INTERMOLECULAR FORCE CALCULATIONS
BASED ON THE EXP-6 PAIR POTENTIAL

A thesis submitted for the degree of
Doctor of Philosophy of the University
of London

by

Barry David Utting

of

The Department of Chemistry,
Imperial College of Science and Technology,
London S.W.7.

June, 1968.

Abstract

The EXP-6 pair potential has been incorporated
into the cell theory of Lennard-Jones and Devonshire.
The resulting EXP-6 cell model has been used in its
quantum form to calculate various solid state properties
of neon, argon, krypton and xenon. The appropriate
values of the adjustable parameters in the pair potential
are derived solely from zero point solid state data.
The solution of the radial wave equation is through the
WKB approximation, which has been adapted so that
second derivatives of the energy levels with respect
to volume may be evaluated. Similar calculations
have been performed using the LJ 12:6 cell model.
When calculated values of such properties as specific
heat and entropy, which are considered too model
sensitive to yield useful information, are ignored,
the EXP-6 function exhibits some superiority in
describing the solid state of argon, krypton and
xenon. For solid neon, however, the LJ 12:6 function
seems more suitable.

The effect of including triplet dispersion inter-
actions in the static lattice energy on both the EXP-6
parameters and the EXP-6 solid state properties has
also been investigated. For solid neon the effect of
including triplet interactions is small. For the
heavier inert gas solids, however, the values of the
potential parameters and of the thermodynamic properties
are changed appreciably by the inclusion of triplet
interactions. Nevertheless, the conclusion that the
EXP-6 function shows some superiority over the LJ 12:6
function in describing the heavier inert gas solids is

not altered. For all the substances considered the
EXP-6 parameters derived by including triplet effects
are more in line with those calculated from second
virial data than are those derived from "pairwise
additive" solid state calculations. For neon, argon
and krypton the "triplet" parameters give better
predictions of the second virial coefficient than
do the "pairwise additive" ones.

Dedication

To Sue and Sarah

Acknowledgements

I should like to thank Dr. John Walkley for his guidance and encouragement in supervising the work described in this thesis during the two years prior to his emigration to Canada in 1966. I should also like to thank Dr. Neville Parsonage who kindly agreed to supervise my work on Dr. Walkley's departure. Dr. Parsonage's ready advice on a topic not directly related to his own interests has at all times been warmly appreciated.

The award of a research studentship by the Science Research Council which enabled this research to be completed and the use of the facilities of the University of London Institute of Computing Science are gratefully acknowledged.

Finally I offer special thanks to my many friends at Imperial College for making my career there a happy one and to Professor Buckingham of Bristol University for preventing my family from starving while this thesis was being written.

B. D. Utting

Contents

Contents (cont.)

Chapter 1

An Introduction to the Intermolecular Pair Potential

The mutual potential energy of an isolated pair of
molecules may be expressed as a function of their
relative position and orientation with respect to one
another. This function is called the intermolecular
pair potential function.

This thesis is concerned solely with inert gas
molecules, which are monatomic (i.e. in this case,
the words "atom" and "molecule" may be used inter-
changeably), spherical and electronically saturated
and, for these, the question of orientational depend-
ence does not arise, so that the potential may be
written as a function of only the centre to centre
distance of the pair of molecules under consideration.
Because of their simplicity, the inert gas molecules
provide a useful testing ground for the fundamental
theory of molecular interactions uncomplicated by
orientation, electrostatic charge and permanent di-
pole effects.

There are two different lines of approach for
the formulation of the pair potential. Either, with
a knowledge of the physical properties of a macro-
scopic system we may attempt the inversion of the
equations of statistical mechanics to give the pair
function, or, by the consideration of an isolated
pair of molecules we may attempt the derivation from
first principles.

Let us consider first the interaction between an isolated pair of molecules. The mutual potential energy of a pair of inert gas molecules may be separated into two main parts:

    (1) short range repulsive forces, which dominate when electron overlap is large;

    (2) long range attractive forces, which dominate when electron overlap approaches zero.

The short range forces arise from a first order perturbation and consist of Coulombic and exchange terms. They are less well understood than the long range forces and most information as to their nature comes from the quantum mechanical study of specific interactions between electronically simple molecules. For instance, the helium-helium interaction has been widely studied (see, for example, Slater 1928, Rosen 1950, Griffing and Wehner 1955, Sakamoto and Ishiguiro 1956, Phillipson 1962, Kestner and Sinanoglu 1966), but even in such a simple case as this, considerable approximations are needed to make the mathematics tractable. From calculations such as these, it seems that the short range potential energy varies in some exponential manner with distance, although, in general, the exact dependence is uncertain. For many purposes the repulsive energy is written in the highly simplified form:

$$\phi(r) = be^{-ar} \qquad (1.1)$$

where r is the distance between molecular centres and a and b are constants.

The long range attractive forces are termed "dispersion" forces and arise from a second order perturbation. They were first treated theoretically by London (1930) who showed that the leading term in the dispersion energy varies as r^{-6} (r again being the intermolecular distance). This term represents the attraction of the dipole moments instant-aneously induced in each molecule by the electronic motion in the other. Induced multipole interactions give rise to further terms varying as r^{-8}, r^{-10} etc. (Margenau 1939a), but since these are small compared with the r^{-6} term, we may neglect them to a first approximation. London's expression for the induced dipole-induced dipole energy may be written as:

$$\phi(r)^{dis}_{AB} = -C^{AB}/r^6 \qquad (1.2)$$

where C^{AB} is a positive coefficient, invariant to permutation of the molecules A and B, which depends on the energies and dipole oscillator strengths for the excitation of the molecules from their ground states to excited states. London approximated this coefficient by writing some of its terms as ionisation energies, but other workers (e.g. Slater and Kirkwood 1931, Margenau 1939b, Dalgarno and Kingston 1961, Bell and Kingston 1966) have calculated its value for various interactions from quantum mechanical first principles.

The theory of dispersion forces is for zero electron overlap. If overlap is allowed for in the second order perturbation, additional attractive forces called "second order exchange forces" appear

(see Margenau 1939b, McWeeny 1959,1960, Murrell, Randic
and Williams 1965, Salem 1965). Such interactions come
into play at "intermediate" intermolecular separations
and are most important for molecules without inner
electron shells. As is the case with the short range
repulsion, their evaluation is very difficult except
for the simplest systems. From Margenau's calculations
for helium, the second order exchange energy appears to
show some sort of exponential dependence on intermol-
ecular distance. For our purposes, however, second
order exchange effects may be considered small and
will not be discussed in any detail.

Let us now consider the second line of investi-
gation, that of calculating the pair potential from
the physical properties of a macroscopic system. To
invert the equations of statistical mechanics to
give the pair potential as an explicit function is an
impracticable task and a very much simpler but more
empirical approach is taken.

A pair potential function containing two or more
adjustable parameters is proposed. The potential is
"characterised" for the molecules under consideration
by evaluating the parameters from suitable experi-
mental data and tested by comparing values of physical
properties predicted by the characterised function
with experiment.

We may write the potential function for the
interaction of a pair of inert gas molecules as:

$$\phi(r) = \phi(r)_{s.r.} + \phi(r)_{l.r.} \qquad (1.3)$$

where $\phi(r)_{s.r.}$ is the short range repulsive potential and $\phi(r)_{l.r.}$ is the long range attractive potential. The function (1.3) has a minimun at some value of intermolecular distance, r_m.

Fig. 1. The mutual potential energy of a pair of inert gas molecules as a function of internolecular distance
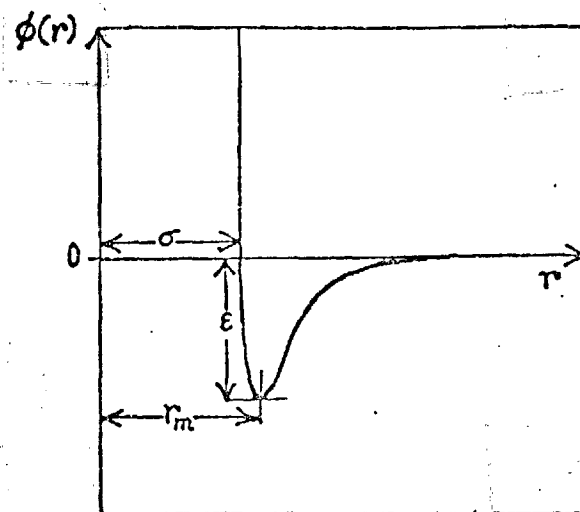
Fig. 1 is a sketch of the dependence of the pair potential on intermolecular distance given by an expression such as (1.3). Marked in the fugure are:

(1) σ, the value of r when $\phi(r)$ is zero;

(2) r_m, the value of r when $\phi(r)$ is a minimun;

(3) ε, the depth of the potential minimun below zero.

A mathematical function suitable for the description of the inert gas pair interaction must give the general form shown in Fig. 1. The function is usually written in such a way that ε and either σ or r_m are two of its adjustable parameters. Which of σ and r_m is chosen as a parameter is mainly a matter of convenience, since, for simple functions, there is

a mathematical relationship between them.

Many functions have been proposed for the inert
gas pair potential. For examples of these the reader
is referred to Hirschfelder, Curtiss and Bird 1954,
p.31 et seq. Some of the functions are more realistic
than others and some (e.g. the square well and Suther-
land potentials) are gross approximations to what must
be the true state of affairs. The reason for preferred
use of one particular potential function rather than
another is very often just mathematical expediency,
especially if not too accurate results are required.

For example, the Mie-Lennard-Jones bireciprocal
potential (Mie 1903, Lennard-Jones 1924) has been
widely used in inert gas intermolecular force calc-
ulations, mainly because of its mathematical simplicity.
It may be written as:

$$\phi(r) = C \varepsilon \left[(\sigma/r)^m - (\sigma/r)^n \right] \qquad (1.4)$$

where C is a constant given by

$$C = \left(\frac{m}{n} \right)^{\frac{n}{(m-n)}} \left(\frac{m}{m-n} \right)$$

and, in order to give the form required by (1.3),
$m > n$.

The attractive term in this potential is in
accordance with London's treatment of dispersion
forces provided that $n=6$, but the mathematical form
of the repulsion has no theoretical foundation what-
ever. Nevertheless, the function is very simple and
lends itself to straightforward calculations of

macroscopic properties of assemblies of simple molecules.

The value of m giving the best representation of the LJ m:6 potential for the inert gas pair inter-action has been the subject of much discussion. For example, recent calculations by Zucker (1968 - but privately communicated to the author prior to pub-lication) of solid state isotherms using solid state data alone to evaluate ε and σ indicate that 12 is the best value of m for neon, argon and krypton and that m=11 is most suitable for xenon. Also, calculations by Walkley and co-workers (Hillier and Walkley 1965, Jenkins and Walkley 1965) show that the use of the LJ 12:6 function gives a good picture of the solid state properties of solid argon and solid neon. These results agree with earlier ones from calculations by Corner (1948) for neon and argon, in which the potential was characterised using solid state experimental data and the best value of m was determined by predicting second virial coeff-icients and gas viscosities. However, they contra-dict the results of Horton and Leech (1963), who per-formed detailed calculations for the inert gas solids, neon, argon, krypton and xenon and found that 'no m=12 calculation comes near to experiment'.

Other physical properties suggest other values for m. For example, Brown and Rowlinson (1960) using a thermodynamic discriminant satisfying a "Schwarz Inequality" suggest that $m \geqslant 13.3$ for liquid argon near the triple point. This is in agreement with the suggestion by Rossi and Danon (1965) that a repulsion steeper than that given by m=12 is necess-ary to account fully for the second virial coefficient

of the inert gases (see discussion of the Kihara core
potential appearing on later pages of this chapter).
On the other hand, the results of molecular scatter-
ing experiments performed by Amdur and Mason (1958)
give repulsions considerably less steep than that
given by m=12. Amdur's and Mason's values of m for
the inert gases lie between 5 and 10, the "softest"
repulsion being that of krypton (m=5.42) and the
"hardest" that of neon (m=9.99). Since scattering
experiments such as these are a direct measure of the
repulsive energy at very small intermolecular distances
where any attraction is negligible, insertion of these
small m values in LJ m:6 potentials cannot be expected
to give reliable predictions of, for example, the solid
state properties at normal pressures, which are
sensitive to the region of the potential around
the minimum. Indeed, substitution of m=5.42 (the
value for krypton) into an LJ m:6 potential would
lead to nonsensical results, since this gives a pair
potential with the repulsion as a longer range force
than the attraction, in direct contradiction to the
basic and justifiable assumption that the repulsion
is very short range in nature and that the attraction
is reasonably long range. It is interesting to note,
however, that the results of Amdur and Mason indicate
that the repulsion softens considerably as very small
intermolecular separations are reached.

We see therefore that the value of m giving
the best representation of the inert gas pair inter-
action is not universal and, indeed, varies even for
the prediction of different properties of the same
substance. However, as we have seen, calculations

by Zucker point, in general, to a value of m=12 for the
best description of the solid state of the inert gases
and, with m=12 and n=6, (1.4) becomes:

$$\phi(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^{6} \right] \qquad (1.5)$$

which is the LJ 12:6 potential, the most commonly
encountered bireciprocal function.

The LJ m:n function is a particular case of the
Kihara core m:n potential (Kihara 1951,1953,1955).
The Kihara core function is similar in form to the
LJ 12:6 function, but involves a quantity $\bar{\varsigma}$, which
is the diameter of a spherical hard core situated
around the centre of each molecule. It may be written:

$$\phi(r) = D\varepsilon \left[\left(\frac{\sigma-\varsigma}{r-\varsigma} \right)^{m} - \left(\frac{\sigma-\delta}{r-\varsigma} \right)^{n} \right] \qquad (1.6)$$

where D is a constant depending only on m and n and
m and n are usually assumed to be 12 and 6 respectively,
as in the case of the LJ m:n function. If $\delta = 0$, (1.6)
becomes the LJ m:n potential, (1.4). Each term in
an expression such as (1.6) may be written as a sum
of terms given by the binomial expansion. The expansion
of (1.6) for m=12, n=6 is:

$$\frac{\phi(r)}{D} = \left(\frac{\sigma-\delta}{r} \right)^{12} \left[1 + 12\left(\frac{\delta}{r} \right) + 78\left(\frac{\delta}{r} \right)^{2} + \cdots \right]$$

$$\left(\frac{\sigma-\delta}{r} \right)^{6} \left[1 + 6\left(\frac{\delta}{r} \right) + 21\left(\frac{\delta}{r} \right)^{2} + \cdots \right] \qquad (1.7)$$

The Kihara core function was originally proposed
to describe the behaviour of spherocylindrical molecules,

but, of late, it has found favour in the description
of the spherical inert gas molecules. The attractive
term in the 12:6 form is somewhat more realistic than
that of the LJ 12:6 potential, in that, on expansion
(see (1.7)), it gives terms in r^{-8}, r^{-10} etc., in
accordance with multipole considerations. It should
be noted, however, that it also gives terms in r^{-7},
r^{-9} etc., for which there is less theoretical justi-
fication in the case of spherical molecules, although
it is known that, if the distance between two molecules
is so great that retardation effects come into play,
the r^{-6} dependence breaks down and the attraction
varies as r^{-7} (Casimir and Polder 1948). The re-
pulsion in the Kihara core 12:6 potential gives, on
expansion (see (1.7)), a sum of terms varying as r^{-12},
r^{-13}, r^{-14} etc. Therefore, at small intermolecular
distances, the repulsion is steeper than that of the
LJ 12:6 potential, but is no less empirical as far
as its mathematical form is concerned.

The hard core diameter, δ, may be calculated
in one of two ways. Either it may be considered as
an adjustable parameter of the potential to be calc-
ulated from suitable experimental data - in this case
the potential is a three parameter one - or it may
be calculated using a formula derived by Danon and
Pitzer (1962) - in this case the function is a two
parameter one, as is the LJ potential.

Rossi and Danon (1965), using the latter pro-
cedure, have found that the Kihara core 12:6 function
is far better than the LJ 12:6 function for the pre-
diction of the second virial coefficient of argon,
krypton and xenon over the whole temperature range

of experimental measurements, in spite of the fact
that no extra flexibility is introduced by the in-
clusion of $\tilde{\mathcal{E}}$ as a third parameter. This work seems
to indicate that a repulsion steeper than that given
by m=12 is required for an adequate description of the
behaviour of the second virial coefficient, especially
at low temperatures. Rossi and Danon also found that
agreement between the value of the coefficient of r^{-6}
calculated from quantum mechanical first principles
and the value of the same coefficient given by the
potential parameters evaluated by a consideration of
the experimental second virial coefficient is far
better for the Kihara core 12:6 than for the LJ 12:6
function. The corresponding values of the r^{-8} coeff-
icient are also in fair agreement for the Kihara 12:6
potential.

On the other hand, work by Zucker (1968), which
considers $\tilde{\mathcal{E}}$ as an adjustable parameter and which
characterises the potential from solid state data
only, shows that there is no significant improvement
in the prediction of solid state isotherms when a
Kihara core potential is used rather than a bireciprocal
LJ form, in spite of the inclusion of the third param-
eter.

A function which is capable of very good pre-
dictions of the solid state properties of argon is that
originally proposed by Guggenheim and McGlashan (1960)
and later studied more thoroughly by McGlashan (1965).
These authors took the step of dividing the pair
potential into three parts:
      (1) the long range part where it is known that, to
          a first approximation, the function varies as
          r^{-6} and that the coefficient of this term is

calculable from quantum mechanics;

(2) the part near the minimum of the curve, where
the potential may be represented as an an-
harmonic oscillator:

$$\phi(r) = -\varepsilon + K\left(\frac{r-r_m}{r_m}\right)^2 - \alpha\left(\frac{r-r_m}{r_m}\right)^3 + \beta\left(\frac{r-r_m}{r_m}\right)^4 - \ldots$$

(1.8)

(3) the short range part, of which the detailed
mathematical form is uncertain. Guggenheim
and McGlashan assumed that, since the potential
in this range is very steep, it can be re-
presented by an infinite cutoff at some value
of intermolecular distance, d.

This "piece-wise" formulation of the potential is
sensible from some points of view. The long range
part of the function is in accordance with London's
theory of dispersion forces and the formulation of the
part near the minimum is perfectly general if ε, K, α,
β, etc. are all adjustable parameters. Guggenheim and
McGlashan truncated the series after the four terms
given in expression (1.8). This should give a good
representation of the region of the curve near the
minimum.

However, the repulsion is again highly empirical.
In this case the repulsion is an even more gross
approximation than that of the LJ potential. Since
Guggenheim and McGlashan proposed this potential in
order to predict only normal pressure solid argon
properties, which are most sensitive to the region
of potential around the minimum and relatively in-
sensitive to the repulsion at small intermolecular

distances, the approximate form given by the infinite
cutoff did not worry them unduly. Use of this potential
for the prediction of properties sensitive to the re-
pulsion cannot be expected to give good results, how-
ever. Also since the potential is mathematically de-
fined only in three specific regions, parts of the
potential lying outside these regions have to be guess-
ed and, if the function is to be constructed over the
whole range of intermolecular distance, the undefined
parts have to be drawn freehand. As well as these
points, the characterisation of the Guggenheim-McGlashan
potential function requires the evaluation of six
parameters. Although the use of functions involving
too few parameters may place artificial restraints
on the potential, the use of as many as six to predict
only solid state properties confers so much flexibility
that the function becomes almost "tailor made" for a
specific interaction (in this case the argon-argon
interaction), and using a potential form such as this
makes it very difficult to say anything about the
mathematical form of the general interaction between
a pair of inert gas molecules.

Dymond, Rigby and Smith (1965) have forwarded
the five term, two parameter function:

$$\phi(r) = \epsilon \left[0.331(r_m/r)^{28} - 1.7584(r_m/r)^{24} + 2.07151(r_m/r)^{18} \right.$$
$$\left. -1.74552(r_m/r)^8 - 0.39959(r_m/r)^6 \right] \quad (1.9)$$

as a representation of the inert gas pair interaction.
This function is capable of giving a good description
of the second virial coefficients and, if triplet

interactions are allowed for (see Chapter 5), of the
crystal properties of neon, argon, krypton and xenon
at 0°K. Once again, however, the repulsive terms in
r^{-28} and r^{-18} are highly empirical. Also, Dymond,
Rigby and Smith themselves admit that the five coeff-
icients of the powers of $1/r$ - obtained by a machine
fit - have little physical meaning and that the r^{-24}
attractive term is included only to give the breadth
of potential well required by experiment. Nevertheless,
the function does not suffer from the disadvantage of
involving discontinuities and, further, contains only
two adjustable parameters, thus avoiding unreasonable
flexibility.

All the pair potential functions mentioned so
far have the disadvantage of containing an unrealistic
repulsive term. As we have seen, quantum mechanical
calculations point to an exponential repulsion of some
kind and, although the detailed nature of this repulsion
is uncertain, it seems logical to cast it into an ex-
ponential form. With this in mind, perhaps the most
realistic function which has been suggested to represent
the inert gas interaction potential is that proposed by
Buckingham and Corner (1947). This function may be
written:

$$\phi(r) = b\exp\left[-\alpha(r/r_m)\right] - (cr^{-6} + c'r^{-8})\exp\left[-4(r_m/r-1)^3\right] \quad r_m \geq r$$

$$\phi(r) = b\exp\left[-\alpha(r/r_m)\right] - (cr^{-6} + c'r^{-8}) \qquad\qquad r \geq r_m$$

$$(1.10)$$

$$\text{where } b = \left[-\varepsilon + (1+\beta)cr_m^{-6}\right]\exp\alpha$$
$$c = \varepsilon\alpha r_m^6\left[\alpha(1+\beta) - 6 - 8\beta\right]^{-1}$$
$$c' = \beta r_m^2 c$$

This is a two part potential with four parameters $\hat{\varepsilon}$, r_m, α, β and contains an exponential short range repulsive term in accordance with quantum mechanical indications. Also second order exchange forces are allowed for (somewhat arbitrarily admittedly) in the term $(cr^{-6}+c'r^{-8})\exp\left[-4(r_m/r-1)^3\right]$ and the induced quadrupole-induced dipole dispersion energy is included (in the r^{-8} term) as well as induced dipole-induced dipole energy (in the r^{-6} term). However, the gain in realism over other potentials has been accompanied by a considerable loss in simplicity and the function (1.10) is mathematically rather unwieldy.

Considerable simplification is effected by writing the potential as (see Kihara and Koba 1952):

$$\phi(r) = \frac{\alpha \varepsilon}{\alpha - 6}\left[\frac{6e^{\alpha}}{\alpha}\exp(-\alpha r/r_m) - (r_m/r)^6\right] \qquad (1.11)$$

which is the EXP-6 potential and involves three adjustable parameters ε, r_m and α. ε and r_m have their usual significance (see Fig. 1) and the value of α is a measure of the steepness of the repulsive branch of the potential. This function contains an exponential repulsion and an r^{-6} attraction, both of which are quite realistic from a quantum mechanical point of view. Also the mathematical form of (1.11) is quite simple and the EXP-6 potential seems to offer the best compromise between realism and simplicity in the description of the inert gas pair interaction.

Although both terms in (1.11) are reasonable in themselves, their mathematical interaction gives rise to the appearance in the function of a spurious maximum at a small value of intermolecular distance (r_{max}). This is removed by writing the potential in

two parts, thus (see Hirschfelder, Curtiss and Bird 1954, p.33):

$$\phi(r) = \frac{\varepsilon}{\alpha - 6} \left[\frac{6e^{\alpha}}{\alpha} \exp(-\alpha r/r_m) - (r_m/r)^6 \right] \qquad r \geqslant r_{max} \qquad (1.12a)$$

$$\phi(r) = \infty \qquad\qquad\qquad\qquad\qquad r \leqslant r_{max} \qquad (1.12b)$$

Generally the maximum occurs at such a small intermolecular distance that the potential is high enough on the repulsive branch for the assumption of an infinite cutoff to be valid. Indeed, for many purposes the potential energy at r_{max} is so high that the maximum may be ignored completely. When working with the EXP-6 function, however, this anomaly should always be remembered and allowance made for it where necessary. A fuller discussion of the spurious maximum will be given in Chapter 4.

In spite of its realism and simplicity, the use of the EXP-6 potential has been rather limited in the past, mainly because calculations by Mason and Rice (1954) seemed to indicate that an exponential repulsion term predicts inert gas properties only marginally better than an inverse twelfth power repulsion.

Mason and Rice used measurements of zero point solid state properties, second virial coefficients and gas viscosities to characterise the EXP-6 function and they predicted only gas properties to test the potential. No test was made by performing detailed solid state calculations. Since the solid state data used has now been largely superseded and, for reasons which will become clear in later chapters, the use

of a mixture of solid state and gas properties to characterise and test a potential function must be viewed with some suspicion, their conclusions must be doubtful until further proof is available.

Characterisation of the EXP-6 function for the inert gases argon, krypton and xenon by a consideration of the second virial coefficient alone·shows that this potential gives far better predictions of this property than does the LJ 12:6 potential (Sherwood and Prausnitz 1964). It should be pointed out, however, that the Kihara core 12:6 potential, assuming $\ddot{a}$ to be an adjustable parameter, is capable of predicting the second virial coefficients of these gases to the same accuracy as the EXP-6 function (Sherwood and Prausnitz 1964) and, therefore, the better representation of the interaction may be due to the inclusion of three parameters rather than two. On the other hand, we should remember that Rossi's and Danon's work shows that the Kihara core potential, treated as a two parameter function, is also more capable of predicting the second virial coefficient of the heavier inert gases, than is the LJ 12:6. Whatever the reason for the markedly superior prediction of the second virial coefficient by these more complicated functions, there seems little doubt that a function so simple as the LJ 12:6 is not adequate for the description of this property. Nevertheless, we have seen that the LJ potential is capable of giving a fair picture of at least some of the solid state properties of some of the inert gases; and that comparison with the results given by the Kihara core shows that little improvement is apparent with this more complicated function, as far as the prediction of solid state isotherms is

concerned. However, detailed calculations of solid
state properties based on the EXP-6 pair potential
have not been performed and the LJ 12:6 function
awaits comparison with the EXP-6 as far as its ability
to predict the properties of the inert gas crystals is
concerned.

Detailed EXP-6 calculations of the solid state
properties of neon, argon, krypton and xenon have
therefore been undertaken. Some second virial coeff-
icient calculations have also been performed. Later
chapters of this thesis describe these calculations,
and present and attempt to interpret their results.
Some comparison is made with results calculated from
the LJ 12:6 pair function.

Chapter 2

The Cell Theory as a Single Particle Model

The many body problem

If we consider any macroscopic system, we need to calculate the system partition function before the equations of statistical mechanics can be used to calculate the thermodynamic properties of the assembly.

In the classical formulation of statistical mechanics the canonical partition function may be written:

$$Z_{NCl} = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \int \cdots \int \exp[-W(R_1, R_2, \ldots, R_N)/(kT)] dR_1 dR_2 \cdots dR_N \quad (2.1)$$

where m is the mass of each molecule in the system, N is the number of molecules present, T is the temperature, $W(R_1, R_2, \ldots, R_N)$ is the potential energy of the configuration of the system represented by the position vectors R_1, $R_2, \ldots, R_N$ of the molecules, k and h are the Boltzmann and Planck constants respectively and the integration is carried out over all phase space. The expression:

$$Q = \frac{1}{N!} \int \cdots \int \exp[-W(R_1, R_2, \ldots, R_N)/(kT)] dR_1 dR_2 \cdots dR_N \quad (2.2)$$

is called the configurational integral of the system.

Using quantum statistical mechanics, the partition
function may be written as the sum over states expression:

$$Z_{NQu} = \sum_{j} \exp\left[-E_j/(kT)\right] \qquad (2.3)$$

where E_j, the jth energy state of the system, is given
by the Schroedinger equation:

$$\sum_{i=1}^{N} \nabla_i^2 \psi_j (R_1, R_2, \ldots, R_N) + \frac{8\pi^2 m}{h^2}\left[E_j - W(R_1, R_2, \ldots, R_N)\right]$$

$$\times \psi_j (R_1, R_2, \ldots, R_N) = 0 \qquad (2.4)$$

It should be noted at this point that here and elsewhere
in the this thesis, unless otherwise stated, the term "quan-
tum statistical mechanics" refers to Boltzmann statistics,
which takes account of the quantum mechanical concept
of energy taking discrete values, but takes no account
of molecular spin, as do Fermi-Dirac and Bose Einstein
statistics.

It is very difficult to elicit an real information
from expressions (2.1) and (2.3) which depend on com-
plicated potential functions depending on the co-ordinates
of all the molecules of the system. Therefore, con-
siderable simplifications have to be made before useful
results can be obtained. A way of simplifying the
expressions for a molecular assembly at high density
is to use the cell theory of Lennard-Jones and Devonshire
(1937, 1938). In its original form this theory
was for classical systems interacting according
to an LJ 12:6 potential. It is, however, straight-
forwardly extended to quantum systems (see Levelt
and Hurst 1960, Hillier and Walkley 1964) and

to other potential functions, provided that they are
not too complicated. In our work we extended it to
the EXP-6 function.

The cell theory of Lennard-Jones and Devonshire(LJD)

The LJD cell theory formulates an equation of state
and thermodynamic properties of molecular systems for
which three assumptions are valid. These assumptions
are:

(1) that the volume available to the system may
be divided into identical cells, each cell
being occupied by one molecule;

(2) that the centres of the cells lie on a regular
lattice;

(3) that each molecule moves independently of all
others in the system.

These assumptions mean that we may write the expression
for the potential energy of a system of N molecules at
vector displacements R_1, R_2,..., R_N from their cell
centres as a sum of terms each of which depends on the
vector displacement R_i of a single molecule i from its
cell centre. Thus:

$$W(R_1,R_2,\ldots,R_N) = W(0) + \sum_{i=1}^{N} \overline{w(R_i)} \qquad (2.5)$$

where $W(R_1,R_2,\ldots,R_N)$ is the total potential energy of
the configuration, $W(0)$ the potential energy when all
molecules are at their cell centres and $\overline{w(R_i)}$ the change
in the potential field experienced by a molecule i when
it is displaced from its cell centre by a vector R_i with
all other molecules remaining at their cell centres.

Substitution of the potential energy given by (2.5) in the configurational integral (2.2) gives an expression in terms of the co-ordinates of one particle only. The configurational integral may now be written:

$$Q = \exp[-W(0)/(kT)] \, v_f^N \qquad (2.6)$$

v_f is called the "free volume integral" of a molecule and is given by:

$$v_f = \int_\Delta \exp[-\overline{w(R)}/(kT)] \, dR \qquad (2.7)$$

where $\int_\Delta$ denotes integration over the interior of the cell occupied by the molecule.

Use of (2.5) also allows the sum over states expression (2.3) to be written in terms of the energy levels of a single particle of the system, thus:

$$Z_{NQu} = \exp[-W(0)/(kT)] \left\{ \sum_j g_j \exp[-\lambda_j/(kT)] \right\}^N \qquad (2.8)$$

where λ_j, the jth molecular energy level, has a degeneracy g_j and is given by the single particle Schroedinger equation:

$$\nabla^2 \psi_j(R) + \frac{8\pi^2 m}{h^2} \left[\lambda_j - \overline{w(R)} \right] \psi_j(R) = 0 \qquad (2.9)$$

where $\psi_j(R)$ falls to zero when the end of the vector R falls outside the boundary of the cell.

Therefore, the LJD cell theory, in both its classical and quantum forms, requires the formulation

of the "cell potential", $\overline{w(R)}$, which depends only on
the co-ordinates of a single molecule of the system.
The 3N dimensional problem has now been reduced to one
of 3 dimensions, but $\overline{w(R)}$ is still a complicated function
of all three co-ordinates of a particle in its cell and
further simplification is necessary in order to make
the evaluation of (2.7) and the solution of (2.9)
possible.

If the lattice occupied by the cell centres is
face centred cubic (f.c.c.) - the structure under normal
conditions of all the inert gas crystals except helium -
each molecule at its lattice point is surrounded by
12 nearest neighbours at the vertices of a dodecahedron.
Lennard-Jones and Devonshire approximated the potential
in this dodecahedral cell by assuming the neighbours to
be uniformly distributed over a sphere centred on the
lattice site of the central molecule and of radius a_1,
the nearest neighbour distance.

For a spherically symmetric environment the cell
potential, $\overline{w(R)}$, may be written as a function of $|R|$ (=R)
only, provided that "pairwise additivity" is assumed - i.e.
that the potential field experienced by the central
molecule is the sum of all pair interactions between it
and all the molecules on the sphere. The "sphericalised"
cell potential is given by:

$$\overline{w(R)} = z_1 \left\{ \frac{1}{2} \int_0^{\pi} \phi(\sqrt{a_1^2 + R^2 - 2Ra_1\cos\theta})\sin\theta\, d\theta - \phi(a_1) \right\} \quad (2.10)$$

where ϕ is the pair potential function, R is the distance
of the central molecule from its lattice point, a_1 is the
nearest neighbour distance and z_1 is the number of near-

est neighbours.

Consideration of further neighbours gives the expression:

$$\overline{w(R)} = \sum_i z_i \left\{ \frac{1}{2} \int_0^\pi \left[\phi(\sqrt{a_i^2 + R^2 - 2Ra_i \cos\theta}) \right] \sin\theta \, d\theta - \phi(a_i) \right\}$$

$$(2.11)$$

where a_i is the distance of the ith shell of neighbours from the central lattice site and z_i is the number of neighbours in the ith shell.

For the f.c.c. lattice structure:

$$a_i/a_1 = i^{\frac{1}{2}} \qquad (2.12)$$

and values of z_i have been tabulated by Kihara and Koba (1952) for i=1,2,...,65. For this structure, the volume, V, of a system of N molecules is related to the nearest neighbour distance, a_1, by:

$$V = Na_1^3/2^{\frac{1}{2}} \qquad (2.13)$$

and the length of the side of the crystallographic unit cell (the cell constant) is given by:

$$a_o = 2^{\frac{1}{2}} a_1 \qquad (2.14)$$

The volume of a cell of the system is equal to the volume per molecule of the system. The cell radius, R_c, is the radius of the sphere whose volume is equal to the volume per molecule. By virtue of (2.13), R_c for a f.c.c. lattice is given as:

$$R_c = \left(\frac{3}{4\pi 2^{\frac{1}{2}}} \right)^{\frac{1}{3}} a_1$$

or $\quad R_c = 0.55267 a_1$ (2.15)

Now that the cell potential depends only upon the displacement R, we may transform expression (2.7) for the free volume and the single particle Schroedinger equation, (2.9), to spherical polar co-ordinates and separate out the angular dependence to give equations depending only on R.

The classical free volume integral becomes:

$$v_f = 4\pi \int_0^{R_c} \exp\left[-\overline{w(R)}/(kT)\right] R^2 dR \qquad (2.16)$$

The upper limit of integration is $R=R_c$ because the cell theory requires that each molecule is confined to its cell and, therefore, the furthest distance that a molecule can move from its lattice site is R_c. This upper limit is more correct than $R=0.5a_1$, which was used by Lennard-Jones and Devonshire in their original paper, although, at high densities, the integrand in (2.16) is effectively zero at distances greater than $0.5a_1$.

In the quantum mechanical formulation, the energy levels are now given by the radial wave equation:

$$\frac{d^2 S_{1,n}(R)}{dR^2} + \left[\frac{8\pi^2 m}{h^2} \lambda_{1,n} - \frac{1(1+1)}{R^2} - \frac{8\pi^2 m \overline{w(R)}}{h^2}\right] S_{1,n}(R) = 0 \quad (2.17)$$

where $S_{1,n}(R) = RU_{1,n}(R)$, $U_{1,n}(R)$ being the radial component of the wave function corresponding to quantum numbers 1 and n. Since $U_{1,n}(R)$ must be finite everywhere and since each particle is confined

to its cell, the boundary conditions on (2.17) are:

$$S_{1,n}(0) = S_{1,n}(R_c) = 0 \qquad (2.17a)$$

n and l are the principal and azimuthal quantum numbers respectively for the eigenvalue $\lambda_{1,n}$ and may independently take any integer value, 0,1,2,3,... etc. Each energy level is (2l+1) degenerate by virtue of the magnetic quantum number m, which may take values -l, -(l-1), ..., 0, ..., (l-1), l for each value of l. Thus the sum over states expression (2.8) becomes:

$$Z_{NQu} = \left[\sum_{l,n} (2l+1)\exp\left[-\lambda_{1,n}/(kT)\right] \right]^N \exp\left[-W(0)/(kT)\right] \qquad (2.18)$$

The calculation of the equation of state and thermodynamic properties of the system is now possible provided that the integration in (2.11) may be performed for the chosen pair potential ϕ. Both the integration required for the calculation of classical thermodynamic properties and the solution of the radial wave equation (2.17) in the quantum case can be carried out, but, even with the simplified cell potential, numerical and/or approximate methods need to be used. The evaluation of the W(0) term is effected by assuming pairwise additivity and performing a lattice sum over all pairs of particles in the system. W(0) may thus be written:

$$W(0) = Nw(o)/2 \qquad (2.19)$$

where w(o) is given by:

$$w(o) = \sum_{i}' z_i \phi(a_i) \qquad (2.20)$$

Reduced quantities

Before we consider the cell model in more detail, it is convenient to introduce the concept of "reduced variables", the use of which considerably simplifies many of the expressions derived in the course of intermolecular force calculations.

As we have seen in Chapter 1, the pair potential may be written in terms of a characteristic energy parameter, ξ, and a characteristic length parameter, d, which is usually one of the two quantities σ and r_m (see Fig. 1). The parameters ξ and d enable molecular quantities and bulk properties to be reduced to dimensionless form.

By making the transformation, $r^* = r/d$, the pair intermolecular distance r is reduced to the dimensionless quantity r^* and the pair potential $\phi(r)$ may be replaced by $\phi(r^*)$, where the functional dependence is now upon r^* rather than upon r. Similarly, $\overline{w(R)}$ may be replaced by $\overline{w(R^*)}$, where $R^* = R/d$.

The pair potential can be written in dimensionless form, thus:

$$\phi^*(r^*) = \phi(r^*)/\xi \qquad (2.21)$$

so that the LJ 12:6 ((1.5)) and the EXP-6 ((1.10a) and (1.10b)) functions may be written in terms of reduced variables as:

$$\phi^*(r^*) = 4(r^{*-12} - r^{*-6}) \qquad (2.22)$$

and

$$\phi^*(r^*) = \frac{\alpha}{\alpha-6}\left[\frac{6e^{\alpha}}{\alpha}\exp(-\alpha r^*) - r^{*-6}\right] \qquad r^* \geqslant r_m^* \qquad (2.23a)$$

$$\phi^*(r^*) = \infty \qquad\qquad\qquad\qquad r_m^* \geqslant r^* \qquad (2.23b)$$

respectively, where $d=\sigma$ in the case of the LJ 12:6 function and $d=r_m$ in the case of the EXP-6 function.

Expression (2.11) may be written in reduced form as:

$$\overline{w^*(R^*)} = \sum_i z_i \left\{ \frac{1}{2}\int_0^\pi \phi^*(\sqrt{a_i^{*2}+R^{*2}-2R^*a_i^*\cos\theta})\sin\theta d\theta - \phi^*(a_i^*)\right\}$$

$$(2.24)$$

where $\overline{w^*(R^*)} = \overline{w(R^*)}/\varepsilon$ and $a_i^* = a_i/d$.

Reduction of the free volume integral (2.16) gives:

$$v_f^* = 4\pi\int_0^{R_c^*}\left[\exp\left[-\overline{w^*(R^*)}/T^*\right]\right]R^{*2}dR^* \qquad (2.25)$$

where $v_f^* = v_f/d^3$, $R_c^* = R_c/d$ and $T^* = kT/\varepsilon$.

The sum over states expression may be written in terms of reduced variables, thus:

$$Z_{NQu} = \left\{\sum_{l,n}(2l+1)\exp(-\lambda_{l,n}^*/T^*)\right\}^N \exp\left[-Nw^*(o)/2T^*\right] \quad (2.26)$$

where $\lambda_{l,n}^* = \lambda_{l,n}/\varepsilon$, $w^*(o) = w(o)/\varepsilon$ and $\lambda_{1,n}^*$ is given by the radial wave equation (2.17) expressed in reduced variables:

$$\frac{d^2 S_{l,n}^*(R^*)}{dR^{*2}} + \left[\frac{8\pi^2\lambda_{1,n}^*}{\Lambda^{*2}} - \frac{l(l+1)}{R^{*2}} - \frac{8\pi^2\overline{w^*(R^*)}}{\Lambda^{*2}}\right]S_{l,n}^*(R^*)=0$$

$$(2.27)$$

together with the boundary conditions:

$$S^*_{1,n}(0) = S^*_{1,n}(R^*_c) = 0 \qquad (2.27a)$$

Λ^* is called the quantum parameter and is given by:

$$\Lambda^* = \frac{h}{(m\epsilon)^{\frac{1}{2}}d} \qquad (2.28)$$

$w^*(o)$ is given by the reduced lattice sum:

$$w^*(o) = \sum_i z_i \phi^*(a^*_i) \qquad (2.29)$$

which for the LJ 12:6 function may be written:

$$w^*(o) = 4\left[\frac{S(12)}{a^{*12}_1} - \frac{S(6)}{a^{*6}_1}\right] \qquad (2.30)$$

where:

$$S(n)' = \sum_i z_i (a^*_i/a^*_1)^{-n} \qquad (2.31)$$

and for the EXP-6 function:

$$w^*(o) = \frac{\alpha}{\alpha-6}\left[\frac{6e^{\alpha}R(0)}{\alpha} - \frac{S(6)}{a^{*6}_1}\right] \qquad (2.32)$$

where $S(6)$ is given by (2.31) and $R(0)$ by:

$$R(n) = \sum_i z_i (a^*_i/a^*_1)^n \exp(-\alpha a^*_i) \qquad (n=0) \qquad (2.33)$$

As mentioned at the beginning of this section, bulk

properties may be expressed as reduced, dimension-
less quantities. Examples of commonly encountered
bulk properties expressed as reduced quantities are
given below.

(1) Volume

$$V^* = V/(Nd^3) \qquad (2.34a)$$

(2) Helmholtz Free Energy

$$F^* = F/(N\varepsilon) \qquad (2.34b)$$

(3) Internal Energy

$$U^* = U/(N\varepsilon) \qquad (2.34c)$$

(4) Specific heat at constant volume
    or constant pressure

$$C^* = C/(Nk) \qquad (2.34d)$$

(5) Entropy

$$S^* = S/(Nk) \qquad (2.34e)$$

(6) Pressure

$$p^* = pd^3/\varepsilon \qquad (2.34f)$$

(7) Volume expansivity

$$\beta^* = \varepsilon\beta/k \qquad (2.34g)$$
$$\text{where } \beta = (1/V)(\partial V/\partial T)_p$$

(8) Isothermal compressibility

$$\chi_T^* = \chi_T/d^3 \qquad (2.34h)$$
$$\text{where } \chi_T = -(1/V)(\partial V/\partial p)_T$$

(9) Second virial coefficient

$$B^* = B/(\tfrac{2}{3}\pi Nd^3) \qquad (2.34i)$$

Reduced quantities will appear often in this
thesis and will always be denoted by a superscripted
star.

The sphericalised reduced cell potential, $\overline{w^*(R^*)}$ for the LJ 12:6 and EXP-6 functions

Use of the reduced LJ 12:6 function (2.22) as the pair potential function ϕ^* in the expression for the reduced cell potential (2.24) leads to a straight-forward integration if we make the transformation, $x=(a_i^{*2}+R^{*2}-2R^*a_i^*\cos\theta)^{\frac{1}{2}}$. With this transformation, the integrands in the cell potential corresponding to the attractive and repulsive terms in the pair potential are inverse 11th and inverse 5th powers of x respectively, giving $\overline{w^*(R^*)}$ as:

$$\overline{w^*(R^*)} = \frac{1}{R^*a_1^*}\left[\frac{T(10)_{12}}{5} - \frac{T(4)_6}{2}\right] - \frac{4S(12)}{a_1^{*12}} + \frac{4S(6)}{a_1^{*6}}$$

(2.35)

where $S(n)$ is given by (2.31) and $T(n)_m$ by:

$$T(n)_m = \sum_{i} \frac{1}{i}(a_i^*/a_1^*)^{(n-m+1)}\left[(a_i^*-R^*)^{-n}-(a_i^*+R^*)^{-n}\right]$$

(2.36)

Expressions (2.23a), (2.23b) and (2.24) give the reduced EXP-6 cell potential as:

$$\overline{w^*(R^*)} = \frac{\alpha}{\alpha-6}\left\{\frac{6e^\alpha}{\alpha^2}\left[\frac{A\sinh(\alpha R^*)}{R^*} - \frac{R(-1)\cosh(\alpha R^*)}{a_1^*}\right]\right.$$
$$\left. - \frac{T(4)_6}{8a_1^*R^*} - \frac{6e^\alpha R(0)}{\alpha} + \frac{S(6)}{a_1^{*6}}\right\} \quad R^*_{max} \geqslant R^*$$

(2.37a)

$$\overline{w^*(R^*)} = \infty, \quad R^* \geqslant R^*_{max}$$

(2.37b)

where $R(n)$ is given by (2.33), $T(n)_m$ by (2.36), $S(n)$ by (2.31) and A by:

$$A = R(0) + \frac{R(-1)}{a_1^*\alpha}$$

(2.38)

R^*_{max} is the reduced distance from the cell centre of the spurious maximum in the cell potential corresponding to the one at r^*_{max} in the EXP-6 pair potential.

As we shall see later (Chapter 4), inert gas densities for which the cell model is valid give a cell potential maximum well beyond the cell radius for physically reasonable values of α and therefore can generally be ignored. Nevertheless, the reduced EXP-6 potential should properly be expressed in terms of the two parts given by (2.37a) and (2.37b).

The integration required to obtain the expression (2.37a) is more complicated than that required to derive the reduced LJ 12:6 cell potential (2.35), but is still readily effected by making the transformation, $x=(a_i^{*2}+R^{*2}-2R^*a_i^*\cos\Theta)^{\frac{1}{2}}$, as before. Integration by parts gives the cell potential term corresponding to the repulsive term in the EXP-6 pair function and the integrand corresponding to the attractive term is an inverse fifth power of x, as in the case of the LJ 12:6 treatment. The detailed derivation of the reduced EXP-6 cell potential is given in Appendix 1.

For some purposes it is convenient to cast $\overline{w^*(R^*)}$ into open form by expanding it as an infinite Taylor series. Because of the sphericalisation procedure used in the derivation of $\overline{w^*(R^*)}$, only even powers of R^* appear in the expansion, which may be written:

$$\overline{w^*(R^*)} = \sum_{k=1}^{\infty} C_{2k}^* R^{*2k} \qquad (2.39)$$

where the coefficients C_{2k}^* (k=1,2,...) are functions only of nearest neighbour distance (and therefore of density) and of the pair potential parameters other than ϵ and d. Since the first term in the expansion of $\frac{1}{2}\int_0^\pi \phi^*(\ a_i^{*2}+R^{*2}-2R^*a_i^*\cos\Theta)\ \sin\Theta d\Theta$ is identically

equal to $\phi^*(a_i^*)$, no constant term appears in (2.39).
(2.39) represents the potential experienced by an
anharmonic oscillator. The first term in R^{*2} represents
the harmonic contribution to the cell field and higher
terms represent anharmonic contributions.

The coefficients C_{2k}^* (k=1,2,...) for the LJ 12:6
and EXP-6 potentials are:

$$C_{2k}^*=4\left[\frac{(2k+10)!S(2k+12)}{10!(2k+1)!a_1^{*(2k+12)}} - \frac{(2k+4)!S(2k+6)}{4!(2k+1)!a_1^{*(2k+6)}}\right] \quad (2.40)$$

and

$$C_{2k}^*=\frac{\alpha}{\alpha-6}\left\{\frac{6e^{\alpha}\alpha^{(2k-2)}}{(2k)!}\left[\frac{\alpha A}{2k+1} - \frac{R(-1)}{a_1^*}\right] - \frac{(2k+4)!S(2k+6)}{4!(2k+1)!a_1^{*(2k+6)}}\right\}$$

$$(2.41)$$

respectively, where S(n) is given by (2.31), R(n) by
(2.33) and A by (2.38).

The cell theory as a model of the solid state

Having derived the simplified spherically symmetric
cell potential for molecules interacting according to
an LJ 12:6 pair potential, Lennard-Jones and Devonshire
derived an equation of state by the use of classical
statistical mechanics. They considered only nearest
neighbour interactions in the formulation of the cell
potential and for the static lattice energy term they
used the expression given by Lennard-Jones and Ingham
(1925), viz:

$$w^*(o) = 6(1.0109V^{*-4} - 2.4090V^{*-2})$$

As originally conceived, the cell theory was intended to formulate an equation of state and thermodyamic properties of the liquid and dense gas states of simple molecules. In support of this, Lennard-Jones and Devonshire found that the LJ 12:6 classical cell theory predicted the existence of both "condensed" and "gaseous" phases at low temperatures and also the existence of a critical isotherm. For substances whose intermolecular pair potential might be expected to follow a dependence such as the LJ 12:6 (e.g. the inert gases) the calculated densities and boiling points of the condensed phase were reasonably close to the experimental properties of the liquid. They were, however, even closer to the solid properties. The temperature of the critical isotherm was close to that given by experimental measurements on suitable substances, but the critical density and pressure differed considerably from their experimental values.

Barker (1963, p.56 et seq.), by a detailed comparison of the experimental properties of solid and liquid argon at and around the triple point with those predicted by the LJ 12:6 classical cell model, has clearly shown that the cell model is more properly a theory of the solid rather than of the liquid and gas states. He interprets the critical isotherm as pertaining to solid-expanded solid transition rather than to a liquid-gas transition, as originally supposed by Lennard-Jones and Devonshire, and explains (p.75 et seq.) how the applicability of the model to the solid state follows directly from the assumptions on which it is based. The conclusion that the cell model is really a description of the solid state was in fact indicated by the

later work of Lennard-Jones and Devonshire
(Lennard-Jones and Devonshire 1939a, b, Devonshire
1940, Corner and Lennard-Jones 1941), who
propounded an order-disorder theory of melting
to explain the difference between the solid
and liquid states.

Briefly, the reason we cannot apply the cell
theory, as presented in this chapter, to the
liquid state is that the lattice concept inherent
in the cell model gives long range order in the
system, a property typical of the solid, but not
of the liquid, in which we expect to find short
range order but long range disorder around any
representative molecule. To make the picture of
the liquid state more clear, let us compare the
molecular behaviour of an ideal gas with that of
an ideal crystal. In an ideal gas the whole
volume of the system is available to any molecule
in the system - the molecules are "delocalised" -
and this leads to a "communal entropy" term of
value Nk in the description of the assembly.
In the ideal crystal, on the other hand, where
the molecules are localised around their lattice
sites (the situation given by cell theory), the
communal entropy is zero, since the volume
available to a molecule is equal to the volume
per molecule. Somewhere between these extremes
lies the liquid state. It has been suggested (Eyring
1936) that multiplication of the partition function of
a lattice by a factor e^N could give a better descrip-
tion of the liquid state, but this gives the communal

entropy of an ideal gas and it is more likely that this term appears gradually as we move from the solid, through the liquid, to the gas state (Alder 1962).

Various workers have attempted to account for the communal entropy, either by employing a cell model in which the cells are allocated in such a way that they may be occupied by more than one molecule (Janssens and Prigogine 1950, Pople 1951, Barker 1955,1956,1957), or by considering the behaviour of molecules in clusters of cells (de Boer 1954, Cohen, de Boer and Salsburg 1955,1957, Salsburg, Cohen, Reithmeyer and de Boer 1957, Cohen and Reithmeyer 1958). Such treatments, however, involve many approximations and the problem of communal entropy in the liquid remains largely unsolved.

The cell model, then, represents a system of molecules in restricted oscillatory motion about a set of lattice points and is therefore a model of the solid state. Further, it is a model which is capable of taking explicit account of anharmonicity in the molecular vibrations (see (2.39)). However, even as a description of the solid state, it is still an approximation by virtue of the assumption of independent molecular motion - the Einstein approximation (Einstein 1907, 1911a,b) - and the sphericalisation procedure required to make the cell potential spherically symmetric.

The error introduced by sphericalisation has been studied by Barker (1956). He calculated the classical 12:6 free volume given by the correct three dimensional cell potential and compared it to that given by the

sphericalised cell potential. He found that the error
passes through a maximum $(v_f(\text{correct})/v_f(\text{sphericalised})=1.4)$
in the region of the critical density and that, on
proceeding to high densities, the sphericalisation
procedure becomes progressively more exact, until,
in the imit of high density, the correct and spherical-
ised cell potentials become identical. He therefore
came to the conclusion that the error introduced by
sphericalisation is negligible at solid state densities.

The Einstein approximation of independent mol-
ecular motion undoubtedly leads to some error in the
calculation of thermodynamic properties. These would
be expected to be most pronounced in such properties
as specific heat and entropy, which are independent
of the static lattice energy (see following chapter)
and therefore particularly sensitive to the molecular
motion in the solid. Correlation of molecular motion
in classical statistics may be allowed for by the
method of Barker (1955,1956), who considered binary
and tenary correlations. A more rigorous approach
is the lattice dynamical method pioneered by Born
and von Karman (1912,1913), which considers the motion
of the complete lattice in quantum statistics. The
lattice dynamical method is, however, mathematically
complicated, even in the simplest case of harmonic
lattice vibrations (see Montroll 1942,1943, Montroll
and Peaslee 1944). The complexity of the lattice
dynamical treatment of an anharmonic crystal is greater
still and, although there exists a formal framework for
the treatment of anharmonic lattice vibrations to any
degree of accuracy (Cowley 1963), the difficulties
of the mathematics are so great that, to date, detailed

theory has been developed only for first order anharmonic effects (see Leibfried and Ludwigg 1961). In consequence, even the most modern lattice dynamical calculations (see, for example, Feldman and Horton 1967) take account of only such effects. Further, lattice dynamical calculations usually consider only nearest neighbour interactions, although some workers (Wallace 1963, Reissland 1965) have attempted to allow for more distant neighbours.

On the other hand, with the use of an Einstein model such as the cell model, it is comparatively simple to take explicit account of even high order anharmonic effects, as well as interactions between non-nearest neighbours. From the point of simplicity, then, the cell model has much to recommend it and it is felt that it can be used to good effect, so long as suitable care is taken not to stretch the theory beyond its limits.

Chapter 3

The Quantum Cell Model and the Solution of the Radial Wave Equation

Quantum effects in the inert gas solids

Although classical statistics may serve as a
convenient approximation at high temperatures, any
model purporting to give a complete description of the
solid state of any substance right down to absolute
zero temperature must involve the use of quantum
statistical methods. Indeed, it is well known that
classical methods, no matter how refined, fail com-
pletely to give even qualitatively correct results
for the low temperature values of such non-static
lattice dependent properties as specific heat and
entropy; and it was not until Einstein (1907, 1911a,b)
used the concept of "quantised oscillators" to explain
the experimentally observed decrease in the specific
heat of solid substances from the classical Dulong-
Petit value of $C_v=3R$ mole^{-1} at high temperature to
$C_v=0$ in the limit of absolute zero temperature, that
a realistic picture of the temperature variation of
these properties could be obtained. It has been
mentioned in Chapter 2 that such properties as specific
heat and entropy would be expected to be particularly
sensitive to the model used to represent the solid
state and, indeed, Einstein's theory, with its assump-
tion of independent molecular motion, was found to lead
to errors in the low temperature values of specific
heat. Similar errors would be expected from the use

of the cell model, which is simply an Einstein model
which makes allowance for anharmonic effects. They
may be removed by allowing for correlated molecular
motion (Debye 1912, Born and von Karman 1912, 1913).

Properties expected to be less model sensitive
are those, such as free energy and molar volume, dep-
ending strongly on the static lattice energy, which
is unaffected by the vibrational motion of the crystal.
By virtue of the purely classical nature of the static
lattice, these properties are also less sensitive to
quantum effects and their low temperature behaviour
can be described, at least qualitatively, in terms
of classical statistics.

Quantum effects in the static lattice dependent
properties are governed by the value of the zero
point vibrational energy, E_0, and a simple and
convenient way of judging their relative importance
in the inert gas solids is to compare, for each
substance, how much E_0 contributes to F_0, the total
free energy of the crystal at 0^OK.

A method of estimating the zero point energy of
a crystal from experimental data is to use the relation:

$$E_0 = (9/8) R \, \Theta_{D,\infty}$$

(3.1)

which is derived from a Debye model of the solid
(Debye 1912) in which Θ_D is taken to be the limiting
high temperature value, $\Theta_{D,\infty}$. The use of (3.1) was
originally proposed by Domb and Salter (1952) who
showed that, whereas the previously accepted
expression involving the T=0 value of Θ_D

led to a substantial error in the evaluation of E_o,
the replacement of Θ_E by $\Theta_{(\infty)}$ in a Debye solid re-
produced exactly the second moment of the correct
frequency distribution as given by the lattice
dynamical methods of Born and von Karman (1912,1913)
and, consequently, led to a value of E_o in very close
agreement with the correct one. For the f.c.c. lattice,
which is the one pertinent to the present work, nearest
neighbour considerations revealed the value of the zero
point energy as given by (3.1) to be a mere 0.5%
different from the correct value, while the use of
the T=0 value of Θ_0 leads to a result some 15% in
error. The use of an Einstein model of the solid leads
to a value of $E_o \sim 3\%$ different from that given by (3.1).

An objection that might be raised against the use
of (3.1) in the context of the inert gas solids is that
it is based on the assumption that the zero point
vibrations of the crystal are harmonic. Now, while
this may be assumed valid for the heavier inert gases,
this is not the case for molecules as light as those
of neon (see Reissland 1965). However, since at the
moment we are not concerned with an evaluation of E_o
for its own sake but wish only to demonstrate the
effects of quantum behaviour, we take (3.1) to be a
convenient approximation even when anharmonic effects
are present and in such a situation assume that $\Theta_{(\infty)}$
defines an effective harmonic lattice corresponding
to the anharmonic one.

An experimental value of $\Theta_{D,\infty}$ for any solid can
be derived either from the temperature variation of
the specific heat or from the elastic constants of
the solid, and E_o is simply given by the negative of

the value of the sublimation energy extrapolated to absolute zero temperature. Using the data quoted by Pollack (1964) it is found that E_o expressed as a percentage of F_o (paying no regard to positive and negative signs) has values of 34, 10, 5 and 3 for neon, argon, krypton and xenon respectively. It is clear that quantum deviations are apparent in the $0^o K$ free energies (and, by inference, in the $0^o K$ values of other static lattice dependent properties) of all the inert gas solids. As expected from molecular weight considerations, they are most pronounced in solid neon and least in solid xenon, but even in the case of the latter substance the zero point energy is readily detectable in the total free energy.

Another way of looking at quantum effects in the static lattice dependent properties of the inert gas solids is in terms of the quantum parameter, Λ^*, previously mentioned in Chapter 2 and given by expression (2.28). This quantity is the reduced de Broglie wave length corresponding to an energy of ε, the depth below zero of the minimum in the pair potential, and, as its name implies, is directly related to quantum behaviour. It was first introduced into the theory of intermolecular forces by de Boer (1948) who considered the classical and quantum statistical behaviour of pairwise additive systems of molecules interacting according to a two parameter potential function of the type $\phi = \varepsilon f(r/d)$. He showed that if classical statistics are obeyed, then the reduced thermodynamic properties of such systems may be expressed as universal functions of reduced volume V^* and reduced temperature T^*. Thus for any property:

$$X^*_{classical} = X^*(V^*, T^*) \qquad (3.2)$$

and for the equation of state:

$$p^*_{classical} = p^*(V^*, T^*) \qquad (3.3)$$

If, on the other hand, quantum statistics are obeyed, the reduced thermodynamic properties are now universal functions of Λ^* as well as of V^* and T^*, so that (3.2) and (3.3) become:

$$X^*_{quantum} = X^*(V^*, T^*, \Lambda^*) \qquad (3.4)$$

and

$$p^*_{quantum} = p^*(V^*, T^*, \Lambda^*) \qquad (3.5)$$

respectively. These revert to their classical analogues when $\Lambda^* = 0$.

It is clear that values of the reduced thermodynamic properties at $0^{\circ}K$ and zero pressure of systems for which (3.4) and (3.5) hold may be calculated as functions of Λ^* only. Such calculations have been widely undertaken (e.g. by de Boer and Blaisse 1948, Salter 1954, Dugdale and MacDonald 1954, Bernardes 1960, Hurst and Levelt 1961, Zucker 1961) with particular reference to the inert gas solids. Calculations of this type generally make use of the LJ 12:6 potential and a simple quantum model of the solid state to give plots of $0^{\circ}K$, zero pressure values of such properties as reduced free energy, reduced volume and reduced isothermal compressibility as functions of Λ^*. Such plots give substantial agreement with experimental data (see Figs.2 and 3 below), but comparison of the experimental points with $\Lambda^*=0$ (i.e. classical) values of the properties shows that such agreement is possible only if quantum behaviour is accounted for. This is the case even for xenon, which comes closest

to classical behaviour.

Fig.2. Reduced equilibrium vol-
ume at $0^{\circ}K$ and zero pressure
(V_0^*) as a function of the quan-
tum parameter (Λ^*) for the LJ
12:6 pair potential (after
Zucker 1961).
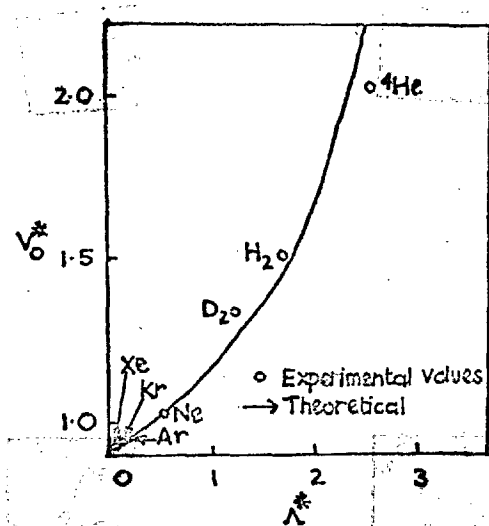
Fig.3. Reduced crystal free
energy at $0^{\circ}K$ and zero press-
ure (F_0^*) as a function of
the quantum parameter (Λ^*)
for the LJ 12:6 pair poten-
tial (after Zucker 1961).
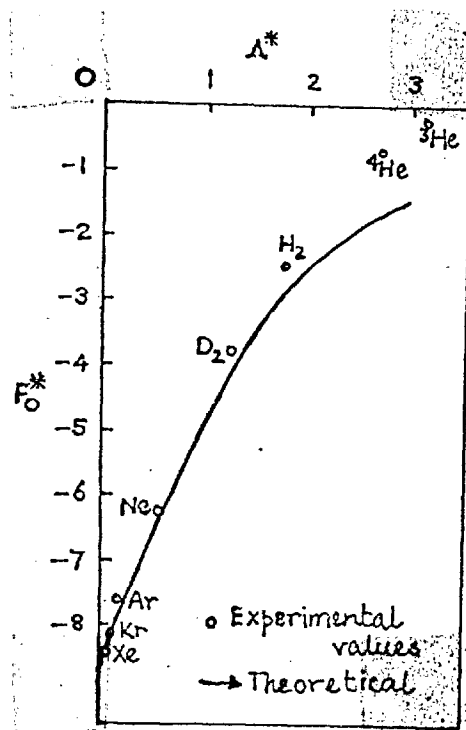
It is quite clear then that the use of a quantum
statistical model is essential, even from the point of
view of the static lattice dependent properties, if a
realistic pictue of the low temperature thermodynamics
of the inert gas solids is to be obtained. The in-
corporation of quantum statistics into the LJD cell
model has been covered in principle in Chapter 2.
The practical application of the theory is described in
the second section of the present chapter.

The thermodynamic properties of a quantum cell model system and the solution of the radial wave equation.

As we have seen in Chapter 2, the quantum form of the cell theory of Lennard-Jones and Devonshire gives the partition function of an N particle, pairwise additive lattice, at a reduced temperature of T* (and an implied reduced volume of V*), as the sum over states expression (2.26):

$$Z_{NQu} = \left[\sum_{1,n} (2l+1) \exp(-\lambda^*_{1,n}/T^*) \right]^N \exp\left[-Nw^*(o)/(2T^*) \right]$$

where w*(o) is the reduced potential energy experienced by a representative particle in the static lattice; and the quantities $\lambda^*_{1,n}$ (l=0,1,2,...; n=0,1,2,...) are reduced single particle energy levels, corresponding to the sphericalised cell field, $\overline{w(R)}$, and determined by the radial wave equation (2.27):

$$\frac{d^2 S^*_{1,n}(R^*)}{dR^{*2}} + \left[\frac{8\pi^2 \lambda^*_{1,n}}{\Lambda^{*2}} - \frac{l(l+1)}{R^{*2}} - \frac{8\pi^2}{\Lambda^{*2}} \overline{w^*(R^*)} \right]$$
$$\times S^*_{1,n}(R^*) = 0$$

under the conditions (2.27a):

$$S^*_{1,n}(0) = S^*_{1,n}(R^*_c) = 0$$

R^*_c being the reduced cell radius.

From the partition function, the bulk thermodynamic properties follow directly by use of standard statistical mechanical relations. For example, the Helmholtz free energy, internal energy, specific heat at constant volume and entropy are given in reduced

form as:

$$F^* = -\frac{T^*}{N} \ln Z_{NQu} = -T^* \ln \left[\Sigma(1) \right] + \frac{w^*(0)}{2} \quad (3.7a)$$

$$U^* = \frac{T^{*2}}{N} \left(\frac{\partial \ln Z_{NQu}}{\partial T^*} \right)_{V^*} = \frac{\Sigma(\overset{*}{\lambda}_{L,n})}{\Sigma(1)} + \frac{w^*(0)}{2} \quad (3.7b)$$

$$C_V^* = \frac{2T^*}{N} \left(\frac{\partial \ln Z_{NQu}}{\partial T^*} \right)_{V^*} + \frac{T^{*2}}{N} \left(\frac{\partial^2 \ln Z_{NQu}}{\partial T^{*2}} \right)_{V^*}$$

$$= \frac{1}{T^{*2}} \left\{ \frac{\Sigma(\overset{*}{\lambda}_{L,n}; \overset{*}{\lambda}_{L,n})}{\Sigma(1)} - \left[\frac{\Sigma(\overset{*}{\lambda}_{L,n})}{\Sigma(1)} \right]^2 \right\} \quad (3.7c)$$

$$S^* = \frac{\ln Z_{NQu}}{N} + \frac{T^*}{N} \left(\frac{\partial \ln Z_{NQu}}{\partial T^*} \right)_{V^*}$$

$$= \ln \left[\Sigma(1) \right] + \frac{1}{T^*} \left[\frac{\Sigma(\overset{*}{\lambda}_{L,n})}{\Sigma(1)} \right] \quad (3.7d)$$

where $\Sigma(a; b; c; \dots) = \underset{L,n}{\Sigma} (2L+1)(abc\dots) \exp\left(-\overset{*}{\lambda}_{L,n}/T^*\right)$

and $\Sigma(1) = \underset{L,n}{\Sigma} (2L+1) \exp\left(-\overset{*}{\lambda}_{L,n}/T^*\right)$

In the same notation the reduced equation of state is given by:

$$p^* = -\frac{T^*}{N} \left(\frac{\partial \ln Z_{NQu}}{\partial V^*} \right)_{T^*} = -\frac{\Sigma(\overset{*}{\lambda}'_{L,n})}{\Sigma(1)} - \frac{w^*(0)'}{2} \quad (3.7e)$$

and reduced isothermal compressibility and reduced volume expansivity by:

$$\chi_T^* = -\frac{1}{V^*} \left(\frac{\partial V^*}{\partial p^*} \right)_{T^*} = \frac{1}{V^* \left\{ -\frac{\Sigma(\overset{*}{\lambda}''_{L,n})}{\Sigma(1)} + \frac{1}{T^*} \left[\frac{\Sigma(\overset{*}{\lambda}'_{L,n} \overset{*}{\lambda}'_{L,n})}{\Sigma(1)} - \frac{\Sigma(\overset{*}{\lambda}'_{L,n})}{\Sigma(1)^2} \right] \frac{w^*(0)''}{2} \right\}} \quad (3.7f)$$

and

$$\mathcal{F}^* = \frac{1}{V^*}\left(\frac{\partial V^*}{\partial T^*}\right)_{P^*} = \frac{1}{V^* T^*}\left\{\frac{\left[\frac{\Sigma(\lambda^*_{l,n}\,\lambda^{*'}_{l,n})}{\Sigma(l)} - \frac{\Sigma(\lambda^*_{l,n})\Sigma(\lambda^{*'}_{l,n})}{\Sigma(l)^2}\right]}{-\frac{\Sigma(\lambda^{*''}_{l,n})}{\Sigma(l)} + \frac{1}{T^*}\left[\frac{\Sigma(\lambda^{*'}_{l,n}\,\lambda^{*''}_{l,n})}{\Sigma(l)} - \frac{\Sigma(\lambda^{*'}_{l,n})^2}{\Sigma(l)}\right] - \overline{w^*(\sigma^*)''}}\right\} \quad (3.7\text{g})$$

where a single prime denotes single differentiation and a double prime double differentiation with respect to V^*. The reduced specific heat at constant pressure is given by substituting expressions (3.7c), (3.7f) and (3.7g) into the reduced thermodynamic relation:

$$C_p^* = C_v^* + \frac{\mathcal{F}^{*2} T^* V^*}{\chi_T^*} \quad (3.7\text{h})$$

Although, in general, because of the complexity of the function, $\overline{w^*(R^*)}$, the radial wave equation (2.27) cannot be solved analytically, it can be solved "exactly" - in the sense that the eigenvalues can be evaluated to any prescribed degree of accuracy - by use of either a series expansion or finite difference technique.

The former approach was adopted by Levelt and Hurst (1960) who wrote the functions $S^*_{1,n}(R^*)$, (related to $U^*_{1,n}(R^*)$, the radial component of the total wave function, by $S^*_{1,n}(R^*) = R^* U^*_{1,n}(R^*)$, see Chapter 2), as a power series in R^*. On substituting this function into the radial wave equation and equating terms involving like powers of R^*, Levelt and Hurst found half the coefficients of the expansion to be identically zero and the others to be related by simple recursion relations, involving the eigenvalue $\lambda^*_{1,n}$, the quantum number 1 and the coefficients

C^*_{2k} (k=1,2,3,...) of the series expansion of
$\overline{w^*(R^*)}$, (see (2.31) in Chapter 2). They determined
the eigenvalues of energy iteratively, by causing
$S^*_{1,n}(R^*)$ to fall to zero at the cell radius in
accordance with the boundary condition, $S^*_{1,n}(R^*_c)=0$.
The other boundary condition, $S^*_{1,n}(0)=0$, is
implicit in the method.

Although this method proved reasonably successful
in treating molecules of high Λ^*, e.g. hydrogen and
deuterium (which, in spite of their lack of spherical
symmetry, may, for many purposes, be considered in
the same context as the inert gas molecules), it is
very cumbersome and time consuming for heavier
molecules. In a later paper, Hurst and Levelt (1961)
estimated that, for argon, over 1000 terms would be
required in the series representation of the wave
function for a reasonably accurate value of the
lowest energy level to be obtained.

The more versatile finite difference method
given by Hillier, Islam and Walkley (1965) transforms
the radial wave equation into four simultaneous, first
order, linear differential equations which may be inte-
grated in a stepwise manner, using a Runge-Kutta
numerical technique. Because of the behaviour of the
term $1(1+1)/R^{*2}$ at $R^*=0$, the initial point of the
integration is chosen as $R^*=10^{-5}R^*_c$ and the initial
values of the function $S^*_{1,n}(R^*)$ and the various
derivatives required by the method are calculated
using the series expansion of Levelt and Hurst, which
is rapidly convergent for such a small value of R^*.
The eigenvalues are calculated by iteration such that

the boundary condition at $R^* = R_c^*$ is satisfied.

Although this technique is of somewhat faster application than that of Levelt and Hurst, it still requires considerable computing time and suffers from a further defect common to both exact methods. This is that neither provides a direct way of determining the volume derivatives of the eigenvalues and, therefore, the evaluation of such properties as pressure, isothermal compressibility and volume expansivity (see (3.7e), (3.7f), (3.7g)) is not possible without recourse to numerical differentiation, either of the eigenvalues themselves or of the logarithm of the partition function. Now, of all mathematical operations, differentiation is perhaps the most awkward to treat by numerical methods, in that a single reasonable evaluation of a derivative requires highly accurate calculations of the quantity to be differentiated at many closely spaced values of the differentiating variable. Such a procedure is both cumbersome and very time consuming and, in the present context, must be considered unsuitable, especially when it is remembered that the calculation of exact eigenvalues is in itself a slow process.

Nevertheless, "exact" methods are useful in testing how well approximate methods evaluate the eigenvalues and the thermodynamic properties not dependent on volume derivatives and, since the finite difference technique has been used for this purpose in this work, a complete treatment of this method is given in Appendix 2.

56.

In the majority of the solid state calculations
described in this thesis, the solution of the radial
wave equation has been effected through the semi-
classical Wentzel-Kramers-Brillouin (WKB) approx-
imation. This method allows rapid evaluation of a
large number of energy levels and reasonably
straightforward calculation of their volume
derivatives. Its application to the quantum cell
model was developed in these laboratories by Hillier
and Walkley (1964) and was later used by them and
others (Hillier, Islam and Walkley 1965, Hillier and
Walkley 1965, Jenkins and Walkley 1965) in detailed
calculations based on the LJ 12:6 potential. A
similar method has been used by Henderson and Reed
(1964). The approach taken here is similar to that
of Hillier and Walkley, but with modifications which
make for greater numerical efficiency and also allow
the second volume derivatives of the energy levels to
be calculated.

The full treatment of the WKB approximation is
covered in most quantum mechanical texts (for example,
see Schiff 1955, p.185 et seq.) and only an outline is
given here. Briefly then, the WKB approximation, as
applied to one dimensional systems, expands the
exponential of i/h (h is Planck's constant) times
the wave function as a power series in h. On
neglecting terms beyond the second in this expansion,
the solution of the Schroedinger equation gives
eigenfunctions which are valid in regions of pos-
itive and negative kinetic energy far removed from
classical turning points of the motion. Approximate
solutions for the two regions are then found that are

reasonably accurate at a turning point and, at the same time, have the correct asymptotic behaviour. The turning point is assumed linear and the solutions connected across it. For a particle moving in a potential well, the asymptotic forms of the solutions arising from the two turning points of the motion are matched in the interior of the well to give a determining equation for the energy levels:

$$\int_{x_1}^{x_2} \frac{2\pi}{h} \left\{ 2m \left[\lambda_n - V(x) \right] \right\}^{\frac{1}{2}} = \left(n + \frac{1}{2} \right) \pi \qquad (3.8)$$
$$(n = 0, 1, 2, \ldots)$$

where m and λ_n are the mass and nth energy level respectively of the particle, $V(x)$ is the potential field and x_1 and x_2 $(x_2 > x_1)$ are the classical turning points of the motion (<u>i.e.</u> the points where $\lambda_n = V(x)$).

Equation (3.8) is straightforwardly extended to three dimensional radial systems by replacing x by r, λ_n by $\lambda_{l,n}$ and $V(x)$ by $V(r) + h^2 (1+\frac{1}{2})^2 / (2mr^2)$. In our notation, the equation determining the reduced energy levels $\lambda_{l,n}^*$ corresponding to the reduced cell potential $\overline{w^*(R^*)}$ may be written:

$$\int_{R_1^*}^{R_2^*} Q^{*\frac{1}{2}} dR^* = \left(n + \frac{1}{2} \right) \pi \qquad (3.9)$$

where

$$Q^* = \frac{8\pi^2}{\Lambda^{*2}} \lambda_{l,n}^* - \frac{(l+\frac{1}{2})^2}{R^{*2}} - \frac{8\pi^2}{\Lambda^{*2}} \overline{w^*(R^*)} \qquad (3.9a)$$

and R_1^* and R_2^* $(R_2^* > R_1^*)$ are the positive roots of the equation:

$$Q^*(R^*) = 0 \qquad (3.9b)$$

The replacement of $l(l+1)$ by $(l+\frac{1}{2})^2$ in the centrifugal part of the kinetic energy of the three dimensional system is necessary to fulfil the boundary condition $S^*_{l,n}(0)=0$ (Langer 1937), and is equivalent to causing the solution of the radial wave equation, written in terms of $S_{l,n}(R)$, to behave in the same way at $R=0$ as does that of the one dimensional Schroedinger equation at $x=-\infty$. The other boundary condition, $S^*_{l,n}(R^*_c)=0$, is not fulfilled in the WKB approximation; instead $S^*_{l,n}(R^*)\to 0$ as $R^*\to\infty$. This is in direct contrast with the 'exact' methods, in which the satisfaction of this condition is inherent in the solution of the wave equation. Nevertheless, as far as the substances considered here are concerned, the use of the WKB formula (3.9) is justified by virtue of R^*_c's being sufficiently large in comparison with R^*_2 for the points $R^*=R^*_c$ and $R^*=\infty$ to be considered equivalent.

With this in mind, the use of (3.9) in calculating the low lying energy levels is justified by the similarity between $\overline{w(R)}$ at small displacements and the harmonic potential $V=C_2R^2$ (see the expansion (2.39) in Chapter 2), for which particular case the WKB approximation gives the energy levels exactly (Fröman and Fröman 1965, p.120 et seq.). (3.9) is also valid for the high energy levels by virtue of the asymptotic nature of the approximation, which makes it generally applicable only when the classical turning points of the motion are well separated.

The numerical accuracy with which the WKB method gives the energy levels of an LJ 12:6 cell model system was initially studied by Hillier and Walkley (1964) who compared the WKB values of the energy levels with the

"exact" finite difference values for hydrogen and
deuterium at various values of V*. The innaccuracies
arising from the use of the WKB method were found to be
small and, for the substances considered here, which,
due to their higher molecular weight more nearly
approach harmonic behaviour, the inaccuracies in the
LJ 12:6 energy levels would be expected to be even
smaller. Although there is no a priori reason to doubt
that the WKB approximation is also applicable to EXP-6
calculations, we felt it advisable to verify that this
is indeed the case and this was done in the course of
the calculations reparted in the next chapter.

Strictly speaking, the use of the WKB approach is
preferable to methods which treat a particle in an
Einstein lattice as a harmonic oscillator perturbed by
anharmonic terms (Henkel 1955, Zucker 1964) because of
its ability to take accurate account of all anharmonic
terms in the evaluation of the high energy levels
where molecular displacements are large. Perturbation
methods, on the other hand, are accurate only in the
evaluation of energy levels for which mean excursions
of the molecules from their lattice points are small
enough to render valid the truncation of the series
expansion of the potential field after a small number
of terms (two in the treatment of Henkel and three in
that of Zucker). However, it should be pointed out that,
even at the triple points of the substances considered
here, the partition function should not be sensitive
enough to the very high energy levels for the second
order perturbation treatment of Zucker to lead to
serious inaccuracies in the evaluation of the thermo-
dynamic properties and the author's preference for

the WKB approximation is only marginal.

Since, for an f.c.c. lattice, $V^* = a_1^{*3}/2^{\frac{1}{2}}$ (see Chapter 2), the first and second reduced volume derivatives of $\lambda^*_{1,n}$ are given by:

$$\frac{d\lambda^*_{1,n}}{dV^*} = \left(\frac{2^{\frac{1}{2}}}{3a_1^{*2}}\right)\left(\frac{d\lambda^*_{1,n}}{da_1^*}\right) \qquad (3.10)$$

and

$$\frac{d^2\lambda^*_{1,n}}{dV^{*2}} = \frac{2}{9a_1^{*4}}\left(\frac{d^2\lambda^*_{1,n}}{da_1^{*2}} - \frac{2}{a_1^*}\frac{d\lambda^*_{1,n}}{da_1^*}\right) \qquad (3.11)$$

respectively.

In the WKB approximation expressions for $d\lambda^*_{1,n}/da_1^*$ and $d^2\lambda^*_{1,n}/da_1^{*2}$ are given by differentiation, under certain conditions, of (3.9) with respect to a_1^*. Although both R_1^* and R_2^* are both dependent on a_1^*, the fact that, by definition, Q^* (and therefore $Q^{*\frac{1}{2}}$) is zero at these points allows the first derivatives to be obtained by straightforward differentiation under the integral sign. This gives:

$$\frac{d\lambda^*_{1,n}}{da_1^*} = \frac{\int_{R_1^*}^{R_2^*} \frac{\partial W^*(R^*)}{\partial a_1^*} Q^{*-\frac{1}{2}} dR^*}{\int_{R_1^*}^{R_2^*} Q^{*-\frac{1}{2}} dR^*} \qquad (3.12)$$

Although this expression, somewhat rearranged, has been used to good effect in the calculations of Walkley and co-workers, in view of the fact that the presence of $Q^{*-\frac{1}{2}}$ leads to infinities in the integrands at R_1^* and R_2^*, it is felt that further comment is required as to its validity.

Let us consider the behaviour of the function $Q*^{-\frac{1}{2}}$ in the region of the turning points R_1^* and R_2^*. Expansion of $Q*$ about each turning point shows that $Q*^{-\frac{1}{2}}$ varies as $(R*-R_1^*)^{-\frac{1}{2}}$ for $R*$ near R_1^* and as $(R_2^*-R*)^{-\frac{1}{2}}$ for $R*$ near R_2^*. (We note as an aside that, if this were not the case, the two turning points would not be linear and the WKB method would not be applicable anyway). Also, since the leading term in each of the expansions of $\overline{\partial w*(R*)}/\partial a_1^*$ about R_1^* and R_2^* are independent of $R*$, the variation of $\left[\overline{\partial w*(R*)}/\partial a_1^*\right] Q*^{-\frac{1}{2}}$ with $R*$ in the regions near the turning points is the same as that of $Q*^{-\frac{1}{2}}$. Since the integration of functions varying as $(R*-R_1^*)^{-\frac{1}{2}}$ and $(R_2^*-R*)^{-\frac{1}{2}}$ leads to ones varying according to the corresponding positive powers, the contribution of the parts of the integrals arising from the regions close to the turning points approach a limiting value of zero. Therefore, in spite of the presence of the infinities in the integrands, the integrals themselves are finite and the use of (3.12) is justified.

However, even though (3.12) is valid in itself, the presence of the infinities in the integrands makes it impossible to obtain the second derivative $d^2\lambda_{1,n}^*/da_1^{*2}$ by straightforward differentiation of this expression. Differentiation of (3.12), as it stands, would require that we find:

$$\frac{d}{da_1^*} \int_{R_1^*}^{R_2^*} \left[\frac{\partial w*(R*)}{\partial a_1^*}\right] Q*^{-\frac{1}{2}} dR* \tag{3.13}$$

and

$$\frac{d}{da_1^*} \int_{R_1^*}^{R_2^*} Q^{*-\frac{1}{2}} dR^* \qquad (3.14)$$

Let us consider the second of these quantities, (3.14). Carrying out the differentiation we should obtain:

$$\frac{d}{da_1^*} \int_{R_1^*}^{R_2^*} Q^{*-\frac{1}{2}} dR^* = -\frac{1}{2}\left(\frac{8\pi^2}{A^{*2}}\right) \int_{R_1^*}^{R_2^*} \left[\frac{d\lambda_{1,n}^*}{da_1^*} - \frac{\partial \overline{W(R^*)}}{\partial a_1^*}\right] Q^{*-\frac{3}{2}} dR^*$$
$$+ \frac{dR_1^*}{da_1^*}\left[Q^{*-\frac{1}{2}}\right]_{R^*=R_1^*} + \frac{dR_2^*}{da_1^*}\left[Q^{*-\frac{1}{2}}\right]_{R^*=R_2^*} \qquad (3.15)$$

Since R_1^* and R_2^* are the zeros of Q^*, the second and third terms in this expression are immediately seen to be of infinite absolute value. The first term is also ill behaved, by virtue of the appearance of $Q^{*-3/2}$ in the integral, which in contrast to integrals involving $Q^{*-\frac{1}{2}}$, has infinite rather than zero contributions in the regions of the turning points. Similarly, formal differentiation in (3.14) leads to terms of infinite value and we conclude that the use of (3.12) must lead to an undefined value for $d^2\lambda_{1,n}^*/da_1^{*2}$.

In view of this, we make use of a suggestion by Munn (private communication) that application of Gauss-Mehler quadrature (see Kopal 1955, p.381 et seq.) to the evaluation of the integrals appearing in (3.12) avoids consideration of infinities in the integrands. Accordingly we make the substitution:

$$R^* = \frac{(R_2^* - R_1^*)}{2} \cos \Theta + \frac{(R_2^* + R_1^*)}{2} \qquad (3.16)$$

(3.14) now becomes:

$$\frac{d\lambda^*_{1,n}}{da^*_1} = \frac{\int_0^\pi \left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a^*_1} Q^{*-\frac{1}{2}} \right]_{R^*=A^*c+B^*} \sin\Theta \, d\Theta}{\int_0^\pi \left[Q^{*-\frac{1}{2}} \right]_{R^*=A^*c+B^*} \sin\Theta \, d\Theta} \qquad (3.17)$$

where, for convenience, A* has been written for $(R^*_2-R^*_1)/2$, B* for $(R^*_1+R^*_2)/2$ and c for $\cos\Theta$. The first non-vanishing terms in the expansions about $\Theta = 0$ and $\Theta = \pi$ of both the integrands in (3.17) are independent of Θ and, therefore, both functions are finite at the limits of the integration. Further, the substitution (3.16) does not give rise to infinities at any other point in the range of integration. Now, differentiation of (3.17) with respect to a^*_1 gives a defined expression for $d^2\lambda^*_{1,n}/da^*_1$. This is:

$$\frac{d^2\lambda^*_{1,n}}{da^{*2}_1} = \left\{ \left\{ \frac{1}{2} \int_0^\pi \left[\frac{d\lambda^*_{1,n}}{da^*_1} - \left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a^*_1} \right]_{R^*=A^*c+B^*} \right] \left\{ \frac{8\pi^2}{\Lambda^{*2}} \frac{d\lambda^*_{1,n}}{da^*_1} + \frac{2(1+\frac{c}{})}{(A^*c+B^*)} \frac{\partial(A^*c+B^*)}{\partial a^*_1} \right] \right. \right.$$

$$- \frac{8\pi^2}{\Lambda^{*2}} \frac{\partial}{\partial a^*} \left[\overline{\omega^*(R^*)} \right]_{R^*=A^*c+B^*} \right\} \left[Q^{*-3/2} \right]_{R^*=A^*c+B^*} \sin\Theta \, d\Theta$$

$$+ \int_0^\pi \left\{ \frac{\partial}{\partial a^*} \left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a^*_1} \right]_{R^*=A^*c+B^*} \right\} \left[Q^{*-\frac{1}{2}} \right]_{R^*=A^*c+B^*} \sin\Theta \, d\Theta \right\}$$

$$\times \left\{ \int_0^\pi \left[Q^{*-\frac{1}{2}} \right]_{R^*=A^*c+B^*} \sin\Theta \, d\Theta \right\}^{-1}$$

$$(3.18)$$

where the quantities $\frac{\partial}{\partial a^*_1} \left[\overline{\omega^*(R^*)} \right]_{R^*=A^*c+B^*}$ and

$\frac{\partial}{\partial a^*_1} \left[\frac{\partial \omega^*(R^*)}{\partial a^*_1} \right]_{R^*=A^*c+B^*}$ are given by:

$$\frac{\partial}{\partial a^*} \left[\omega^*(R^*) \right]_{R^*=A^*c+B^*} = \left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a^*_1} \right]_{R^*=A^*c+B^*} + \frac{\partial(A^*c+B^*)}{\partial a^*_1} \left[\frac{\partial \overline{\omega^*(R^*)}}{\partial R^*} \right]_{R^*=A^*c+B^*} \quad (3.18a)$$

and

$$\frac{\partial}{\partial a_1^*}\left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a_1^*}\right]_{R^*=A^*_c+B^*}$$

$$=\left[\frac{\partial^2 \overline{\omega^*(R^*)}}{\partial a_1^{*2}}\right]_{R^*=A^*_c+B^*} + \frac{\partial(A^*_c+B^*)}{\partial a_1^{*2}}\left[\frac{\partial \overline{\omega^*(R^*)}}{\partial R^*}\right]_{R^*=A^*_c+B^*} \quad (3.18b)$$

Since:

$$\frac{\partial(A^*_c+B^*)}{\partial a_1^*} = \left(\frac{dR_2^*}{da_1^*} - \frac{dR_1^*}{da_1^*}\right)\cos\theta + \left(\frac{dR_2^*}{da_1^*} + \frac{dR_1^*}{da_1^*}\right)$$

we also require the formulation of dR_1^*/da_1^* and dR_2^*/da_1^*.
Remembering that R_1^* and R_2^* are the solutions of:

$$Q^* = \frac{8\pi^2}{\Lambda^{*2}}\lambda_{1,n}^* - \left(l+\frac{1}{2}\right)^2 \frac{1}{R^{*2}} - \frac{8\pi^2}{\Lambda^{*2}}\overline{\omega^*(R^*)} = 0$$

the derivatives are given by:

$$\frac{dR_t^*}{da_1^*} = \frac{\frac{8\pi^2}{\Lambda^{*2}}\left\{\left[\frac{\partial \overline{\omega^*(R^*)}}{\partial a_1^*}\right]_{R^*=R_t^*} - \frac{d\lambda_{1,n}^*}{da_1^*}\right\}}{\left\{\frac{2(l+\frac{1}{2})^2}{R_t^{*3}} - \frac{8\pi^2}{\Lambda^{*2}}\left[\frac{\partial \overline{\omega^*(R^*)}}{\partial R^*}\right]_{R^*=R_t^*}\right\}} \quad (t=1,2)$$

$$\hspace{10cm}(3.18c)$$

In view of the substitution (3.16) required to
give a usable expression for $d^2\lambda_{1,n}^*/a_1^{*2}$, in the
calculations described here, all the integrals required
have been evaluated using the Gauss-Mehler quadrature
formula:

$$\int_0^\pi f(\cos\theta)d\theta = \frac{\pi}{N}\sum_{j=1}^{n} f\left[\cos\left(\frac{2j-1}{2n}\right)\pi\right] \quad (3.19)$$

where 2n is the number of intervals over which integ-
ration is performed.

Since $\sin\theta = (1-\cos^2\theta)^{\frac{1}{2}}$, the integrals appearing
in (3.17) and (3.18) are clearly in the form required
for the application of formula (3.19). To transform
(3.9) to the correct form we again make use of the

substitution (3.16) to give:

$$\int_0^{\pi} [Q^{*\frac{1}{2}}]_{R^* = A^* \mathcal{C} + \mathcal{B}^*} \sin\Theta d\Theta = \left(n + \tfrac{1}{2}\right)\pi \tag{3.20}$$

Now, numerical solution of this equation gives the value
of $\lambda^*_{1,n}$ for the chosen pair potential ϕ and any given
values of l, n, a^*_1 and Λ^*. Use of this value of $\lambda^*_{1,n}$
in (3.17) leads to the value of $d\lambda^*_{1,n}/da^*_1$ and sub-
stitution of the calculated quantities $\lambda^*_{1,n}$ and
$d\lambda^*_{1,n}/da^*_1$ in (3.18) gives the value of $d^2\lambda^*_{1,n}/da^{*2}_1$.
Further details of the numerical procedure used are
left until Chapter 4.

Chapter 4

Pairwise Additive Cell Model Calculations for Solid Neon,
Argon, Krypton and Xenon

The evaluation of characteristic parameters

Before we can perform detailed calculations of the
physical properties of the inert gases, we require
reliable values of the adjustable parameters appearing
in the pair interaction, $\phi(r)$, for each gas. In the
absence of a unique determination of $\phi(r)$ by the second
virial coefficient of the gas alone (Keller and Zumino
1959), it appears necessary to turn to a consideration
of the solid state itself if unambiguous values of
the parameters suitable for solid state investigations
are to be obtained. This is especially the case if we
wish to study, for example, the variation of the
lattice constant of the solid with temperature, which
is so small that the values of the parameters used
become almost critical (Hillier and Walkley 1965,
Jenkins and Walkley 1965, Jenkins 1966).

In contrast to the second virial coefficient,
which by definition represents the interaction of
only two molecules outside the perturbing field of
all others in the system, the properties of the solid
state are multiparticle in nature and require some
assumption as to the additivity of the potential in
their calculation. The assumption generally made is
that the total potential of the system can be taken
as the sum of all pair interactions and it is on this
basis that the cell model treatment described in

Chapter 2 is developed. For the purposes of the present
chapter, we take this assumption to be valid, but recog-
nise that its use in the evaluation of potential parameters
probably leads to an effective $\emptyset(r)$, which reflects the
influence of non-additive effects in the solid, rather
than a true pair function. Since we test this effective
function by calculations performed under the same assump-
tion, our approach is at least self consistent and,
so long as multibody effects are not overbearing, the
use of such an approach would be expected to provide
a fair indication of how well a chosen potential function
represents the true inert gas pair interaction. The
test of whether this is the case or not comes in the
following chapter, where the influence of many body
effects in the inert gas solids is subjected to greater
scrutiny. For the present, we remark only that, if
solid state data is to be used at all for characteris-
ation purposes, it is considered desirable that such
data should be used on its own rather than in conjunc-
tion with second virial and other gaseous data (for
examples of such an approach, see Corner 1948, Mason
and Rice 1954). In view of the comments made above,
not only is the use of such a mixture of solid state
and gaseous data inconsistent in itself, but also
precludes the consideration of non-additivity in the
solid by comparing solid state parameters with second
virial parameters (see Chapter 5).

The solid state data most commonly used for charac-
terisation purposes are $L_o(0)$, the crystal sublimation
energy at $0^{\circ}K$ and effectively zero pressure and $a_{oo}(0)$,
the lattice constant (or, equivalently, $V_o(0)$ the molar
volume) of the crystal at the same temperature and pressure
(Corner 1948, Mason and Rice 1954, Zucker 1956, Hillier,

Islam and Walkley 1965). For two parameter potentials, such as the LJ 12:6, these suffice to determine the interaction completely, the two appropriate equations being:

$$-L_o(0)/(N\varepsilon) = \left[\chi^*_{o,o} + \tfrac{1}{2}w^*(o)\right]_{a_o^* = a_{oo}^*}(0) \qquad (4.1)$$

and

$$0 = \left[d\chi^*_{o,o}/da_1^* + \tfrac{1}{2}(dw^*(o)/da_1^*)\right]_{a_o^* = a_{oo}^*}(0) \qquad (4.2)$$

(4.1) is given by setting $-L_o(0)$ equal to F_o, the crystal free energy at $0^\circ K$ for $a_o = a_{oo}(0)$ and transforming to reduced variables. (4.2) is given by partial differentiation of F_o with respect to volume at constant temperature, followed by setting $(\partial F_o/\partial V)_T (=-p_o)$ to zero for $a_o = a_{oo}(0)$, substituting $Na_1^3/2^{\frac{1}{2}}$ for V (see (2.13)) and transforming to reduced variables. It is remembered that a_o is related to a_1, the nearest neighbour distance in the crystal, by $a_o/2^{\frac{1}{2}} = a_1$ (see (2.14)).

For the EXP-6 function, with its three parameters, ε, r_m and α, a third property is required in addition to $L_o(0)$ and $a_{oo}(0)$ for a complete characterisation. In the light of recent single crystal, X-ray determinations of the isothermal compressibility $(\chi_T = -(1/V)(\partial V/\partial p)_T)$ of solid neon, argon and krypton by Simmons and co-workers — in the first place these results were privately communicated to us, but have since been published (Peterson, Batchelder and Simmons 1966, Batchelder, Losee and Simmons 1967, Urvas, Losee and Simmons 1967) — it was decided to use $\chi_{To}(0)$, the $0^\circ K$, zero pressure value of this quantity, as the third property for these substances. Using $L_o(0)$, $a_{oo}(0)$ and $\chi_{To}(0)$, ε, r_m

and α are given by (4.1) and (4.2), together with:

$$\frac{r_m^3}{\chi_{To}(0)\,\epsilon} = \left\{ \frac{2^{\frac{1}{2}}}{9a_1^*} \left[\frac{d^2\lambda_{o,o}^*}{da_1^{*2}} + \frac{1}{2}\frac{d^2w^*(o)}{da_1^{*2}} \right] \right\}_{a_o^* = a_{oo}^*(0)} \qquad (4.3)$$

(4.3) is obtained by double differentiation of F_o with respect to volume at constant temperature, followed by multiplication by V and putting $V(\partial^2 F_o/\partial V^2)_T = -V(\partial p_o/\partial V)_T = 1/\chi_{To}(0)$ for $a_o = a_{oo}(0)$. The equation is written in terms of a_1^* by substituting $V = Na_1^3/2^{\frac{1}{2}}$, transforming to reduced variables and putting:

$$\frac{2^{\frac{1}{2}}}{3a_1^{*2}} \left\{ \frac{d\lambda_{o,o}^*}{da_1^*} + \frac{1}{2}\frac{dw^*(o)}{da_1^*} \right\} = \frac{-p_o r_m^3}{\epsilon} = 0 \text{ for } a_o = a_{oo}(0)$$

For xenon, we turned to the bulk density p-V measurements of Packard and Swenson (1963) for a suitable third property. This data allows a value of $\chi_{To}(0)$ to be derived, but, owing to the lower accuracy of the experimental method and the fitting procedure used to obtain $\chi_{To}(0)$, this does not approach the accuracy of the single crystal values for neon, argon and krypton. Therefore, we used the zero point isotherm of xenon and chose, as the third property, $a_{oo}(p_o)$, the value of the lattice constant at $0°K$ and the highest pressure, $p_o(=20\text{kbar})$, under which measurements were carried out. In this case the appropriate equations are (4.1), (4.2) and:

$$(-p_o r_m^3)/\epsilon = \left\{ (2^{\frac{1}{2}}/3a_1^{*2})\left[d\lambda_{o,o}^*/da_1^* + \tfrac{1}{2}(dw^*(o)da_1^*) \right] \right\}_{a_o^* = a_{oo}^*(p_o)}$$

$$(4.4)$$

where p_o=20kbar. (4.4) is the non-zero pressure equivalent of (4.2).

A complete list of the various experimental data which we used is given in Table 1.

Table 1

Experimental zero point data used for characterisation purposes

Substance	$L_o(0)$ (cal mole^{-1})	$a_{oo}(0)$ (Å)	$\chi_{To}(0)$ (cm^{2}dyne^{-1})×10^{11}	a_{oo}(20kbar) (Å)
Neon	448[a]	4.4637[d]	9.0[d]	-
Argon	1846[b]	5.3111[e]	3.75[e]	-
Krypton	2666[b]	5.6459[f]	2.91[f]	-
Xenon	3828[c]	6.131[g]	-	5.658[h]

a) Clusius, Flubacher, Piesbergen, Schleich and Sperandio (1960);

b) Beaumont, Chihara and Morrison (1961);

c) Whalley and Schneider (1955);

d) Batchelder, Losee and Simmons (1967);

e) Peterson, Batchelder and Simmons (1966);

f) Urvas, Losee and Simmons (1967);

g) quoted by Pollack, (1964) from the results of Sears and Klug (1962) and Bolz and Mauer (unpublished work);

h) Packard and Swenson (1963).

The results in d), e) and f) were communicated to us prior to their publication.

For the solution of each appropriate set of simultaneous equations, we used the extended Newton-Raphson technique described in Appendix 3. In conjunction with the WKB approximation for the evaluation of $\lambda^*_{0,0}$ and its derivatives, this provides a simple and rapid method of evaluating the parameters to any desired degree of accuracy, so long as reasonable first guesses at the values of the parameters are possible. It is eminently suitable for machine computation and has been programmed by the author for the characterisation of both the LJ 12:6 function, using (4.1) and (4.2), and of the EXP-6 function, using either (4.1), (4.2) and (4.3) or (4.1), (4.2) and (4.4).

A brief outline of the numerical procedure used by the programs is as follows. The values of the appropriate experimental zero point properties, the first guesses at the parameters and the molecular weight of the substance under investigation are input as data. This data is used to calculate the first approximation to the quantum parameter Λ^* (see (2.28)) and the reduced nearest neighbour distance a^*_1 corresponding to the value of $a_{00}(0)$. From this value of a^*_1, values of $w^*(o)$, $dw^*(o)/da^*_1$ and, if necessary, $d^2w^*(o)/da^{*2}_1$ are calculated. For the LJ 12:6 function, expression (2.30) is used for this purpose, together with the values of $S(12)$ and $S(6)$ given by Kihara and Koba (1952). For the EXP-6 function, the appropriate expression is (2.32), the terms corresponding to attraction in $\phi(r)$ being calculated using the same value of $S(6)$ as that used for the LJ 12:6 function and those corresponding to repulsion by summing over sufficient shells of neighbours to give a specified

accuracy.

The next step is the calculation of $\lambda^*_{0,0}$, $d\lambda^*_{0,0}/da^*_1$ and, if necessary, $d^2\lambda^*_{0,0}/da^{*2}_1$ for the value of a^*_1 corresponding to $a_0 = a_{00}(0)$. In these calculations, $\overline{w^*(R^*)}$ and its derivatives are calculated for a number of shells of neighbours specified in the input data, the expressions used to give $\overline{w^*(R^*)}$ for the LJ 12:6 and EXP-6 functions being (2.35) and (2.37a) respectively. Using a first approximation to $\lambda^*_{0,0}$, either read in as data or calculated in the program through the harmonic approximation, the turning points R^*_1 and R^*_2 are roughly located by scanning the function Q^* (see (3.9a) and (3.9b)), noting where it changes sign and applying the method of "similar triangles". The values of R^*_1 and R^*_2 are then refined to a specified accuracy by applying a Newton-Raphson iterative technique to the solution of equation (3.9b). Using the refined values of the turning points, a better value of $\lambda^*_{0,0}$ is calculated by the application of a Newton-Raphson technique to equation (3.20). The necessary integrations are carried out using the Gauss-Nehler quadrature formula (3.19) for some specified number of intervals. The values of the turning points appropriate to the new value of $\lambda^*_{0,0}$ are calculated from the old values of R^*_1 and R^*_2 by again applying a Newton-Raphson technique to equation (3.9b). The new values of R^*_1 and R^*_2 are then employed in the calculation of an even better value of $\lambda^*_{0,0}$. The procedure is repeated until $\lambda^*_{0,0}$ is iterated to some specified accuracy. $d\lambda^*_{0,0}/da^*_1$ is then calculated using (3.17) and, if required, $d^2\lambda^*_{0,0}/da^{*2}_1$ using (3.18), the necessary integrations being performed in the same manner as those in the

calculation of $\lambda^*_{o,o}$. In the case of the character-
isation of the EXP-6 function for xenon, $dw^*(o)/da^*_1$
and $d\lambda^*_{o,o}/da^*_1$ are then calculated in the same way
as before, but for the value of a^*_1 corresponding to
$a_o = a_{oo} (p_o = 20\text{kbar})$.

Now - making use of the notation used in Appendix 3
- the quantities $F_i(P_{1o},\ldots,P_{no})$ ($i=1,\ldots,n$) are
calculated for the appropriate set of equations. By
adjusting in turn the first guess at each parameter
and repeating the calculations, the difference quotients
$(\Delta F_i/\Delta P_j)_o$ ($i=1,\ldots,n$; $j=1,\ldots,n$) are evaluated and,
thence, by the solution of equations (A.3.4), better
values of the parameters obtained. The whole procedure
is repeated until the parameters have been iterated to
a specified accuracy.

In our calculations the parameters were iterated
such that each one was accurate to at least $10^{-2}\%$.
The iteration accuracy for the evaluation of the turning
points R^*_1 and R^*_2 was $10^{-3}\%$ and that for the evaluation
of $\lambda^*_{o,o}$, $10^{-2}\%$. The integrals required were calculated
using 10 Gauss-Mehler quadrature intervals, which
proved capable of giving $\overline{\lambda^*_{o,o}}$ to an accuracy of $10^{-3}\%$.
The calculation of $\overline{w^*(R^*)}$ was for three shells of
neighbours, it being found that the use of "three
shell" parameters in the "three shell" calculation of
thermodynamic properties (see following section but one)
leads to results insignificantly different from calcul-
ations involving more distant neighbours. In the
characterisation of the EXP-6 function, the repulsive

parts of the static lattice terms were calculated to
an accuracy of not less than $10^{-2}\%$.

The results of the calculations for the EXP-6
function are given in Table 2 and those for the
LJ 12:6 function in Table 3.

Table 2

EXP-6 parameters derived from the pairwise additive consideration of the solid state at 0°K

Substance	$\varepsilon(\text{erg})\times10^{15}$	$r_m(\text{Å})$	α	$\Lambda^* = h/\left[(m\varepsilon)^{\frac{1}{2}}r_m\right]$
Neon	5.462	3.090	16.13	0.5012
Argon	17.14	3.808	14.23	0.1632
Krypton	23.89	4.062	14.84	0.08946
Xenon	32.77	4.444	13.55	0.05578

Table 3

LJ 12:6 parameters derived from the pairwise additive consideration of the solid state at 0°K

Substance	$\varepsilon(\text{erg})\times10^{15}$	σ (Å)	$\Lambda^* = h/\left[(m\varepsilon)^{\frac{1}{2}}\sigma\right]$
Neon	5.015	2.774	0.5826
Argon	16.50	3.401	0.1862
Krypton	22.75	3.636	0.1024
Xenon	31.98	3.960	0,06337

The EXP-6 and LJ 12:6 potentials given by these
parameters are plotted as the full and dashed curves
respectively in Figures 4, 5, 6, 7.

Fig.4. Neon - pair potential energy, ϕ, divided by Boltzmann constant, k, as a function of intermolecular distance, r.

ϕ/k
($^\circ$K)

Full curve - EXP-6 function character-ised from solid state data assuming pairwise additivity.
Dashed curve - LJ 12:6 function char-acterised from solid state data assum-ing pairwise additivity.
Dashed-dotted curve - EXP-6 function characterised from solid state data with the triplet dispersion energy included in the static lattice.
Dashed-double dotted curve - EXP-6 function characterised from the sec-ond virial coefficient of the gas.

Fig.5. Argon – pair potential energy, ⌀, divided by Boltzmann's
constant,.k, as a function of intermolecular
distance, r.

Full curve – EXP-6 function characterised
from solid state data assuming pairwise
additivity.
Dashed curve – LJ 12:6 function character-
ised from solid state data assuming
pairwise additivity.   r(Å)

Dashed-dotted curve – EXP-6 function
characterised from solid state
data with triplet dispersion
energy included in the sta-
tic lattice.

Dashed-double dotted
curve – EXP-6 function
characterised from
the second virial
coefficient of the
gas.

Fig. 6. Krypton – pair potential energy, ϕ, divided by Boltzmann's constant, k, as a function of intermolecular distance, r.

Full curve – EXP-6 function character-ised from solid state data assuming pairwise additivity.

Dashed curve – LJ 12:6 function charac-terised from solid state data assuming pairwise additivity.

Dashed-dotted curve – EXP-6 function characterised from solid state data with triplet dispersion energy included in the static lattice.

Dashed-double dotted curve – EXP-6 function characterised from the second virial coeff-icient of the gas.

Fig. 7. Xenon - pair potential energy, ϕ, divided by Boltzmann constant, k, as a function of intermolecular distance, r.

Full curve - EXP-6 function characterised from solid state data assuming pairwise additivity.
Dashed curve - LJ 12:6 function characterised from solid state data assuming pairwise additivity.

Dashed-dotted curve - EXP-6 function characterised from solid state data with triplet dispersion energy included in the static lattice.

Dashed-double dotted curve - EXP-6 function characterised from the second virial coefficient of the gas.

It is seen that, in the case of each of the sub-
stances considered here, the pair potential given
by the EXP-6 function characterised by solid state
data has a somewhat lower, slightly narrower bowl
than that given by the corresponding LJ 12:6 function.

The spurious maximum in the EXP-6 potential

In Chapter 2 it was pointed out that, due to the
spurious maximum in the EXP-6 pair potential at $r^* = r^*_{max}$,
there is a similar anomaly in the reduced cell potential,
$\overline{w^*(R^*)}$, at some reduced distance, $R^* = R^*_{max}$. For this
reason, $\overline{w^*(R^*)}$ is written in two parts given by (2.37a)
and (2.37b), in direct analogy with the description of
$\phi^*(r^*)$ by (2.23a) and (2.23b).

For any given value of α, r^*_{max} is given by the smaller
root of the transcendental equation:

$$-e^{\alpha} \exp(-\alpha r^*) + r^{*-7} = 0 \qquad (4.5)$$

the larger root, $r^* = 1$, being the position of the
minimum of $\phi^*(r^*)$. (4.5) is straightforwardly solved
by numerical methods and values of r^*_{max} and $\phi^*(r^*_{max})$,
the reduced pair energy at the maximum, have been
tabulated for physically realistic values of α by
Hirschfelder, Curtiss and Bird (1954), p.34. Their
results are reproduced in Table 4.

Table 4

The position and energy of the spurious maximum in the EXP-6 potential

α	r^*_{max}	$\phi^*(r^*_{max})$
12.0	0.30247	1705
12.5	0.27304	3518
13.0	0.24697	7110
13.5	0.22382	14115
14.0	0.20319	27585
14.5	0.18476	53170
15.0	0.16825	101222

From this table we see that r^*_{max} decreases and $\phi^*(r^*_{max})$ increases with increasing α, but that, even at the lowest value of α quoted (i.e. 12), the value of r^*_{max} represents an intermolecular distance much less than the equilibrium separation and the maximum appears well up on the repulsive branch of the potential. Consequently we should expect that the presence of the maximum in $\overline{w^*(R^*)}$, if it is to have any effect at all, would influence the calculation of only the higher lying energy levels. For this reason the zero point calculations described in the previous section were performed under the assumption that the maximum could be ignored.

The value of R^*_{max} is given by the largest root of:

$$\frac{\partial w^*(R^*)}{\partial R^*} = \frac{\alpha}{\alpha-6}\left\{\frac{6e^{\alpha}}{\alpha^2}\left[\frac{A}{R^*}\cosh(\alpha R^*)-\frac{\sinh(\alpha R^*)}{R^*}\right]\right.$$
$$\left.-\frac{\alpha R(-1)}{a_1^*}\sinh(\alpha R^*) + \frac{T(4)_6}{8a_1^* R^{*2}} - \frac{T'(5)_6}{2a_1^* R^*}\right\}=0 \qquad (4.6)$$

where (4.6) is given by differentiation of (2.37a),
A being defined by (2.38), R(n) by (2.33), $T(4)_6$
by (2.36) and $T'(5)_6$ by:

$$T'(5)_6 = \sum_i z_i (a_i^*/a_1^*)^{-1} \left[(a_i^*-R^*)^{-5} - (a_i^*+R^*)^{-5} \right] \qquad (4.7)$$

The value of R_{max}^* depends on two variables, α and
a_1^*. However, for any fixed value of a_1^*, we should ex-
pect, from the results in Table 4, that the values of
R_{max}^* and $\overline{w^*(R_{max}^*)}$ would increase with increasing α and,
consequently, we restrict our attention to the lowest
value of α relevant to the present work. Using $\alpha=13.55$
(see Table 2), the rough solution of (4.6) for $a_1^*=0.8$
gives $R_{max}^* \simeq 0.61$ and $\overline{w^*(R_{max}^*)} \simeq 5 \times 10^3$ and, for $a_1^*=1.15$,
$R_{max}^* \simeq 0.98$ and $\overline{w^*(R_{max}^*)} \simeq 3 \times 10^3$. Since all the solid
state densities appropriate to the present calculations
lie between those represented by a_1^* values of 0.8 and
1.15 and since, for fixed α, both R_{max}^* and $\overline{w^*(R_{max}^*)}$
prove to be monotonic functions of a_1^*, these values
may be considered as extreme limits. We see that
in both cases the value of R_{max}^* is well beyond the
reduced cell radius, R_c^* (=0.55267a_1^* - see Chapter 2),
and the energy at the maximum is so high as to be
well above the highest energy level that sould ever
be required for an accurate evaluation of the partition
function, Z_{NQu}. In view of this we felt it quite safe
to ignore the maximum in $\overline{w^*(R^*)}$ altogether and all our
solid state calculations have been performed regarding
$\overline{w^*(R^*)}$ to be given solely by (2.37a).

The only problem that this approach introduced
was the purely numerical one of correctly locating
the turning points R_1^* and R_2^* by scanning the function

Q^*. For the EXP-6 function, Q^*, instead of changing sign only twice as it should do, has a further zero beyond R_2^* caused by the maximum in $\overline{w^*(R^*)}$. Now, it is possible, if the choice of the scanning interval is too large, that the first turning point R_1^* can be missed altogether and the turning points taken to be R_2^* and the position of the anomalous zero. This possibility was ruled out by programming the scanning sequence in such a way that the zeros of Q^* obtained are taken to be R_1^* and R_2^* only if the changes of sign across them are correct, i.e. a change from negative to positive across R_1^* and from positive to negative across R_2^*. If this is not the case, the interval is automatically increased in the program and the scanning process repeated until the correct turning points are obtained.

In the static lattice terms, there is no possibility of the spurious maximum affecting the calculations. For the densities appropriate to our calculations, the nearest neighbour distance in the crystal is always sufficiently large for the maximum to be ignored completely.

The thermodynamic properties

Having calculated the values of the parameters appearing in the LJ 12:6 and EXP-6 pair interactions and having assured ourselves that the spurious maximum in the EXP-6 function may be safely ignored in solid state calculations, the thermodynamic properties of solid neon, argon, krypton and xenon were calculated through the expressions (3.7a) - (3.7h).

Since the expressions (3.7a) - (3.7h), as they
stand, assume volume and temperature to be the independ-
ent variables, whereas experimental measurements are
invariably made at fixed pressure and temperature,
comparison between theory and experiment requires the
solution of (3.7e) for V* at fixed p* and T*. Use of
this value of V* together with the appropriate value
of T* then gives other thermodynamic properties. The
solution of (3.7e) for V* may be performed graphically
(Hillier and Walkley 1965, Jenkins 1966), but in the
work described here use was made of a Newton-Raphson
iterative technique. This allows the calculations to
be peformed completely by machine and to any desired
degree of accuracy. The iteration formula may be
written:

$$V_{k+1}^* = V_k^* \left\{ 1 + \chi_T^*(V_k^*, T^*) \left[p^* - p^*(V_k^*, T^*) \right] \right\} \qquad (4.8)$$

where V_k^* and V_{k+1}^* are, respectively, kth and (k+1)th
approximations to the reduced volume V* corresponding
to a reduced pressure p* and a reduced temperature T*,
and $p^*(V_k^*, T^*)$ and $\chi_T^*(V_k^*, T^*)$ are calculated through
(3.7e) and (3.7f) for a reduced volume V_k^* and reduced
temperature T*.

The numerical procedure for the calculation of
the thermodynamic properties was incorporated in the
same computer programs as were used for the determination
of the potential parameters. It is briefly summarised
below.

The values of p* and T* for which calculations
are to be performed are input as datum numbers, together

with an approximate value of V^*, the value of the quantum
parameter Λ^* and, in the case of EXP-6 calculations, the
value of the parameter α. After calculating the value
of a_1^* corresponding to the input value of V^*, the static
lattice terms, $w^*(o)$, $dw^*(o)/da_1^*$ and $d^2w^*(o)/da_1^{*2}$ are
evaluated from whichever of (2.30) and (2.32) is approp-
riate, using a similar approach to that employed for the
calculation of the static lattice terms in the character-
isation procedure. Following this, the derivatives of
$w^*(o)$ with respect to a_1^* are converted to those with
respect to V^* by use of relations of the same form
as (3.10) and (3.11).

Now the reduced energy levels $\lambda_{1,n}^*$ ($1=0,1,2,\ldots$;
$n=0,1,2,\ldots$) and their first and second derivatives
with respect to V^* are calculated for the value of
a_1^* corresponding to the input value of V^*, using
whichever of (2.35) and (2.37a) is appropriate for the
evaluation of $\overline{w^*(R^*)}$, this quantity being calculated
for a number of shells of neighbours specified in the
input data. For any $(1,n)$, the values of $\lambda_{1,n}^*$,
$d\lambda_{1,n}^*/da_1^*$ and $d^2\lambda_{1,n}^*/da_1^{*2}$ are calculated through
the WKB relations (3.20), (3.17) and (3.18), using the
same iteration procedure for the solution of (3.20) and
the same method of quadrature as was employed for the
calculation of the $1=0$, $n=0$ energy level terms in
the determination of the potential parameters. The
derivatives of $\lambda_{1,n}^*$ with respect to a_1^* are transformed
to the corresponding ones with respect to V^* by use of
(3.10) and (3.11).

The organisation of the computation of the energy
level terms is such that calculations are performed

for $n=0,1,2,\ldots$etc. keeping l constant at $0,1,2,\ldots$etc. in turn. An approximate value of $\lambda^*_{0,0}$ is either input as a datum number or calculated in the program using the harmonic approximation. The first approximation to $\lambda^*_{1,0}$ is calculated by multiplying the previously iterated value of $\lambda^*_{0,0}$ by a constant specified in the input data. For $l>1$, the first approximation to $\lambda^*_{l,0}$ is given by linear extrapolation of the values of $\lambda^*_{l-2,0}$ and $\lambda^*_{l-1,0}$. The approximate values of the turning points, R^*_1 and R^*_2 corresponding to $\lambda^*_{l,0}$ for each value of l are calculated by scanning the function Q^* (see (3.9a)), noting where it changes sign and applying the "method of similar triangles". For $n>0$, the approximate value of $\lambda^*_{l,n}$ is taken as the previously iterated value of $\lambda^*_{l,n-1}$ and the approximate values of R^*_1 and R^*_2 as those corresponding to $\lambda^*_{l,n-1}$. For each l value, the increase of n is terminated when, for some value of n, $\lambda^*_{l,n}$ is greater than or equal to a quantity, λ^*_{max}, input as a datum number. When this is the case, the eigenvalues and their volume derivatives corresponding to the current value of l are stored, n reset to zero, l increased by unity, and the calculations continued. The complete termination of eigenvalue calculations occurs when, for some value of l, $\lambda^*_{l,0} \geqslant \lambda^*_{max}$. Following this, the values of $\lambda^*_{l,n}$, $d\lambda^*_{l,n}/dV^*$ and $d^2\lambda^*_{l,n}/dV^{*2}$ ($l=0,1,2,\ldots$; $n=0,1,2,\ldots$) are removed from store, the appropriate sums over l and n formed and checked to be accurate to a specified accuracy limit and the iteration formula (4.8) applied to give a better value of V^*.

The above procedure is repeated until V^* is iterated to an accuracy specified in the input data, the first approximation to $\chi^*_{o,o}$ for the kth value of reduced volume, V^*_k, being taken as the value of $\chi^*_{o,o}$ appropriate to the (k-1)th value, V^*_{k-1}. Using the values of $\chi^*_{1,n}$, $d\chi^*_{1,n}/dV^*$ and $d^2\chi^*_{1,n}/dV^{*2}$ (l=0,1,2,...; n=0,1,2,3,...) appropriate to the final value of V^*, other thermodynamic properties are evaluated by forming the appropriate sums over l and n and using expressions (3.7a) to (3.7h).

The results of the calculations for the EXP-6 and LJ 12:6 potential functions are tabulated in Appendix 4 and plotted as the full and dashed curves respectively in Figs. 8a-8g for neon, 9a-9g for argon, 10a-10g for krypton and 11a-11g for xenon. In each case, the figures labelled a-f give plots of the zero pressure values of the lattice constant, a_o, isothermal compressibility, $\chi_T(=-(1/V)(\partial V/\partial p)_T)$, volume expansivity, $\beta(=1/V)(\partial V/\partial T)_p)$, isochoric specific heat, C_v, isobaric specific heat, C_p, and entropy, S, respectively as functions of temperature, T. Those labelled g give the variation of molar volume, V, normalised by the zero pressure value, V(0), with pressure, p, at a specified temperature - 4°K for neon, 77°K for argon and krypton and 150°K for xenon. The reason a plot of V/V(0) versus p is given rather than one of V versus p, is that the removal of temperature dependence at zero pressure by normalisation with respect to V(0) gives a clearer picture of the effect of pressure.

The results were obtained by determining sufficient eigenvalues to cause the required sums over l and n to converge to an accuracy of at least 10^{-3}% and using an iteration accuracy of 10^{-2}% for the evaluation of V*. They are consistent with the results of the characterisation calculations in that the parts in the EXP-6 static lattice terms corresponding to repulsion were calculated over sufficient shells of neighbours to give an accuracy of 10^{-2}% and the reduced eigenvalues were iterated to an accuracy of 10^{-2}% using values of the turning points iterated to 10^{-3}%. Again 10 Gauss-Mehler quadrature intervals proved sufficient for the accurate evaluation of the integrals required and the results are for three shells of neighbours included in the calculation of $\overline{w^*(R^*)}$, which, as mentioned before, is sufficient to lead to results insignificanly different from those given by calculations involving more distant neighbours.

Before detailed calculations of thermodynamic properties were undertaken, the accuracy of the WKB solution of the EXP-6 radial equation was verified by comparison with the results given by the "exact" finite difference technique given by Hillier, Islam and Walkley (1965) and fully described in Appendix 2. The comparison was made for solid neon at the triple point, the finite difference calculations being performed by use of the parameters given in Table 1 and the value of V* given by WKB calculations. It was found that agreement between the WKB and finite difference eigenvalues was close for all l and n values considered (l=0-12, n=0-6) and that the accuracy of the WKB approximation, as expected from

its asymptotic nature (see Chapter 3), increased with increasing l and n. For l=0,n=0 the difference between the two results was 1%, for l=0,n=6, 0.1% and for l=12,n=0, 0.06%. Differences of this order in the eigenvalues lead to insignificant changes in the values of thermodynamic properties which are not dependent on volume derivatives, the difference between the results of the two calculations for U, S and C_v being only 0.5%, 0.25% and less than 0.1% respectively. Since the effect of anharmonicity is most pronounced in solid neon at its triple point and it is known that the WKB method becomes progressively more exact as the vibrations become more harmonic (see Chapter 3), we may be sure that the results from our other WKB calculations are accurate within the limits of the cell theory. As mentioned in Chapter 3, the accuracy of the WKB approximation in LJ 12:6 calculations has been established by Hillier and Walkley (1964).

The experimental data plotted in Figures 8a-11g are tabulated in Appendix 5 and are, in the author's opinion, the most reliable at present available. For the sources from which they are taken, the reader is referred either to the figures themselves or to Appendix 5. The experimental points in graphs of C_v and S versus T do not come directly from experimental measurements but are calculated through the thermodynamic relations:

$$C_p = C_v + \beta^2 TV/\chi_T \tag{4.9}$$

and

$$S = \int_0^T (C_p/T)dT \tag{4.10}$$

respectively, using experimental values of C_p, β, V and χ_T. Since it was felt that, in the case of krypton and xenon, the experimental data available are not sufficiently accurate for a reasonable estimate of $\beta^2 TV/\chi_T$ to be made, no experimental points are given in the C_v versus T plots for these substances. Experimental error limits have been indicated where these are quoted and appreciable on the scale of the figures. For the moment, the reader is asked to ignore the dashed-dotted curves in Figs. 8a-11g.

Fig. 8a.   Solid neon — lattice constant, a_o, as a function
of temperature, T, at zero pressure

Full curve — EXP-6 cell model assuming pairwise
additivity.
Dashed curve — LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve — EXP-6 cell model with
triplet dispersion energy included in the
static lattice.
⊙ — Experimental data of Batchelder, Losee
and Simmons (1967).
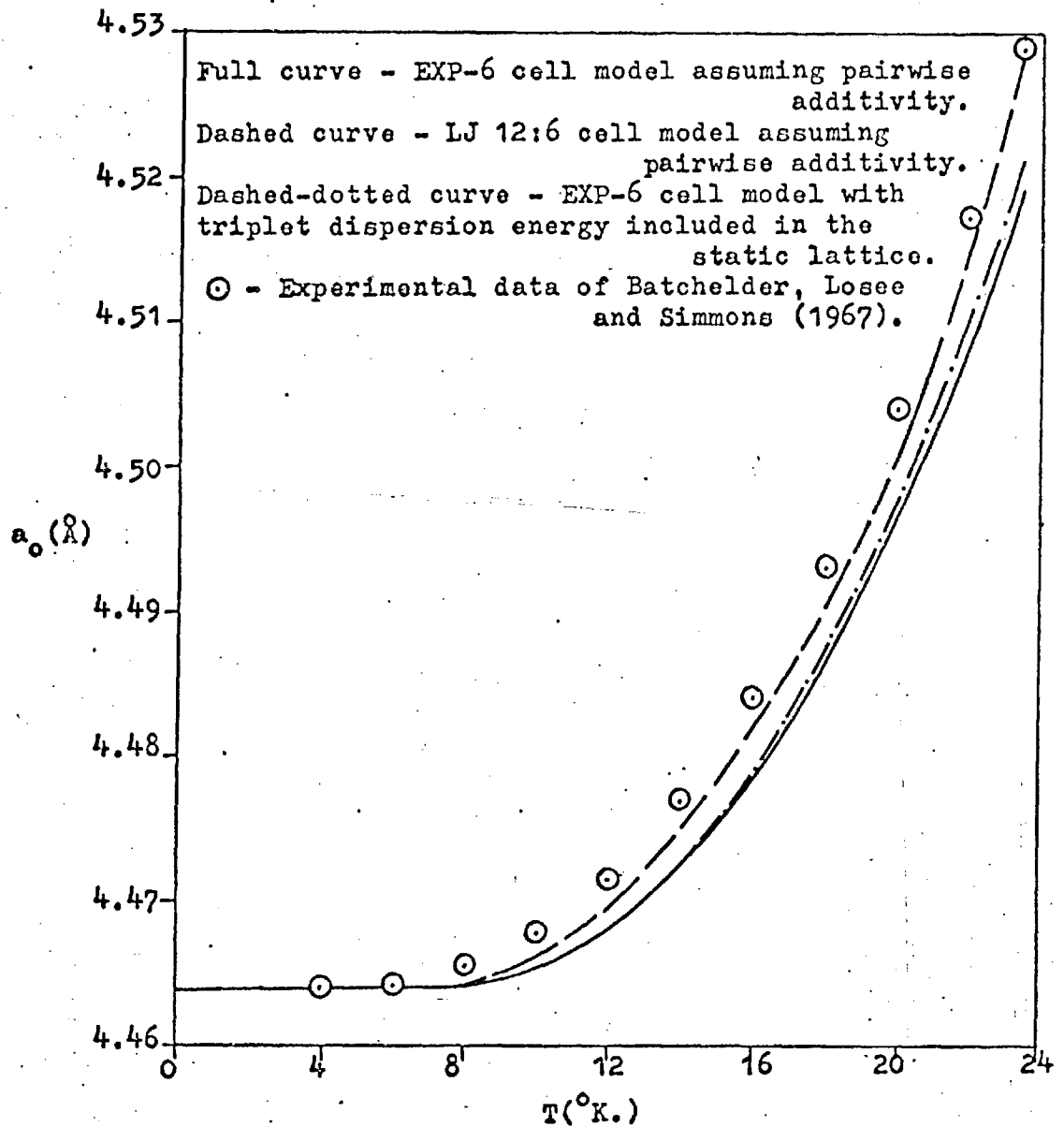
Fig.8b. Solid neon – isothermal compressibility, χ_T, as a function of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming
pairwise additivity.
Dashed curve – LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve – EXP-6 cell model
with triplet dispersion energy included
in the static lattice.
⊙ – Experimental data of Batchelder,
Losee and Simmons (1967).

χ_T
$(cm^2 dyne^{-1})$
$\times 10^{10}$

$T(^{o}K.)$
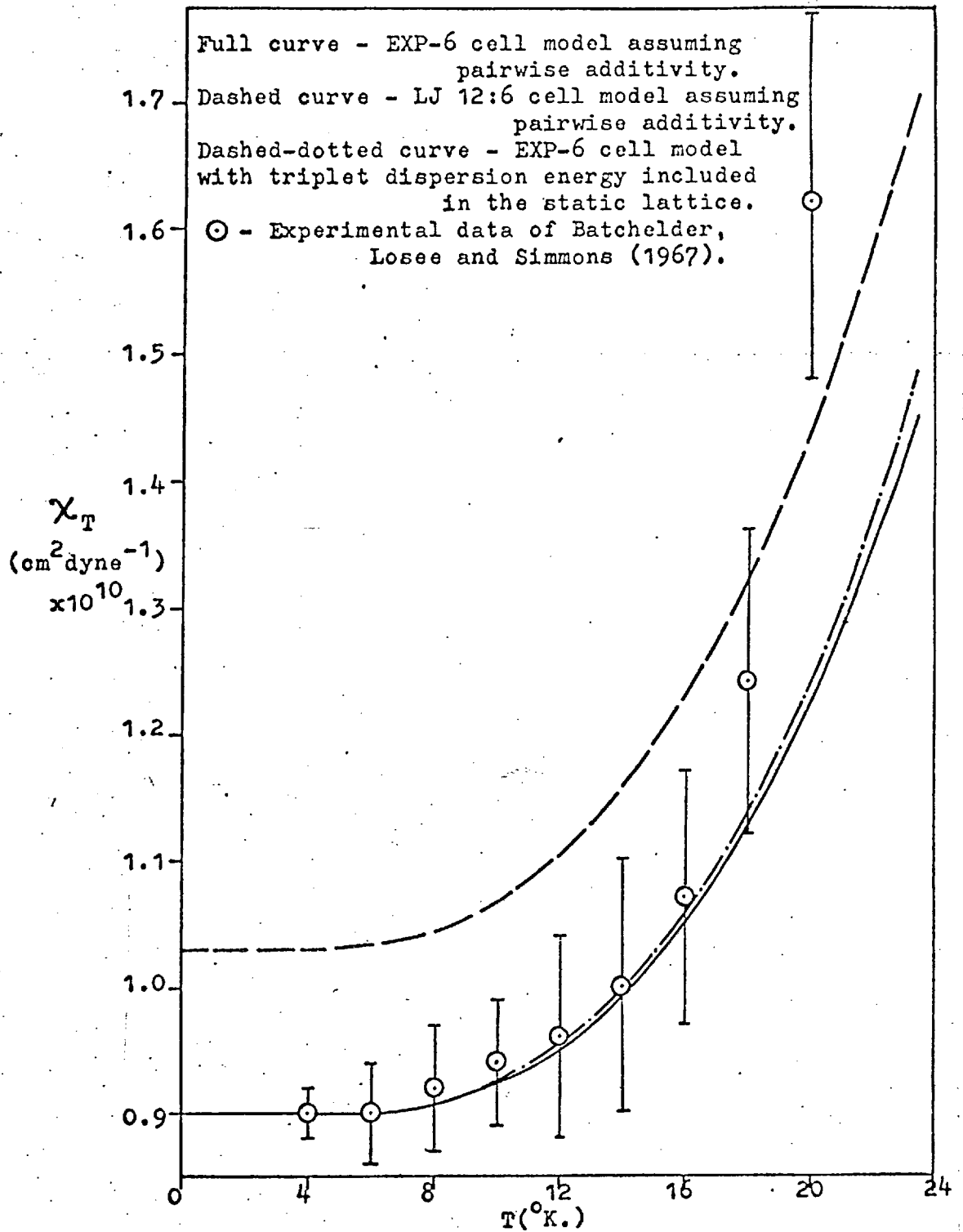
Fig.8c.Solid neon – volume expansivity, β, as a function of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming pairwise additivity.

Dashed curve – LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve – EXP-6 cell model with triplet dispersion energy included in the static lattice.

⊙ – Experimental data of Batchelder, Losee and Simmons (1967).
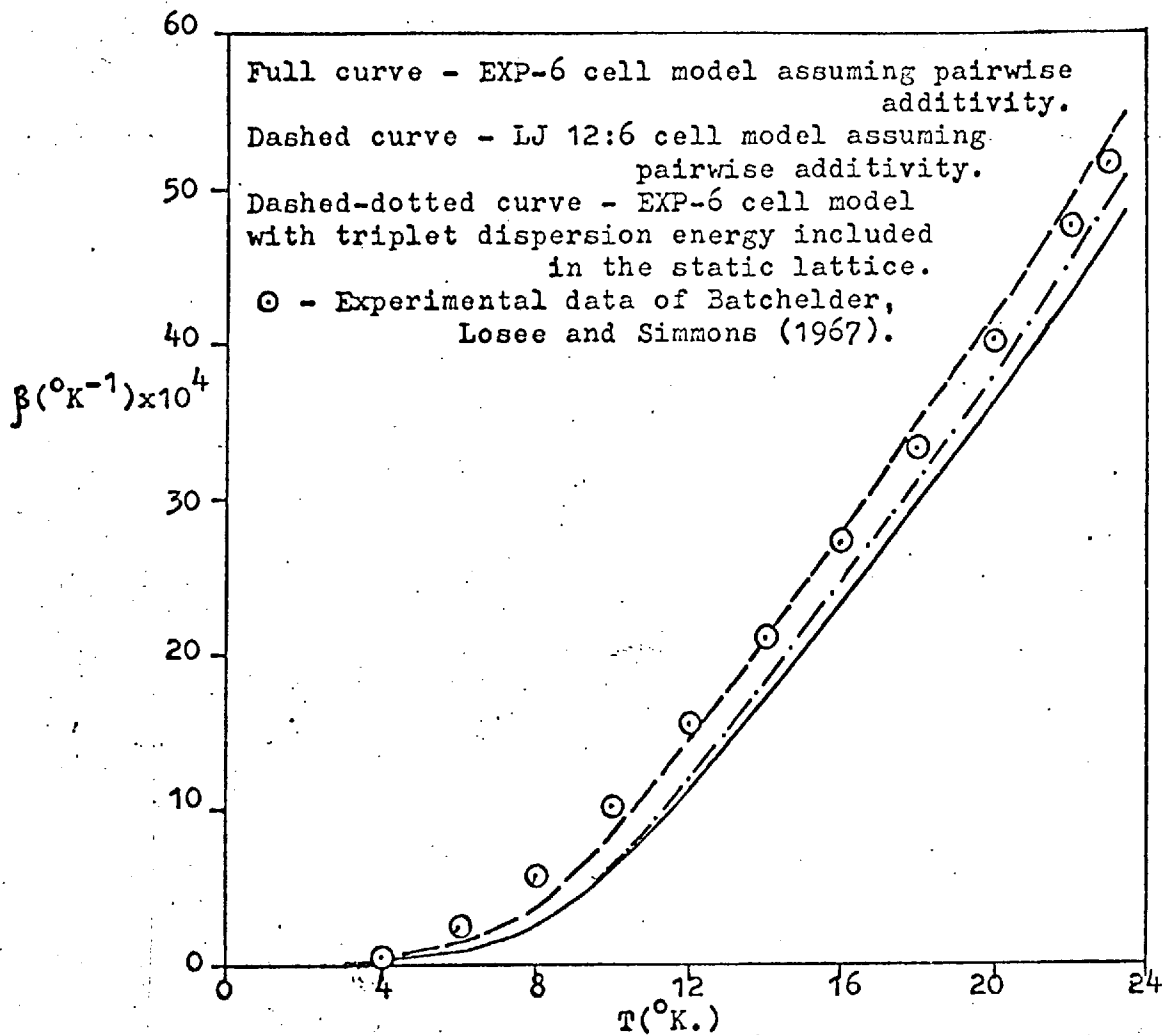
Fig. 8d. Solid neon - isochoric specific heat, C_v, as a function of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise additivity.

Dashed curve - LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve - EXP-6 cell model with triplet dispersion energy included in the static lattice.

⊙ - Calculated by Batchelder, Losee and Simmons (1967) using the experimental C_p data of Fenichel and Serin (1966) and Fagerstroem and Hallet (1965) together with their own experimental values of β, χ_T and V.
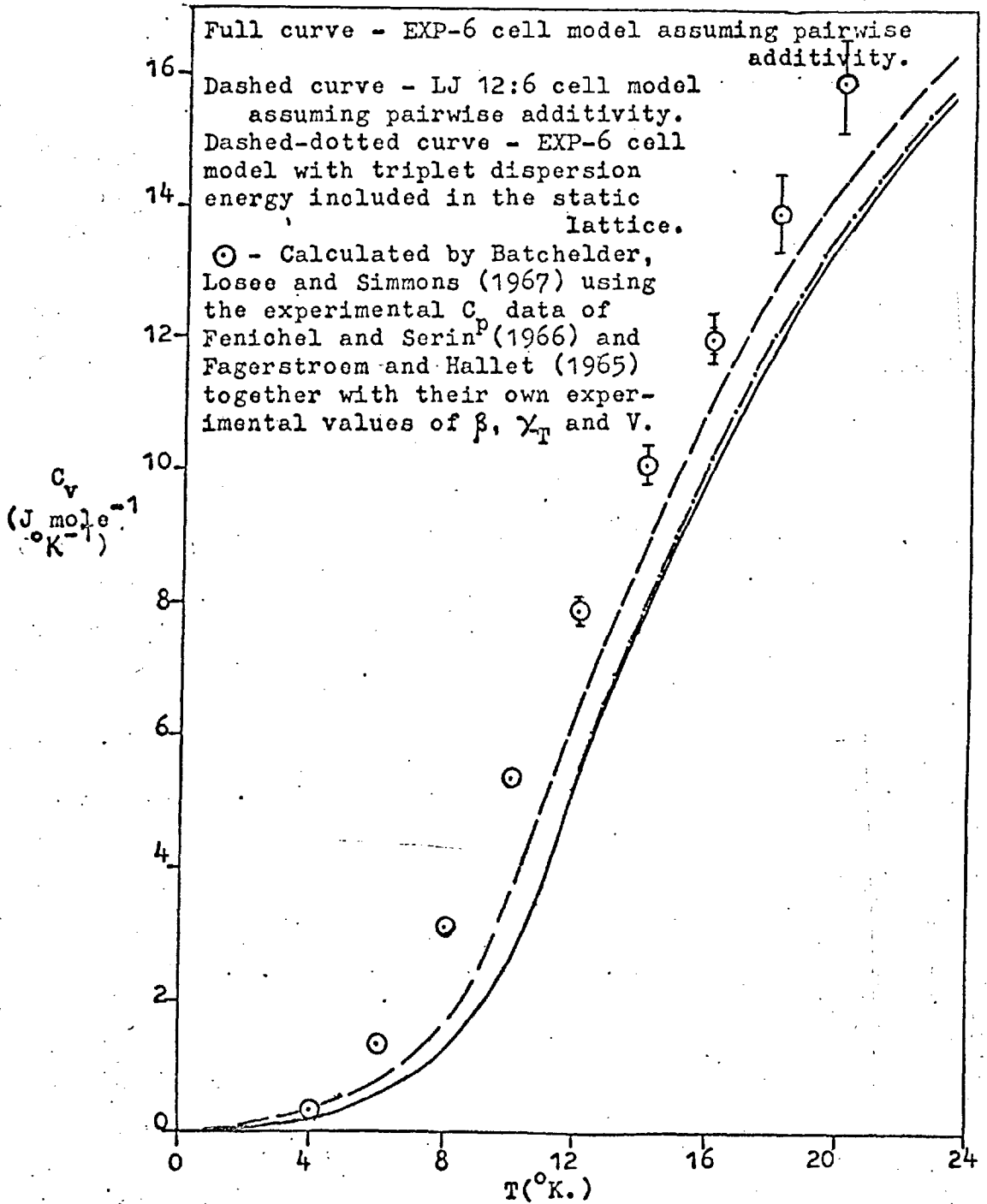
Fig.8e. Solid neon – isobaric specific heat, C_p, as a function of temperature, T, at zero pressure
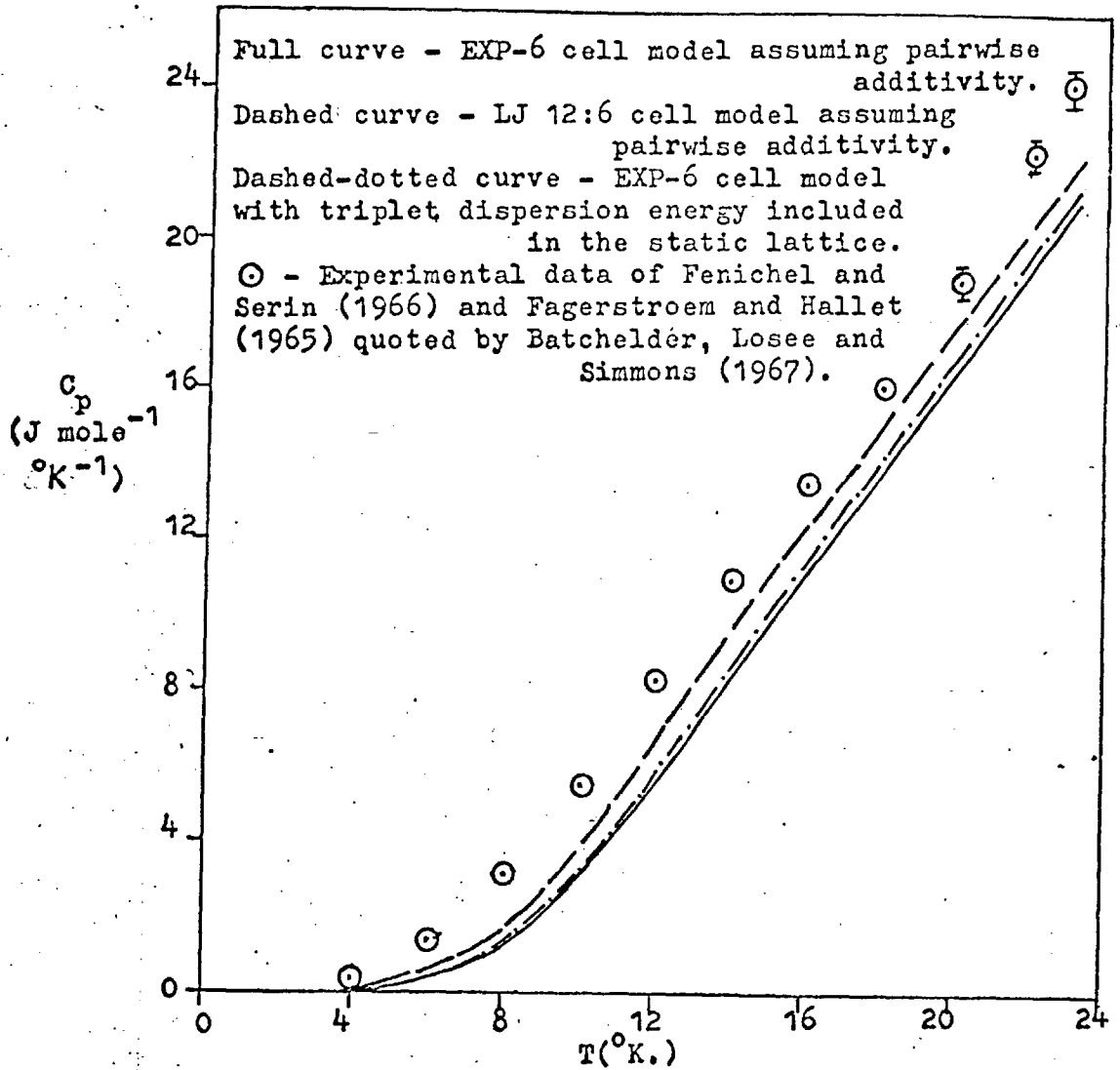
Fig. 8f. Solid neon – entropy, S, as a function of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming pairwise additivity.

Dashed curve – LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve – EXP-6 cell model with triplet dispersion energy included in the static lattice.

⊙ – Calculated from the experimental C_p data of Fenichel and Serin (1966) and Fagerstroem and Hallet (1965) quoted by Batchelder, Losee and Simmons (1967).
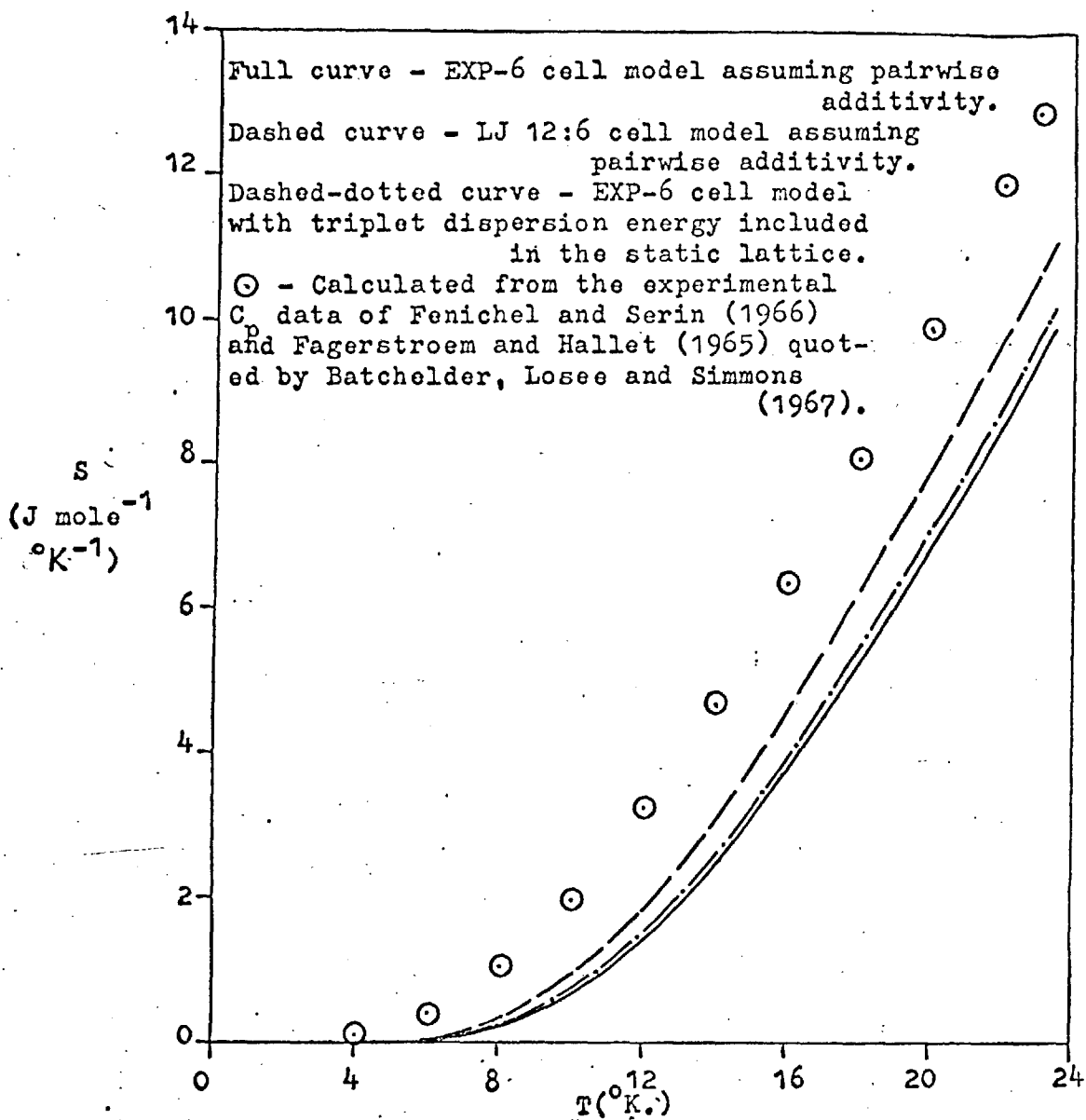
Fig.8g Solid neon — molar volume, V, normalised by the zero
pressure molar volume, V(0), as a function
of pressure, p, at 4°K.

Full curve — EXP-6 cell model assuming pairwise
additivity.
Dashed curve — LJ 12:6 cell model assuming pairwise
additivity.
Dashed-dotted curve — EXP-6 cell model with triplet
dispersion energy included in the static lattice.
-⊙- Experimental data of Stewart (1956).
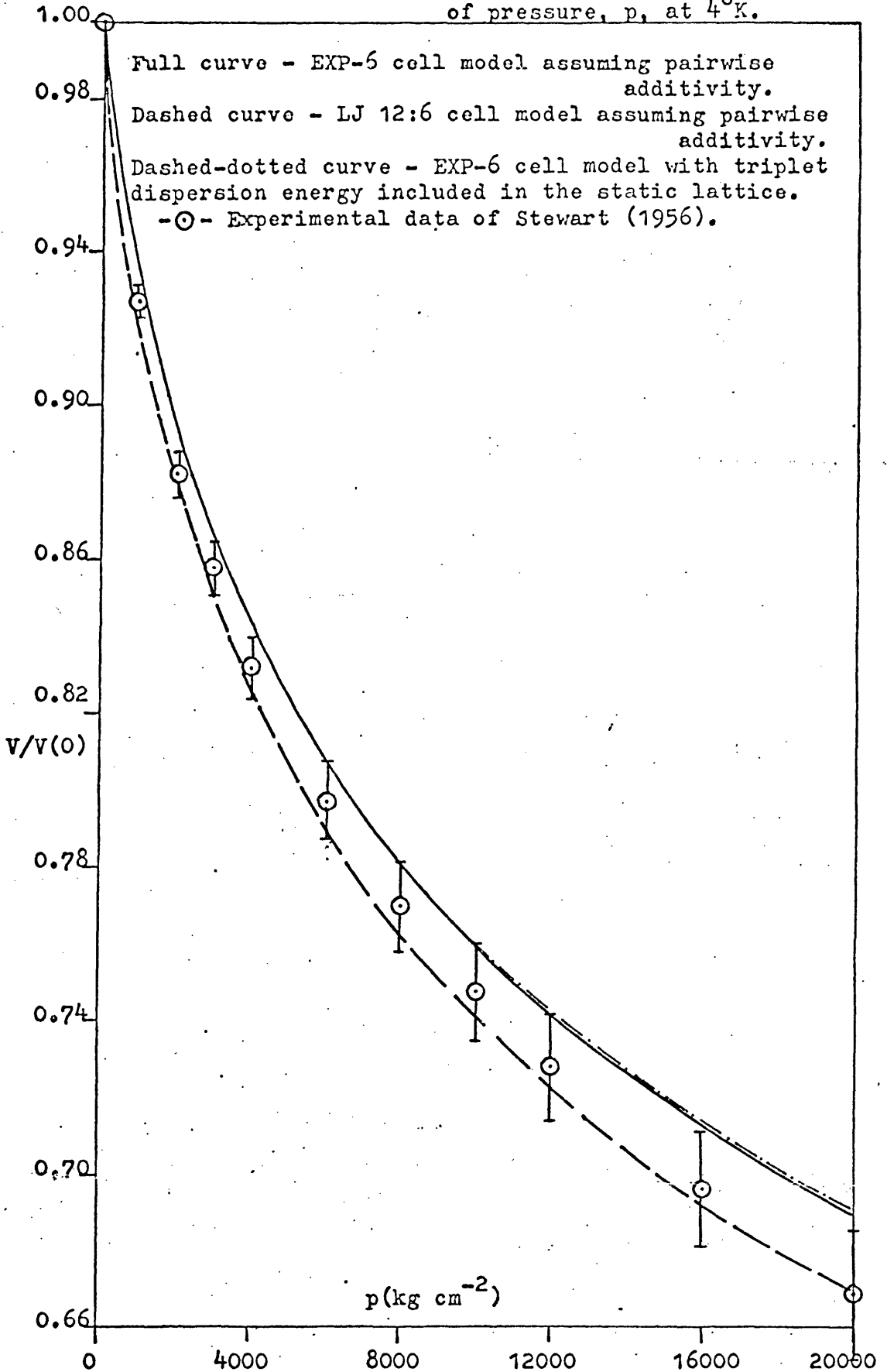
Fig. 9a.   Solid argon – lattice constant, a_o, as a function
of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming pairwise additivity.

Dashed curve – LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve – EXP-6 cell model with triplet dispersion energy included in the static lattice.

$\odot$ – Experimental data of Peterson, Batchelder and Simmons (1966).

$a_o (\overset{o}{A})$

$T(^oK.)$
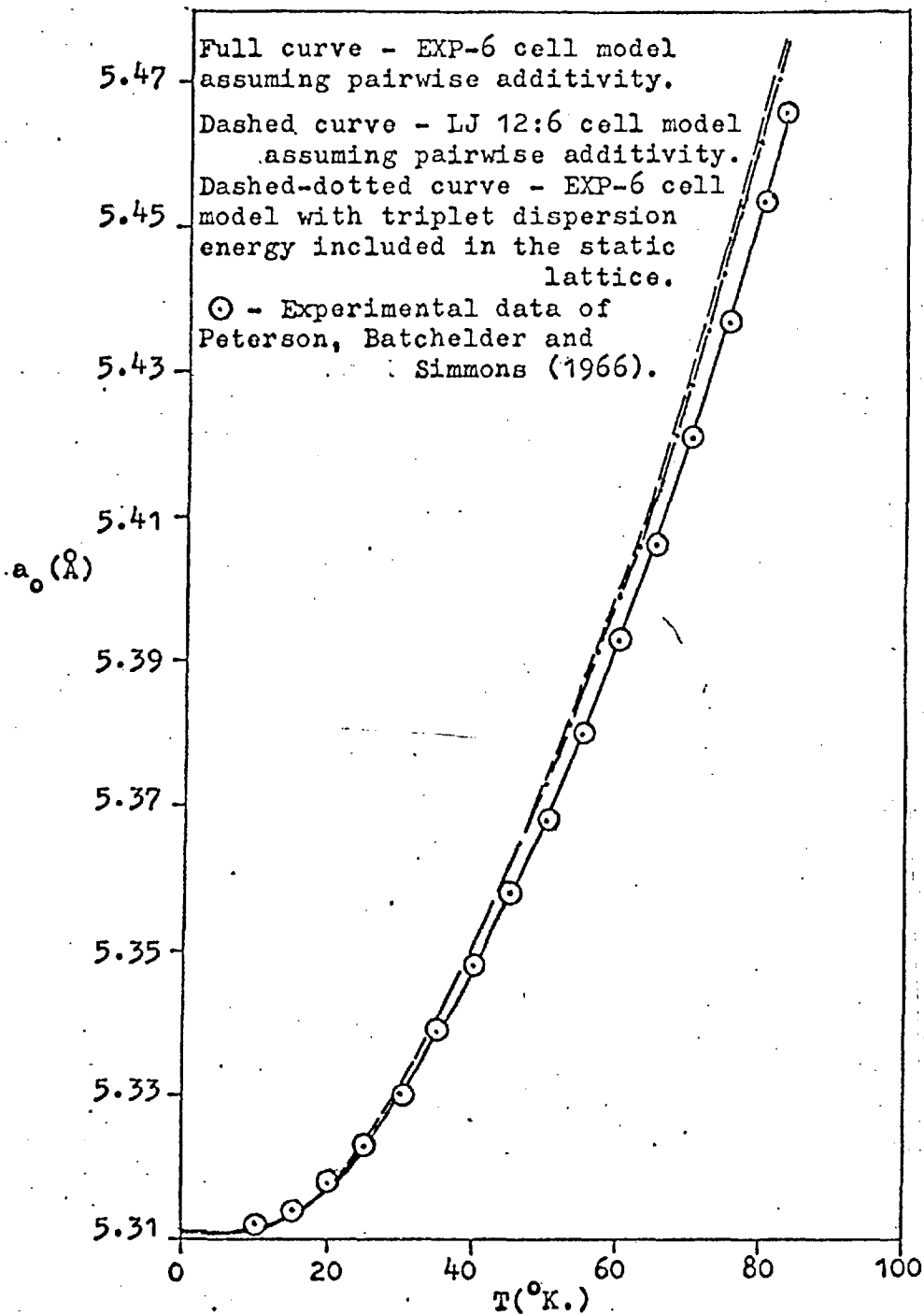
Fig. 9b. Solid argon - isothermal compressibility, χ_T, as a function of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise additivity.

Dashed curve - LJ 12:6 cell model assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell model with triplet dispersion energy included in the static lattice.
$\odot$ - Experimental data from Peterson, Batchelder and Simmons (1967).
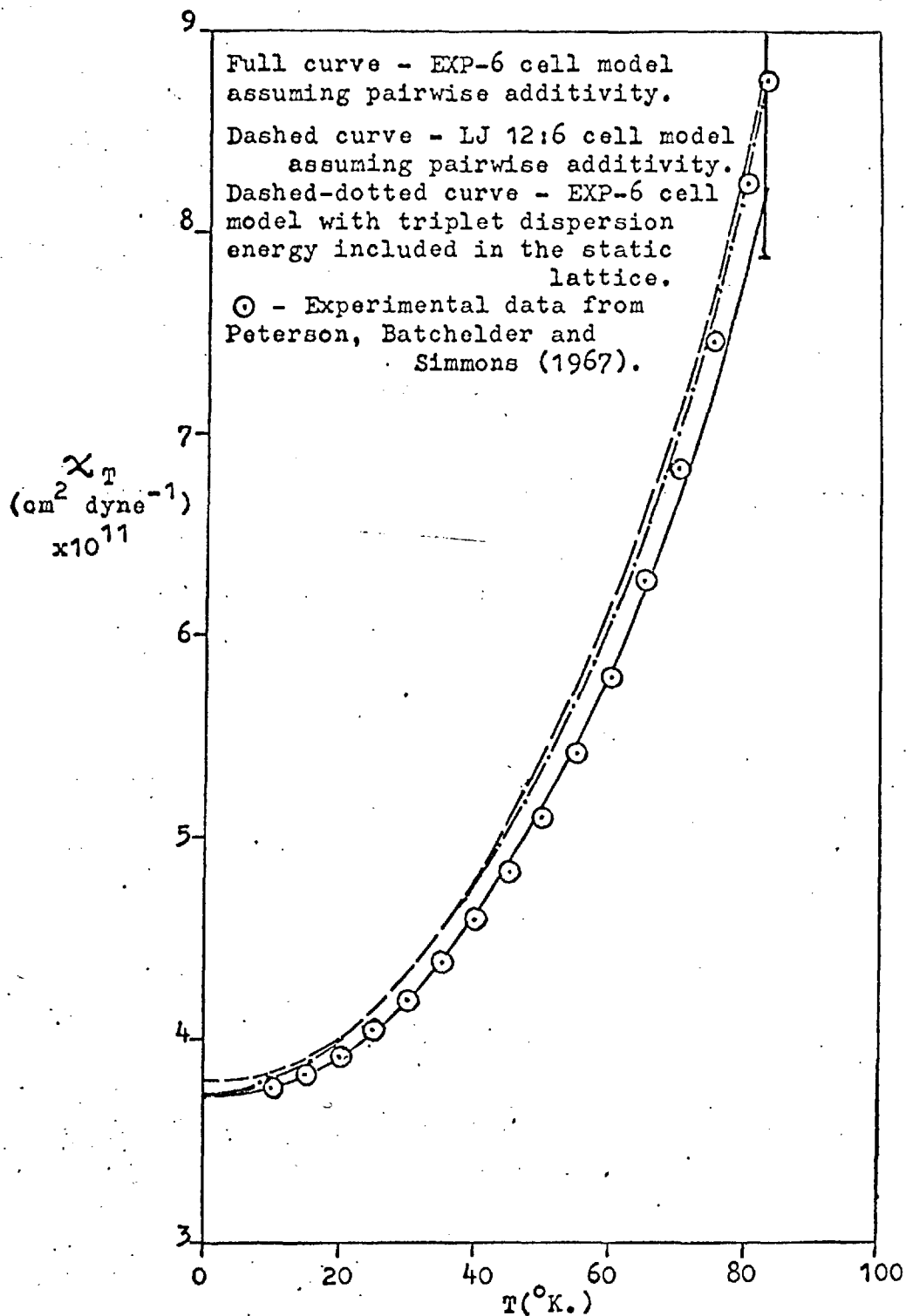
Fig.9c. Solid argon - volume expansivity, β, as a function
of temperature, T, at zero pressure

Full curve - EXP-6 cell model
assuming pairwise additivity.

Dashed curve - LJ 12:6 cell model
assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell
model with triplet dispersion
energy included in the static
lattice.

⊙ - Experimental data of
Peterson, Batchelder and
Simmons (1966).
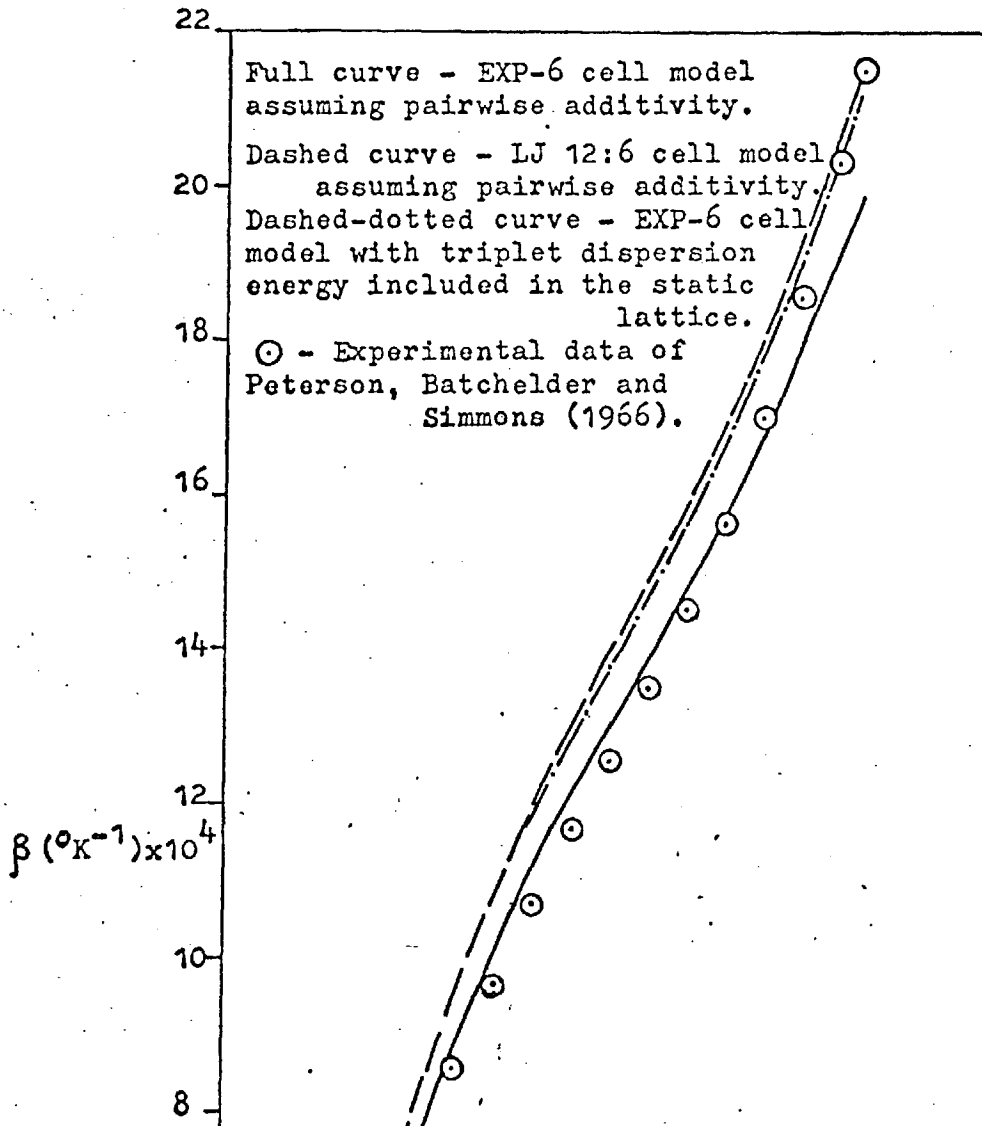
Fig. 9d. Solid argon - isochoric specific heat, C_v, as a function of temperature, T, at zero pressure.

Full curve - EXP-6 cell model assuming
                    pairwise additivity.
Dashed curve - LJ 12:6 cell model assuming
                    pairwise additivity.

Dashed-dotted curve - EXP-6 cell
model with triplet dispersion
energy included in the static
                    lattice.
-⊙- Calculated by Peterson Bat-
chelder and Simmons (1966) using
the experimental C_p data of Flu-
bacher, Leadbetter and Morrison
(1961) together with their own
experimental values of β and V
and their quoted values of χ_T.

Fig.9e. Solid argon – isobaric specific heat, C_p, as a function of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming pairwise additivity.

Dashed curve – LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve – EXP-6 cell model with triplet dispersion energy included in the static lattice.

-⊙- Experimental data of Flubacher, Leadbetter and Morrison (1961) quoted by Peterson, Batchelder and Simmons (1966).

C_p
$(J \ mole^{-1}$
$°K^{-1})$

$T(°K.)$
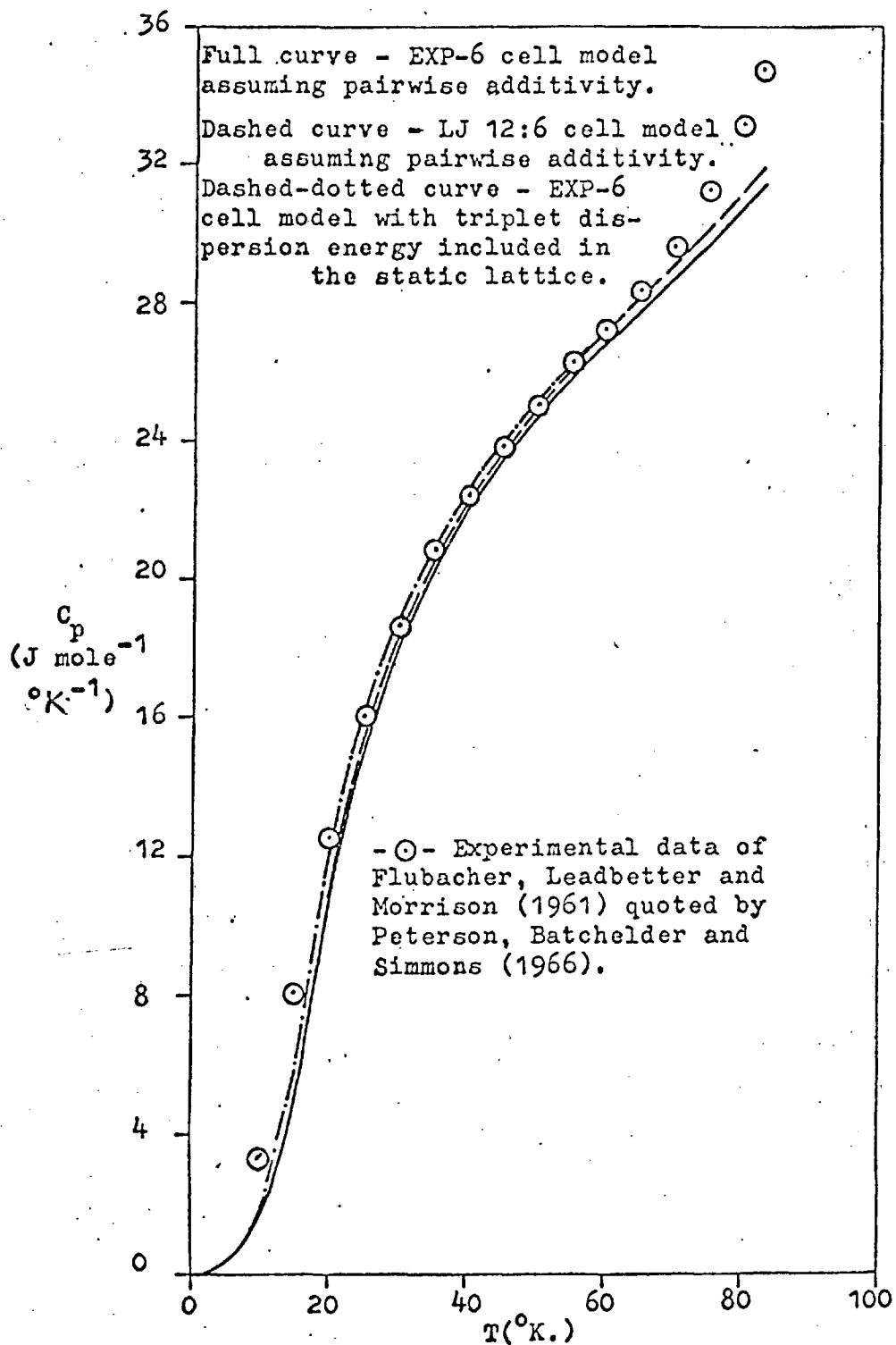
Fig. 9f. Solid argon - entropy, S, as a function of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise additivity.

Dashed curve - LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve - EXP-6 cell model with triplet dispersion energy included in the static lattice.

-⊙- Calculated from the experimental C_p data of Fluhacher, Leadbetter and Morrison (1961) quoted by Peterson, Batchelder and Simmons (1966).
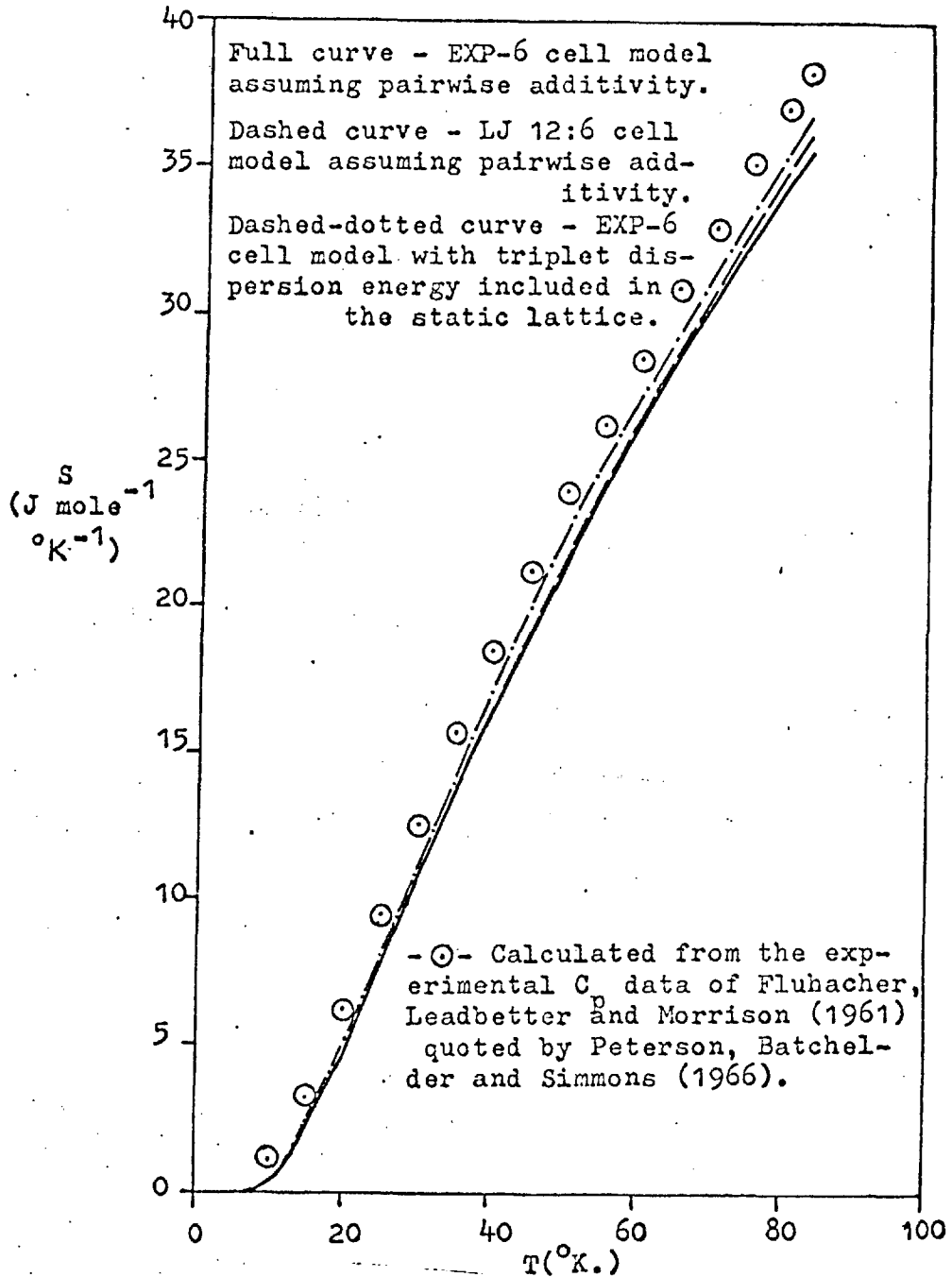
Fig. 9g. Solid argon – molar volume, V, normalised by the zero pressure molar volume, V(0), as a function of pressure, p, at 77°K.

Full curve – EXP-6 cell model assuming pairwise additivity.

Dashed curve – LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve – EXP-6 cell model with triplet dispersion energy included in the static lattice.

-⊙- Experimental data of Stewart (1956).
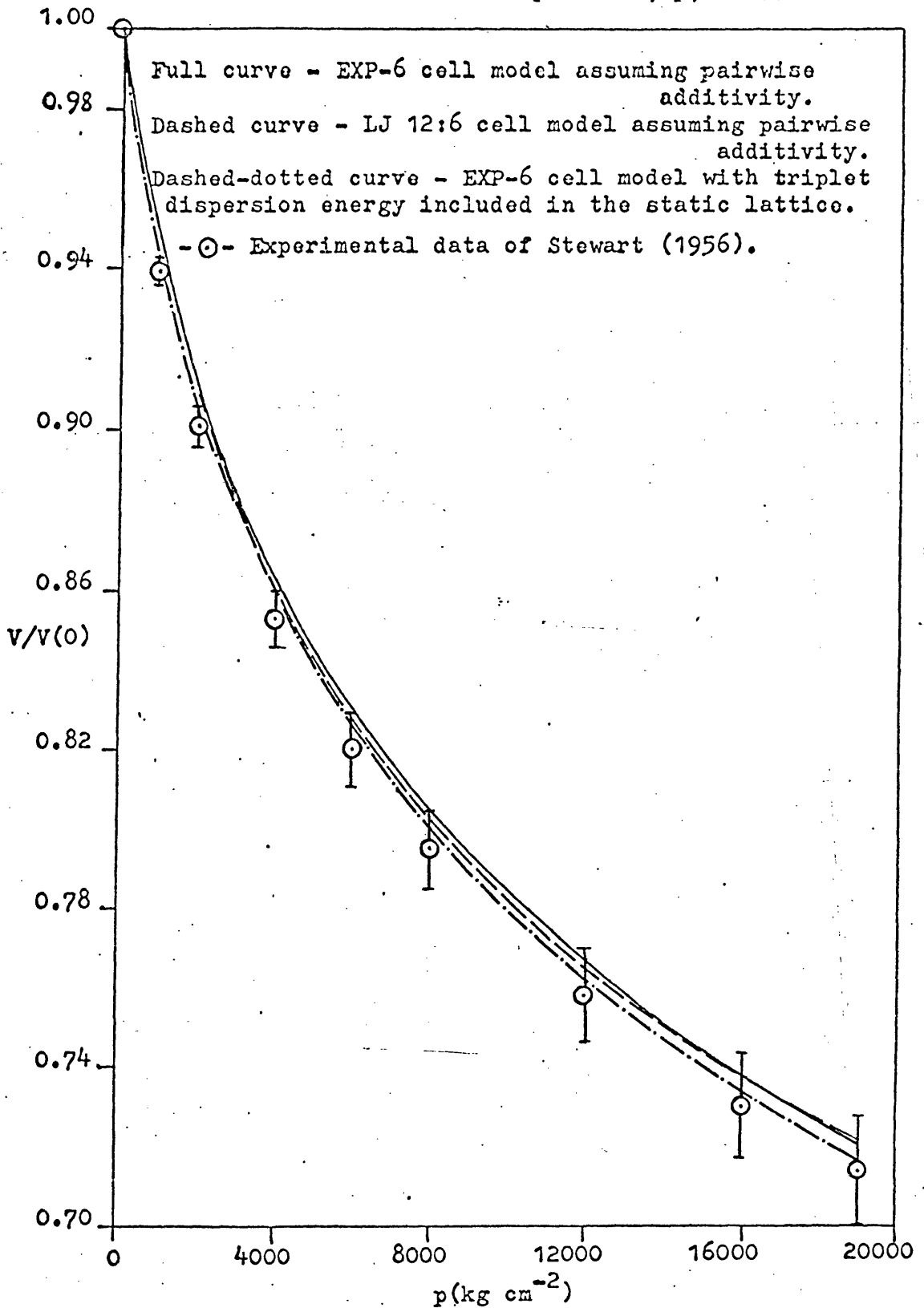
Fig.10a.Solid krypton - lattice constant, a_o, as a function
of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise
additivity.
Dashed curve - LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve - EXP-6 cell model with
triplet dispersion energy included in the
static lattice.
⊙ - Experimental data of Urvas, Losee and
Simmons (1967).
△ -   "   "   " Cheeseman and
Soane (1957).
□ -   "   "   " Figgins and
Smith (1960).
✕ -   "   "   " Clusius and
Weigand (1960)

$a_o(\overset{o}{A})$

T(°K.)
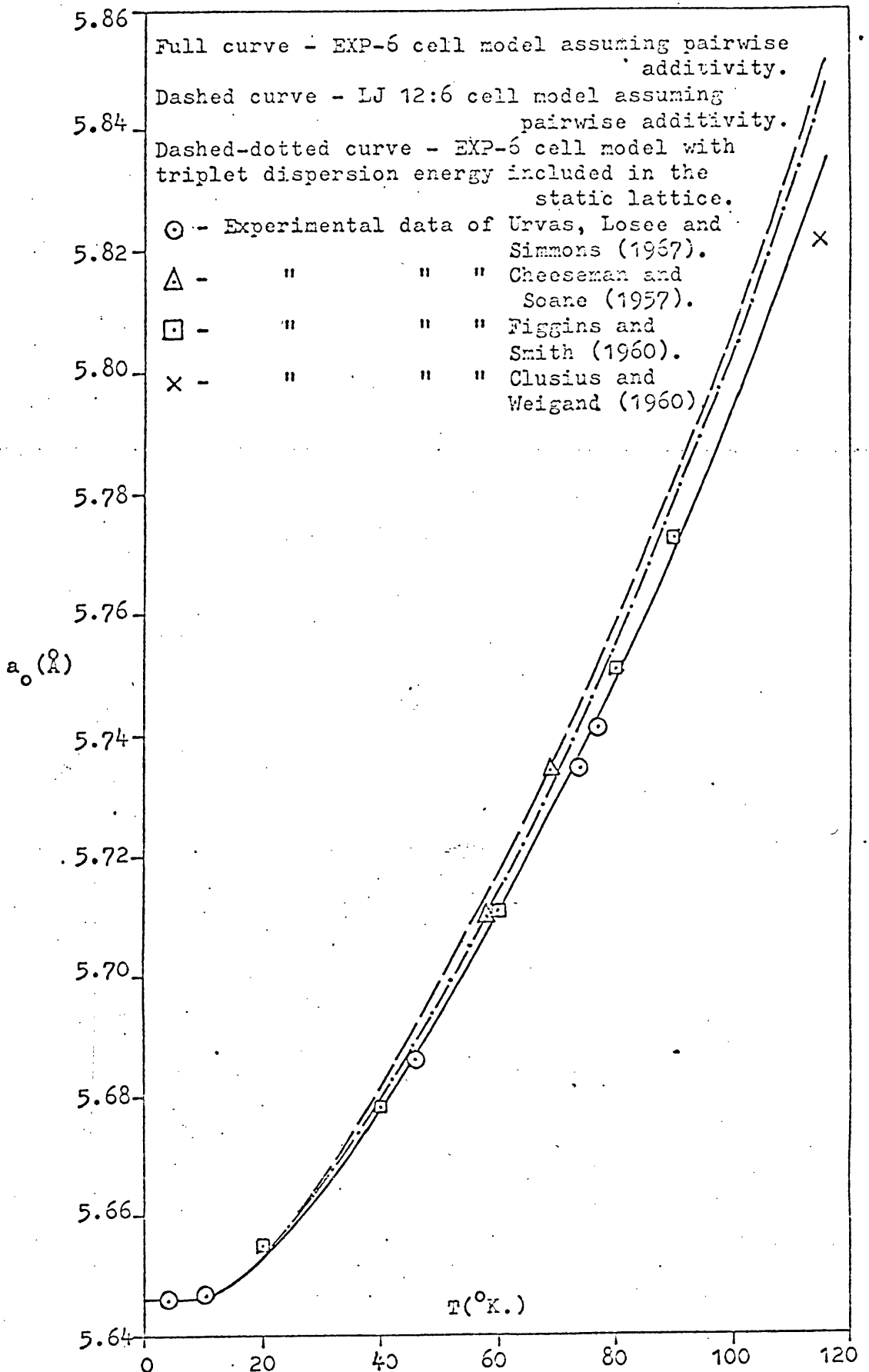
Fig.10b.   Solid krypton - isothermal compressibility, χ_T, as a
function of temperature, T, at zero
pressure

Full curve - EXP-6 cell model assuming pairwise
additivity.
Dashed curve - LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve - EXP-6 cell model with
triplet dispersion energy included in the
static lattice.
⊙ - Experimental data of Urvas, Losee and
Simmons (1967).

χ_T
$(cm^2 dyne^{-1})$
$\times 10^{11}$

$T(^\circ K.)$
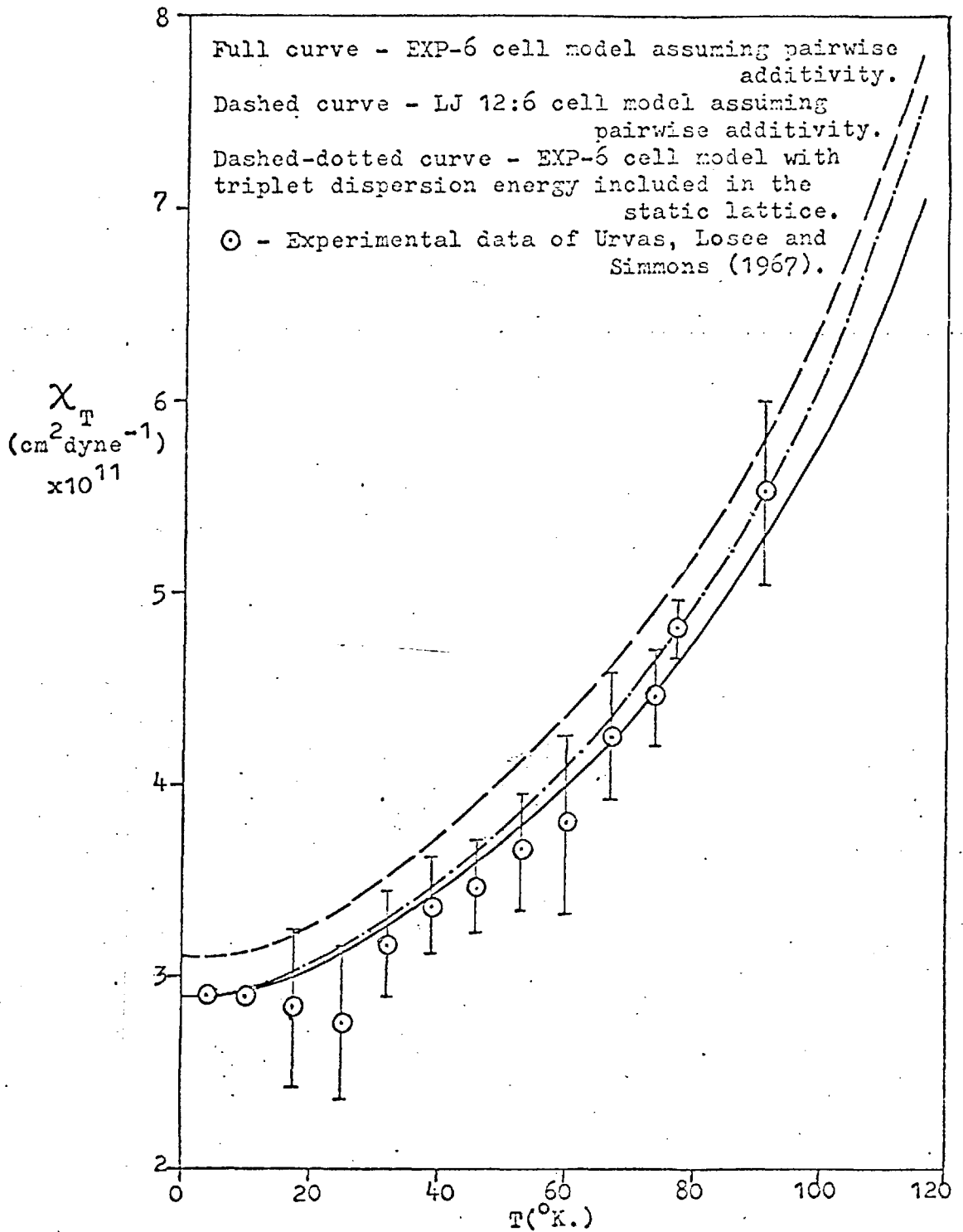
Fig.10c. Solid krypton - volume expansivity, β, as a function
of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise
additivity.
Dashed curve - LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve - EXP-6 cell model with
triplet dispersion energy included in the
static lattice.
⊙ - Experimental data of Figgins and
Smith (1960).
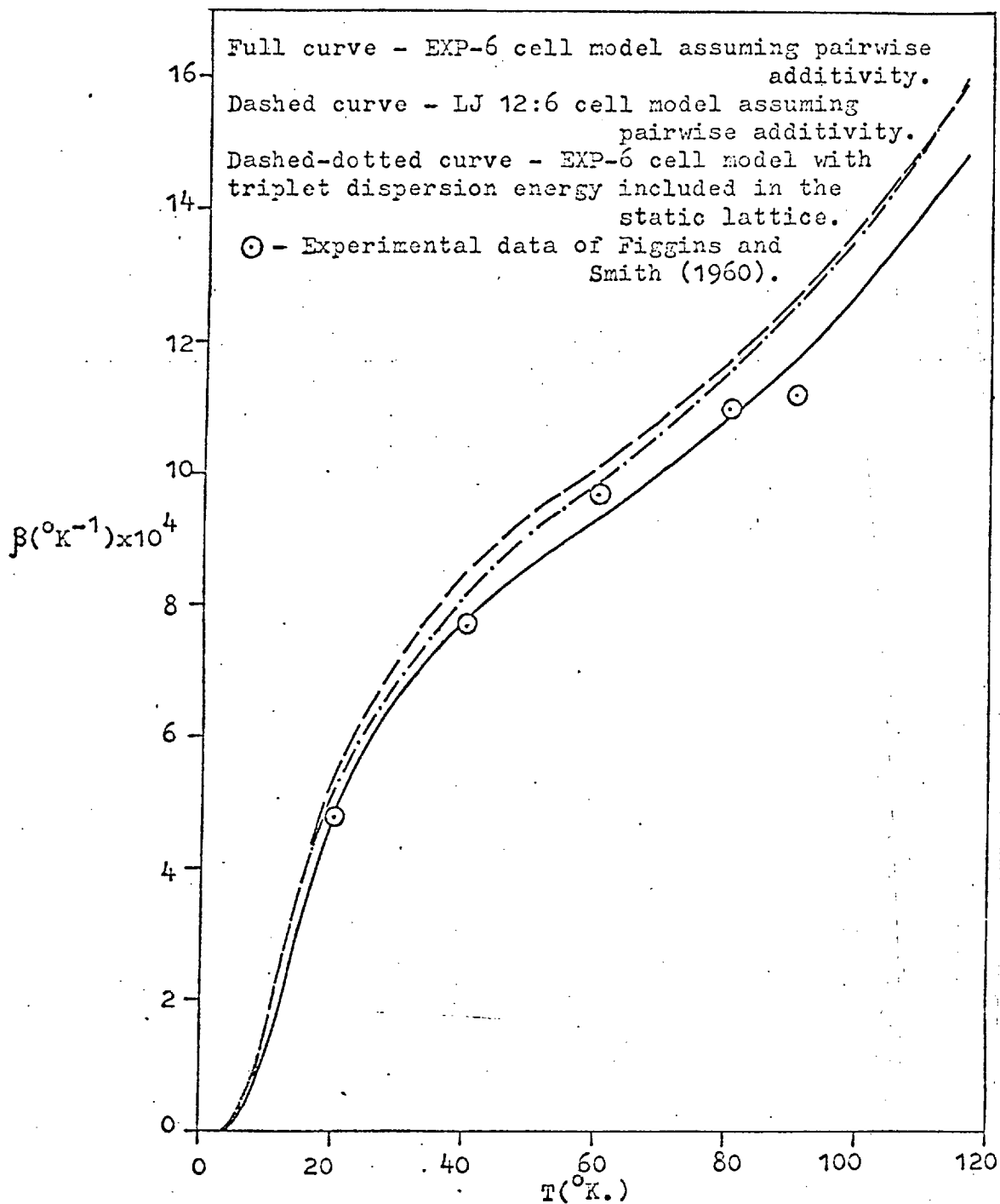
Fig.10d. Solid krypton- isochoric specific heat, C_v, as a
function of temperature, T, at zero
pressure

Full curve – EXP-6 cell model assuming
pairwise additivity.
Dashed curve – LJ 12:6 cell model
assuming pairwise additivity.
Dashed-dotted curve – EXP-6 cell model
with triplet dispersion energy included
in the static lattice.
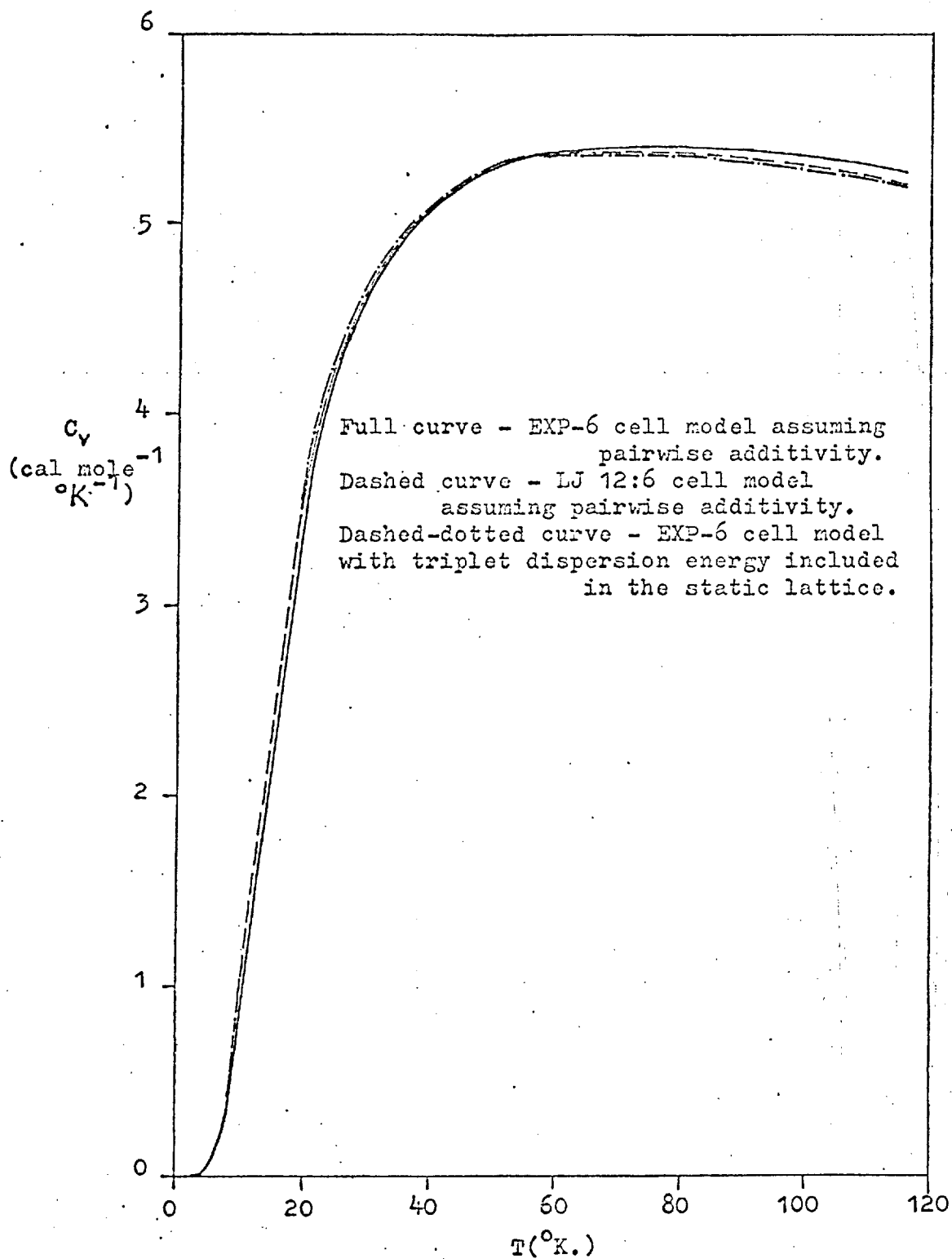
Fig. 10e. Solid krypton – isobaric specific heat, C_p, as a
function of temperature, T, at
zero pressure

Full curve – EXP-6 cell model assuming pairwise
additivity. ⊙

Dashed curve – LJ 12:6 cell model assuming
pairwise additivity. ⊙

Dashed-dotted curve – EXP-6 cell model with
triplet dispersion energy included in the
static lattice.

⊙ – Experimental data of Beaumont,
Chihara and Morrison (1961).

C_p
(cal mole^{-1}
$^\circ$K.$^{-1}$)

T($^\circ$K.)
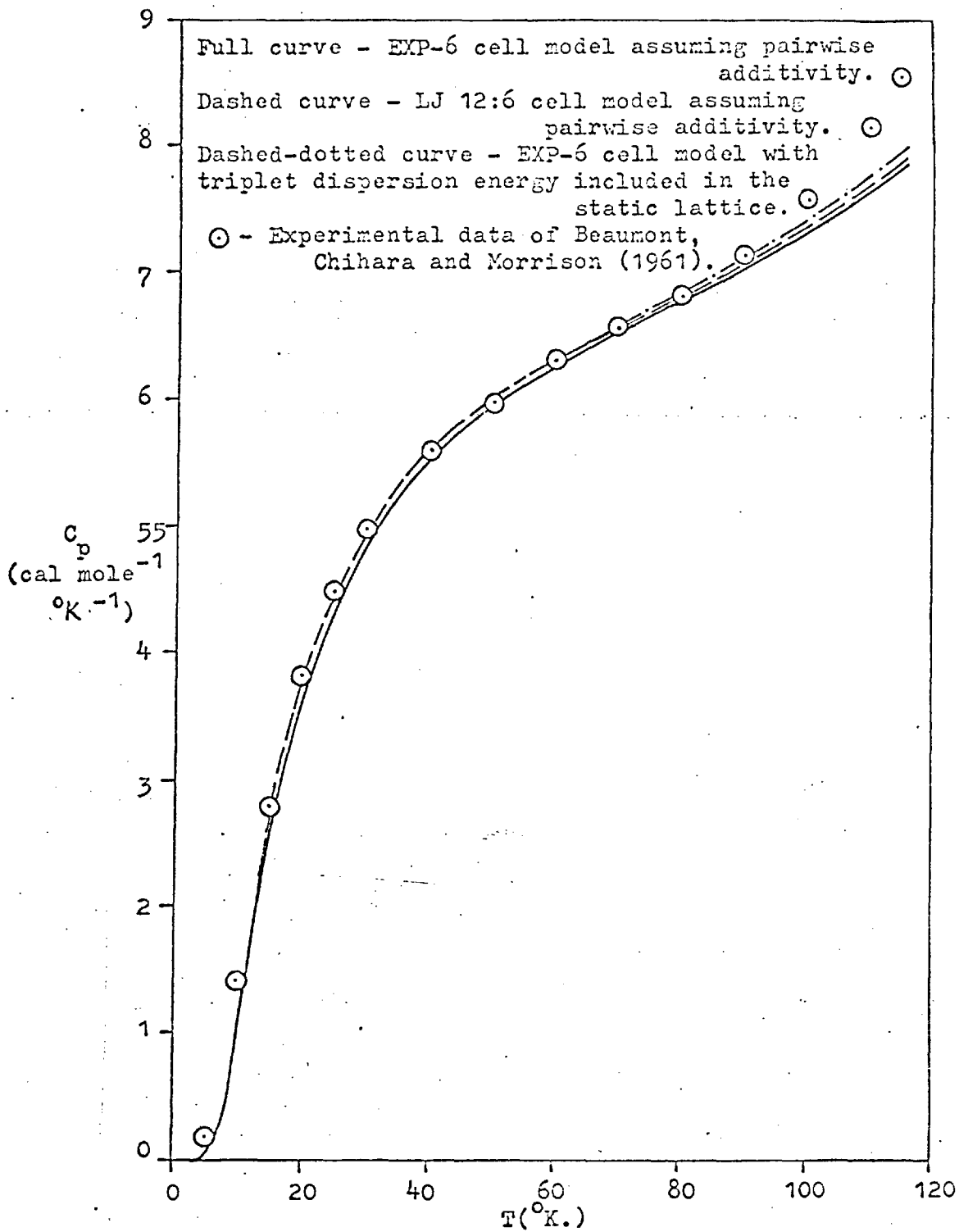
Fig. 10f. Solid krypton - entropy, S, as a function of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise additivity.

Dashed curve - LJ 12:6 cell model assuming pairwise additivity.

Dashed-dotted curve - EXP-6 cell model with triplet dispersion energy included in the static lattice.

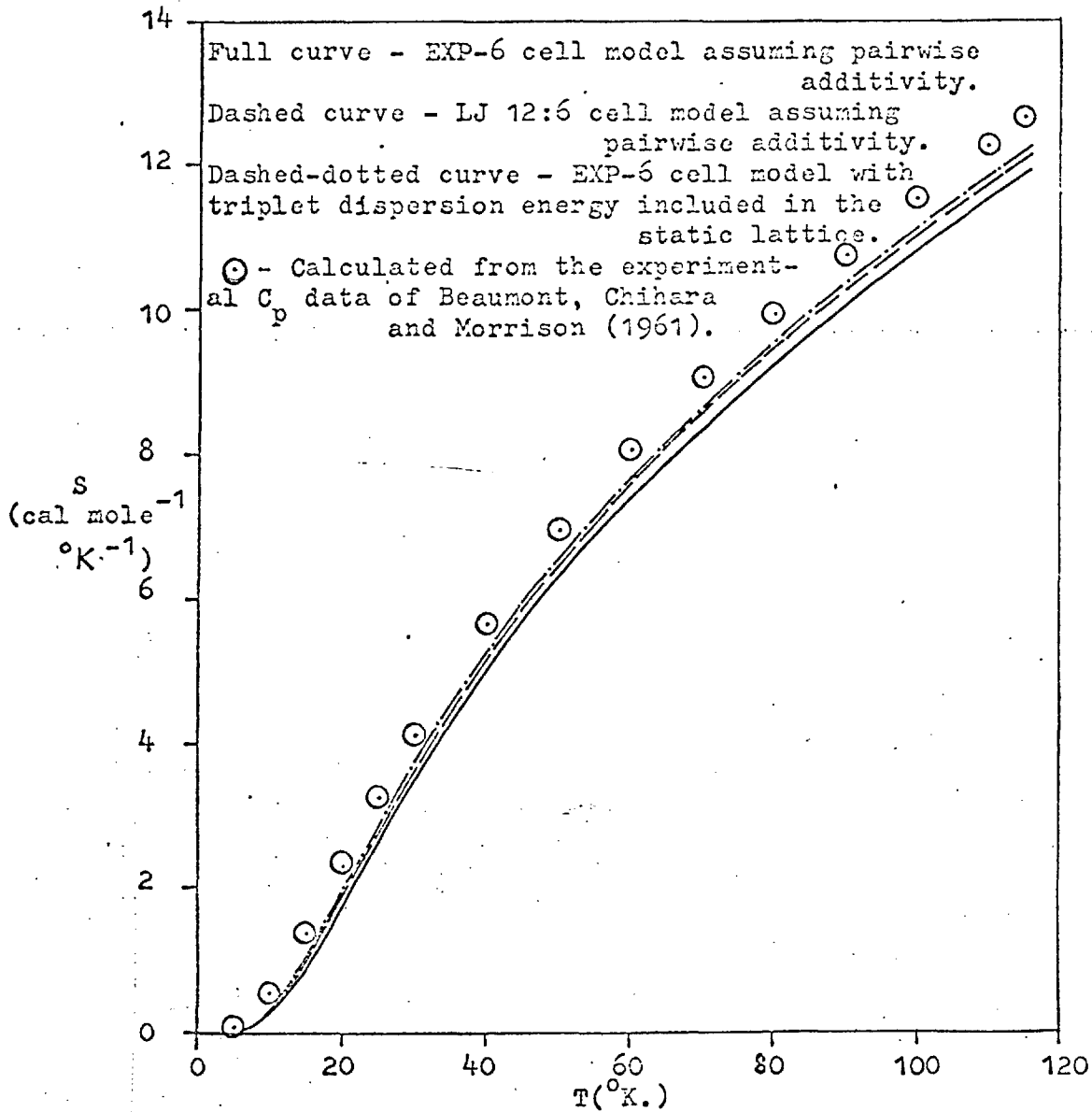⊙ - Calculated from the experimental C_p data of Beaumont, Chihara and Morrison (1961).

Fig.10g.Solid krypton - molar volume, V, normalised by the zero
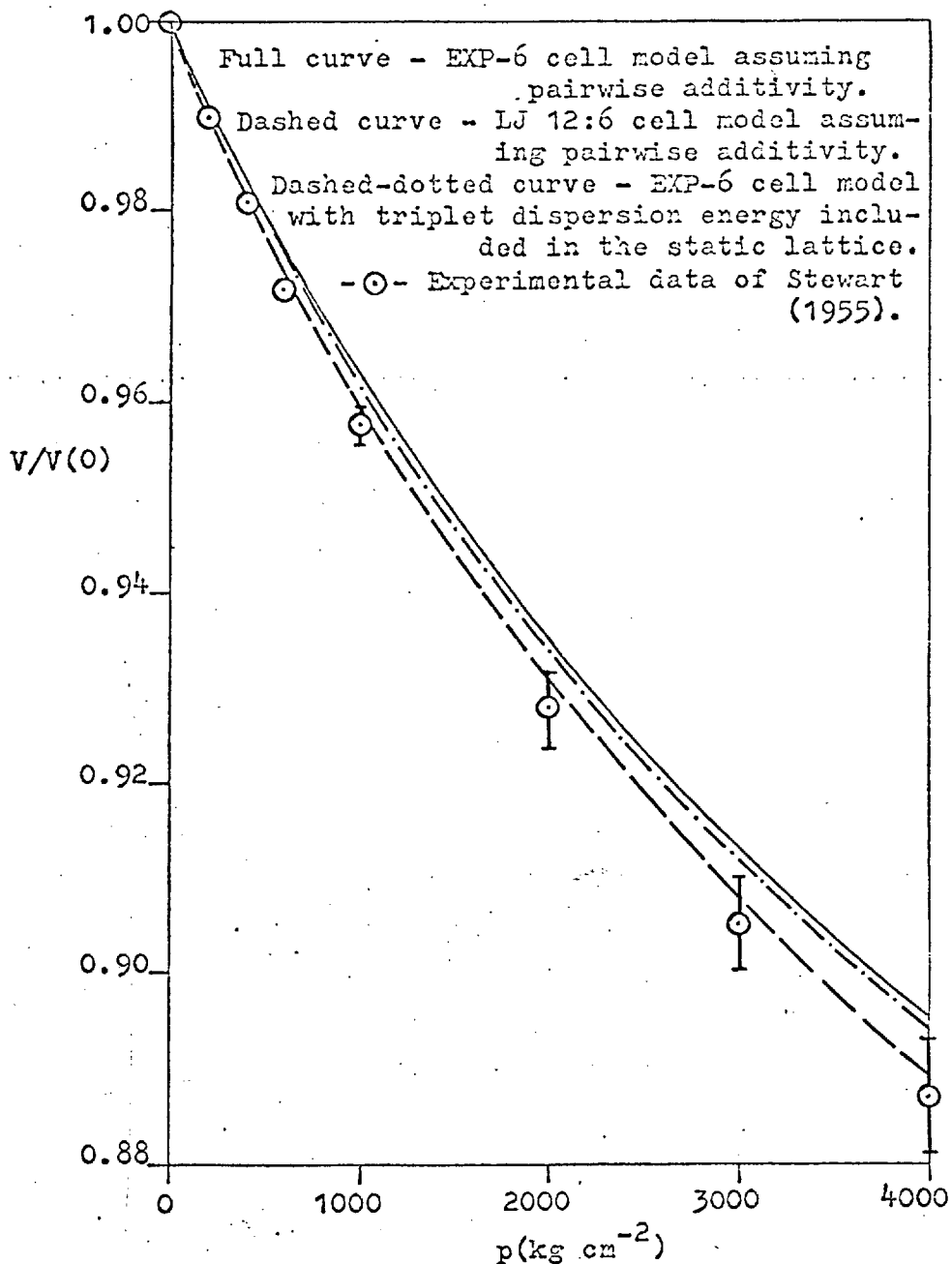pressure molar volume, V(0), as a function
of pressure, p, at 77°K.

Full curve - EXP-6 cell model assuming
pairwise additivity.
Dashed curve - LJ 12:6 cell model assum-
ing pairwise additivity.
Dashed-dotted curve - EXP-6 cell model
with triplet dispersion energy inclu-
ded in the static lattice.
- ⊙ - Experimental data of Stewart
(1955).

Fig. 11a. Solid xenon – lattice constant, a_o, as a function of temperature, T, at zero pressure

Full curve – EXP-6 cell model assuming pairwise additivity.
Dashed curve – LJ 12:6 cell model assuming pairwise additivity or EXP-6 cell model with triplet dispersion energy included in the static lattice.
$\odot$ – Experimental data of Sears and Klug (1962).
$\triangle$ – " " of Packard and Swenson (1963).
$\square$ – " data of Eatwell and Smith (1961).
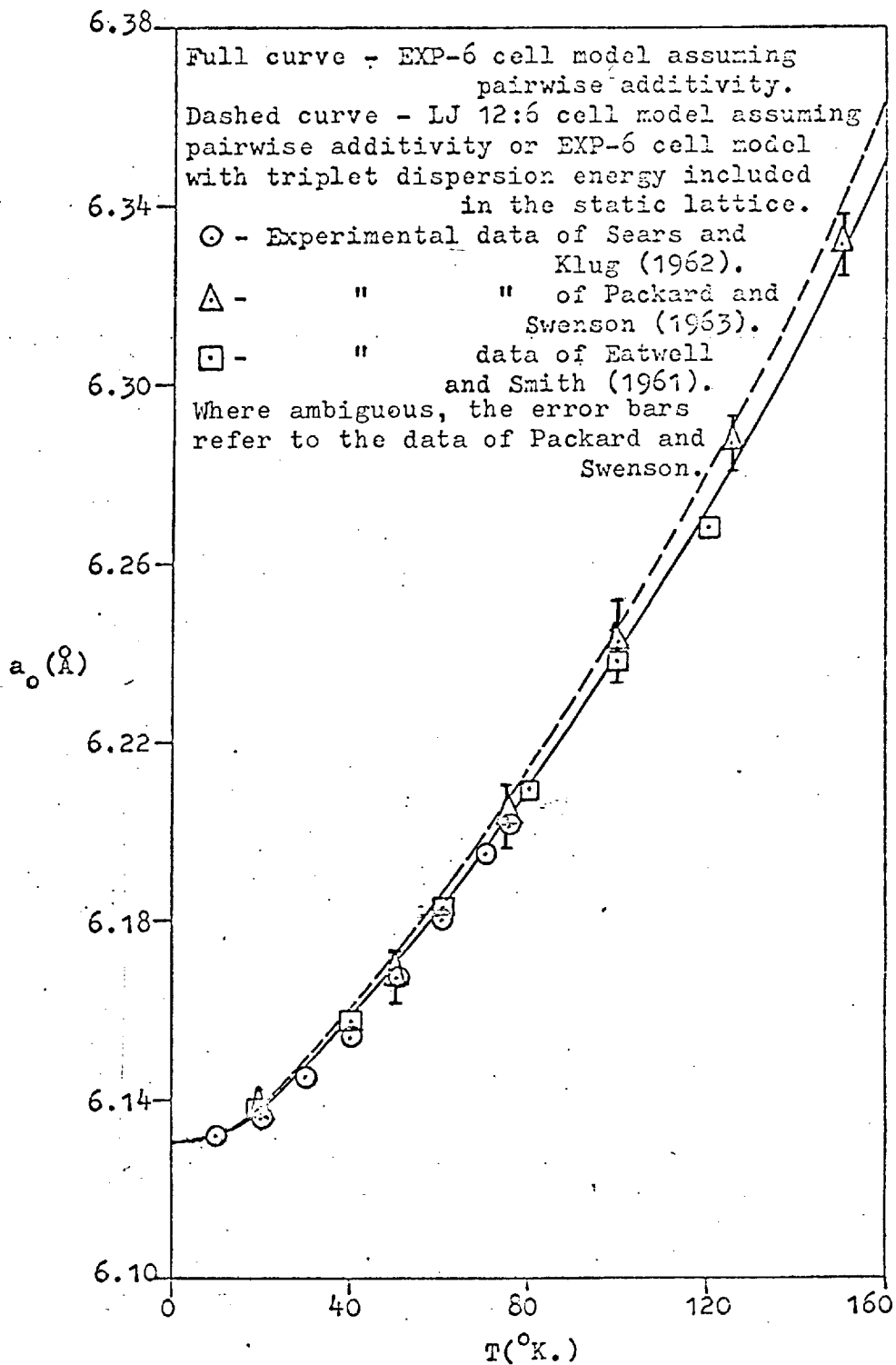Where ambiguous, the error bars refer to the data of Packard and Swenson.

Fig.11b. Solid xenon – isothermal compressibility, χ_T, as a
function of temperature, T, at zero
pressure

Full curve – EXP-6 cell model assuming
pairwise additivity.
Dashed curve – LJ 12:6 cell model assuming
pairwise additivity.
Dashed-dotted curve – EXP-6 cell model
with triplet dispersion energy included
in the static lattice.
⊙ – Experimental data of Packard and
Swenson (1963).

χ_T

$(cm^2\ dyne^{-1})$
$\times 10^{11}$

$T(^{\circ}K.)$
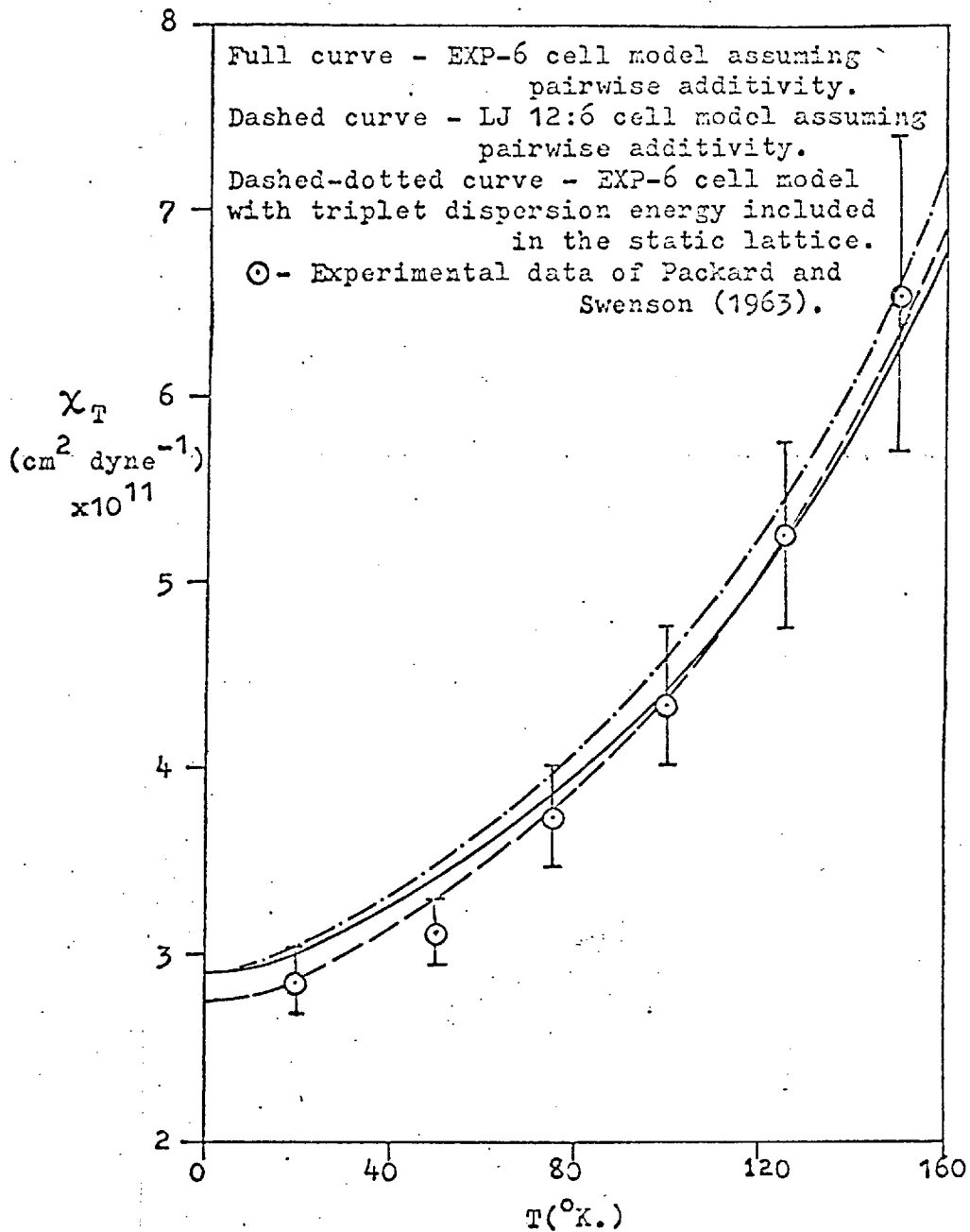
Fig.11$_c$ Solid xenon - volume expansivity, β, as a function
of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming
pairwise additivity.
Dashed curve - LJ 12:6 cell model
assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell model
with triplet dispersion energy in-
cluded in the static lattice.
⊙ - Experimental data of Sears
and Klug (1962).
△ - Experimental data of
Packard and Swenson (1963).

-◘- Experimental data of
Eatwell and Smith (1961).
Where ambiguous, the error
bars refer to the data of
Packard and Swenson

$\beta(^{\circ}K^{-1})\times10^4$

T($^{\circ}$K.)

Fig.11d.Solid xenon - isochoric specific heat, C_v, as a
function of temperature, T, at zero
pressure

Full curve - EXP-6 cell model assum-
ing pairwise additivity.
Dashed curve - LJ 12:6 cell model
assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell
model with triplet dispersion energy
included in the static lattice.
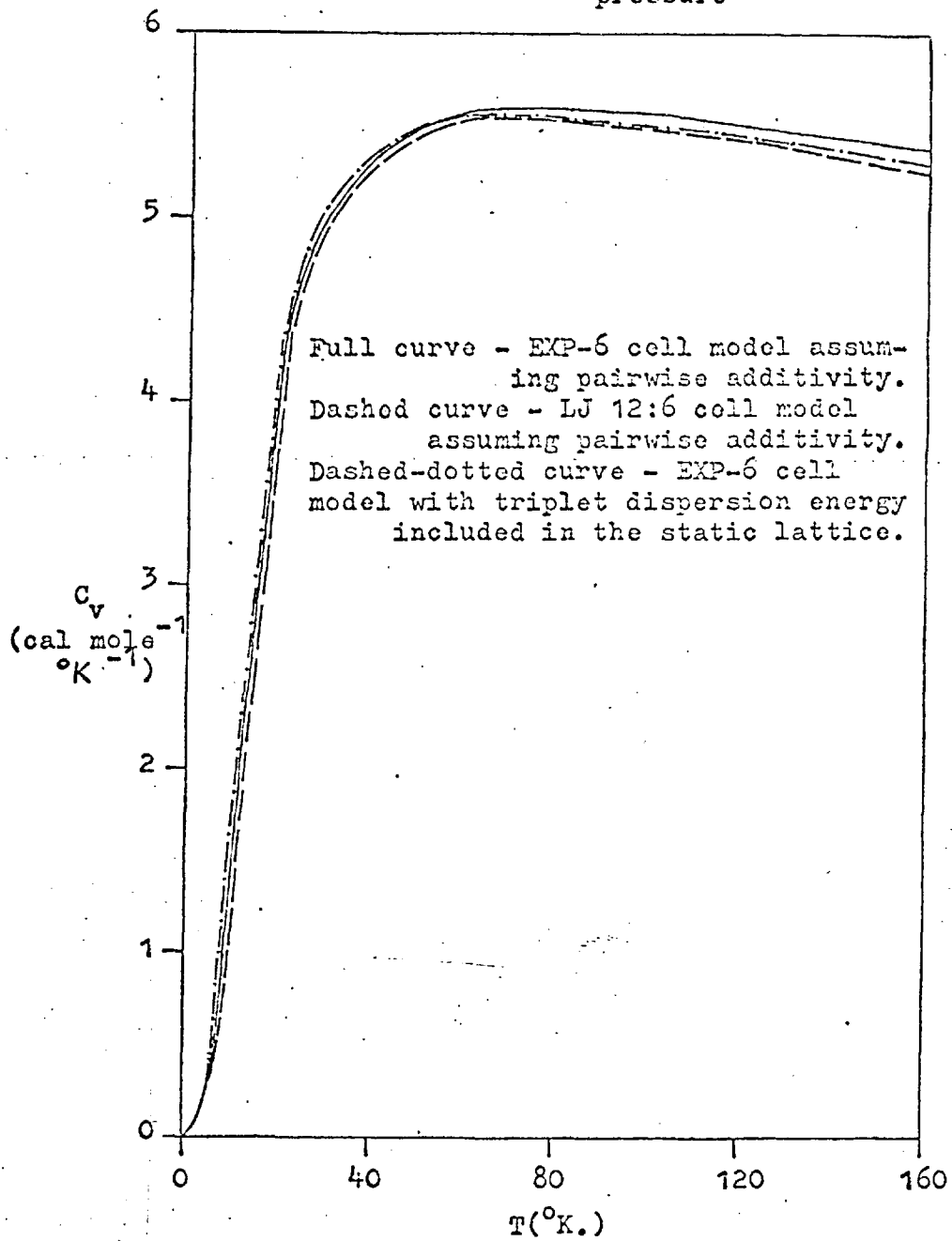
Fig.11a Solid xenon - isobaric specific heat, C_p, as a
function of temperature, T, at zero
pressure

Full curve - EXP-6 cell model assuming
pairwise additivity.
Dashed curve - LJ 12:6 cell model
assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell
model with triplet dispersion
energy included in the static
lattice.

C_p
(cal mole^{-1}
$^\circ$K^{-1})

-⊙- Experimental data of Fenichel
and Serin (1966).
-△- Experimental data of Clusius
and Riccoboni (1938).

$T(^\circ K.)$
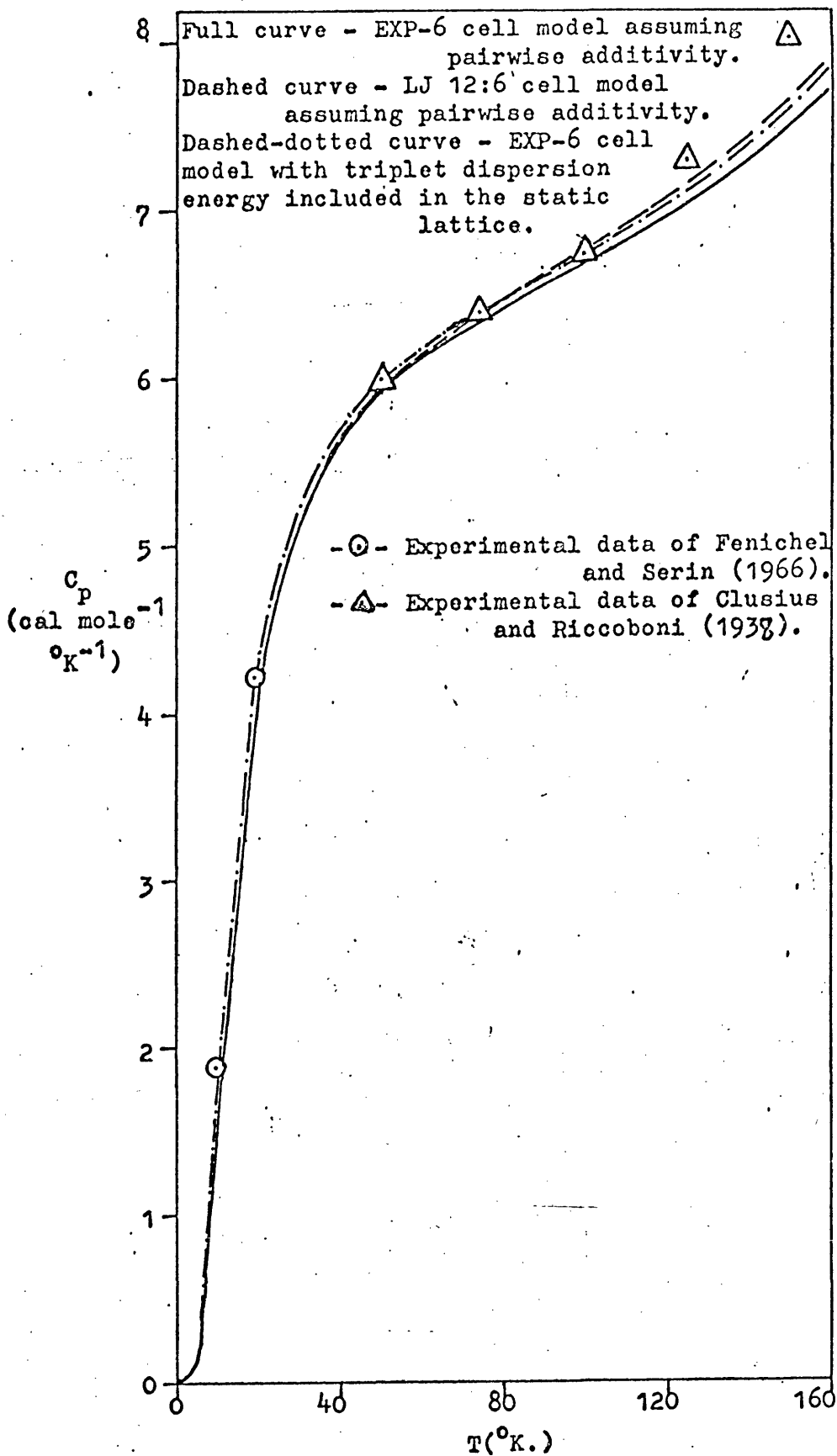
Fig.11f. Solid xenon - entropy, S, as a function of temperature, T, at zero pressure

Full curve - EXP-6 cell model assuming pairwise additivity.
Dashed curve - LJ 12:6 cell model assuming pairwise additivity.
Dashed-dotted curve - EXP-6 cell model with triplet dispersion energy included in the static lattice.
⊙ - Calculated by Packard and Swenson (1963) from the experimental C_p data of Clusius and Riccoboni (1937).
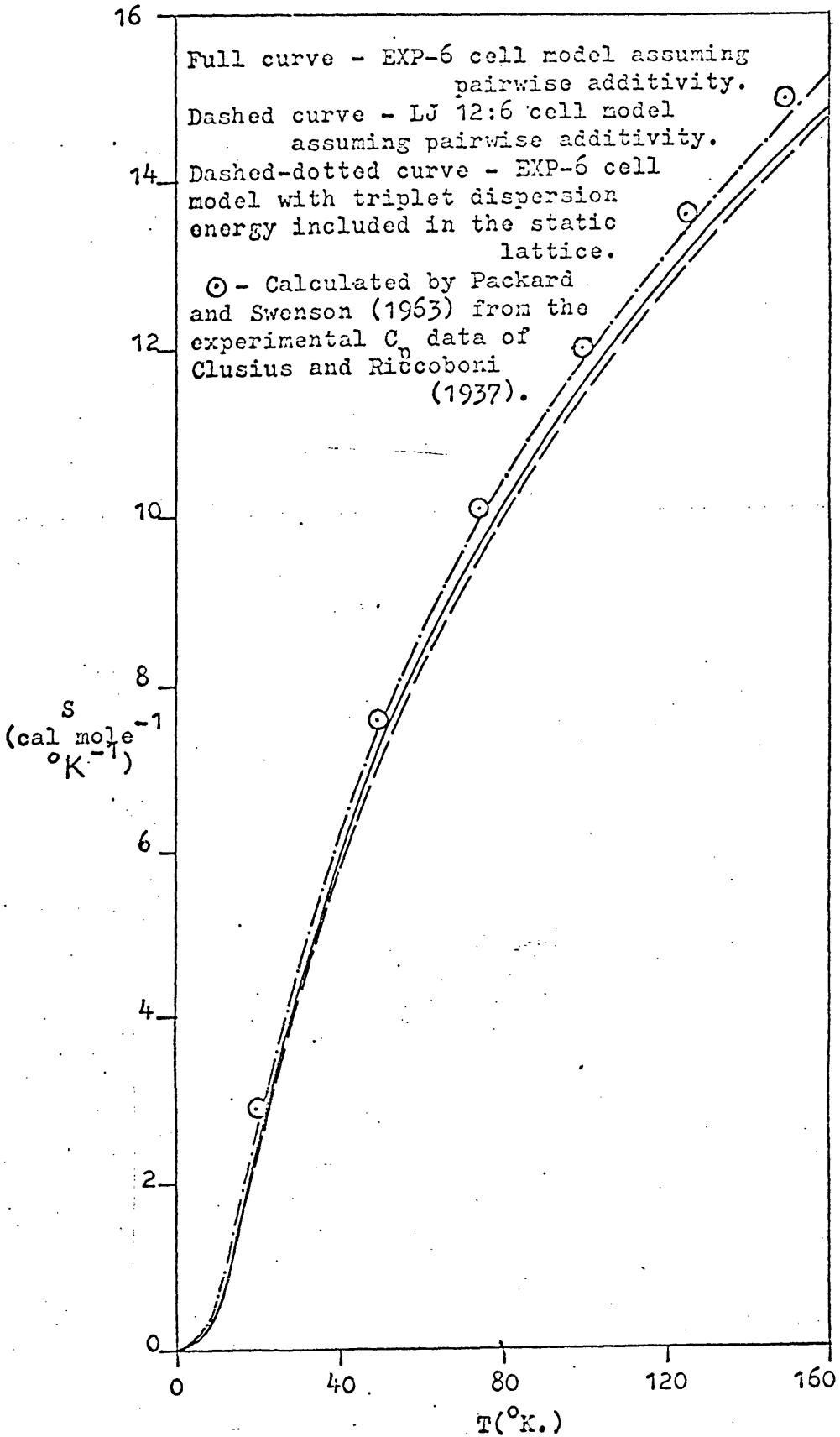
Fig.11g. Solid xenon — molar volume, V, normalised by the zero
pressure molar volume, V(O), as a function
of pressure, p, at 150°K.

Full curve — EXP-6 cell model assuming pairwise
additivity.
Dashed curve — LJ 12:6 cell model assuming pairwise
additivity.
Dashed-dotted curve — EXP-6 cell model with triplet
dispersion energy included in the static lattice.
-⊙- Experimental data of Packard and Swenson
(1963).

V/V(0)

p(kbar)
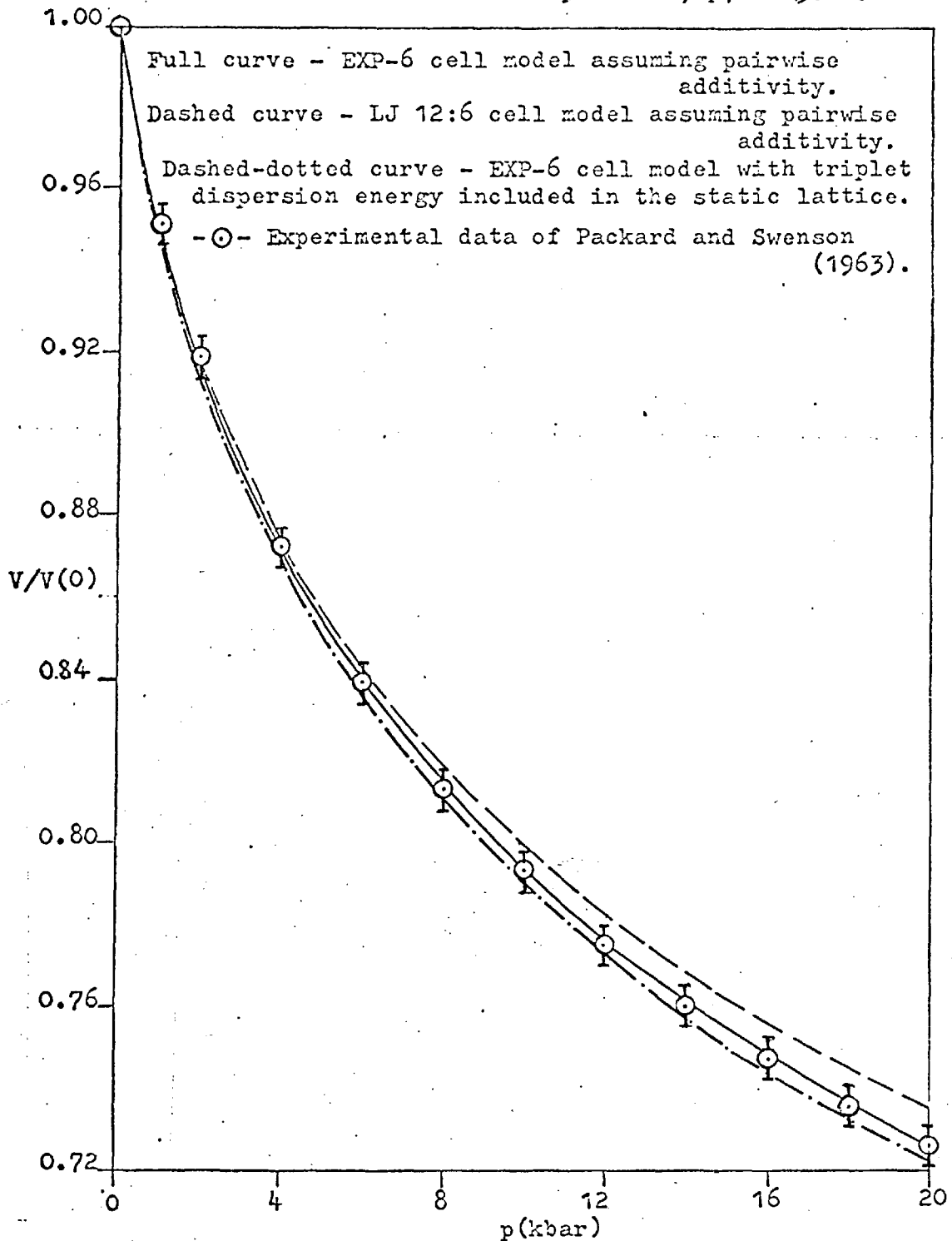
Discussion of results

Solid neon:

In Fig. 8a it is seen that the results given by
the LJ 12:6 cell model for the variation of the lattice
constant of solid neon with temperature are in good
agreement with experiment. On the other hand, the
EXP-6 results are appreciably too low at temperatures
above 8°K. Below this temperature, the agreement
between both theoretical curves and the experimental
results is good, but this is not surprising since the
T=0 value of the lattice constant was one of the
properties used to characterise the potential functions
in the first place.

Fig. 8b shows that, in the range of temperature
from 0°K to 16°K, the EXP-6 model gives results for the
isothermal compressibility of solid neon in agreement
with experiment. The LJ 12:6 results are too large in
this region. This is in direct contrast to the lattice
constant results, but is not entirely unexpected when
it is remembered that the T=0 value of χ_T was used as
the third property in the determination of the EXP-6
parameters, whereas characterisation of the two para-
meter LJ 12:6 function did not require the use of such
a property. At higher temperatures than 16°K the
experimental χ_T increases more rapidly with temperature
than the EXP-6 values and at 18°K the error bar
associated with the experimental result spans both
theoretical curves. At 20°K the experimental χ_T
is higher than both of the theoretical values but
nearer to the LJ 12:6 result.

Referring to Fig. 8c, it is clear that the values
of the volume expansivity of solid neon predicted by
the LJ 12:6 model are in better agreement with experiment
than the EXP-6 results. This is a direct consepquence
of the much better prediction by the LJ 12:6 model of the
a_o versus T curve.

Fig. 8d shows that, although the LJ 12:6 results
are in better agreement with experiment than the EXP-6
results, both models predict too small a value of C_v
over the whole temperature range (excluding of course
T=0 where C_v=0). Such behaviour must be attributed,
at least in part, to the use of an Einstein model of
the solid, the defects of which, as pointed out in
earlier chapters, are expected to be most apparent in
non static lattice dependent properties such as C_v.
For harmonic systems, the errors given by the Einstein
assumption of independent motion are such that predicted
values of C_v are lower than the experimental values.
It is evident that this is the case with our results.
However, the harmonic Einstein values of C_v are in
appreciable error only in the low temperature region
and rapidly become very accurate at temperatures
greater than $\theta_D/4$ ($\simeq 16^{\circ}$K for neon, see Pollack 1964),
whereas neither o f the theoretical curves in Fig. 8d
shows appreciably better agreement with experiment in
the higher temperature range. While this discrepancy
could possibly be attributed to the nature of the
pair interaction, it seems likely that it can largely
be put down to an inability of the Einstein approximation
to take adequate account of anharmonicity, which is
particularly large for solid neon, in such a property
as C_v. Although a direct comparison between our results

and those of lattice dynamical calculations is not
possible - our calculations take account of all an-
harmonic terms and are for three shells of neighbours,
whereas lattice dynamical calculations performed to
date consider only first order anharmonic contributions
and usually only nearest neighbour interactions - Barron
(1965) has pointed out that the Einstein and lattice
dynamical expressions for the first order anharmonic
contribution to C_v are markedly different in the limit
of high temperature.

Turning to the temperature variation of C_p given
in Fig.8e, it is again seen that the LJ 12:6 curve is
closer to the experimental results, but that both sets
of theoretical results are considerably too low. This
is only to be expected from the results predicted for
C_v, which is related to C_p by the thermodynamic relation
(4.9).

C_p is thermodynamically related to entropy by
(4.10) and any discrepancy between the experimental
values of C_p and the theoretical results is automat-
ically carried over into S. In consequence, the dis-
agreement between the theoretical and experimental
entropy values for solid neon shown in Fig.8f is not
surprising. Yet again the LJ 12:6 curve is closer to
the experimental results but both sets of theoretical
results are too low.

In fact, S is sensitive to the defects of the
Einstein approximation at all temperatures, even if it
may be assumed that predicted values of specific
heat are in error only in the low temperature region,
as is known to be the case for harmonic systems. This
is because of the integral appearing in (4.10), which

means that, at any temperature, S is not only dependent on the value of C_p at that particular temperature, but also on the values at lower temperatures. Further, by virtue of the reciprocal temperature in the integrand, low temperature contributions to the integral are significant even at considerable temperatures.

Finally for solid neon, Fig. 8g shows that, with the exception of the value at 2000 kg cm^{-2}, the LJ 12:6 cell model gives a V/V(0) versus p curve which agrees with the experimental points within their quoted un-certainties. The EXP-6 results are not in such good overall agreement with experiment. In the pressure range from 6000 to 12000 kg cm^{-2} the EXP-6 values of V/V(0) are just within the upper experimental accuracy limit, but for pressures outside this range, (except at p=0 where agreement is automatic), they are slightly too large.

Solid argon:

Fig. 9a shows that, in the case of solid argon, it is the EXP-6 a_o versus T curve which is in close agreement with experiment over the whole temperature range. The LJ 12:6 results, after their automatic good agreement with experiment at low temperature, become rapidly too large at temperatures above 20°K.

In contrast with X_T versus T plots relevant to the other inert gas solids, in which experimental accuracy limits are shown over the whole temperature range, it is only for the experimental X_T value at

83°K that an error bar has been included in Fig. 9b for
argon. This is the only value of χ_T for which an explicit
experimental uncertainty is quoted, and the absence of
error bars on the other χ_T values should not be taken
to imply high experimental precision. It is seen that
the error limits ($\pm$ 10%) on the 83°K value span both the
LJ 12:6 and EXP-6 curves and it is almost certain that
such behaviour would be general if experimental in-
accuracies were allowed for at the low temperatures.
In view of this, it appears that the existing experi-
mental data for the isothermal compressibility of solid
argon in the range from 10°K to 83°K is not sufficiently
accurate to distinguish between the LJ 12:6 and EXP-6
results, even though these are significantly different
over the whole temperature range.

The experimental value of χ_T used for characterising
the EXP-6 function was that at 4°K, (T=0 and T=4°K may
be considered as equivalent as far as χ_T is concerned),
obtained by Simmons and co-workers using a single
crystal X-ray technique. This value is of much greater
accuracy – the quoted error is about 1.5% – than those
at higher temperatures which come from sound velocity,
light scattering and torsional vibration measurements
in polycrystalline samples. It is not plotted in Fig. 9b,
since the corresponding EXP-6 result is automatically in
agreement with it, but it is worth noting that even the
use of the LJ 12:6 function, which required no χ_T data
for its characterisation, gives a value of χ_T at this
point which is only marginally outside the quoted
experimental uncertainty limits.

In Fig. 9c, the experimental β versus T results for

solid argon are seen to be reasonably well predicted
by the EXP-6 cell model for temperatures up to 70°K.
Above 70°K the experimental β rises more rapidly with
·temperature than the EXP-6 value. The LJ 12:6 results
are, (not suprisingly, when the a_o versus T results are
considered), appreciably larger than those given by
the EXP-6 calculations at all temperatures and, at
temperatures approaching the triple point (i.e. 80°K
to 83°K), the LJ 12:6 curve is the one which shows
better agreement with experiment.

Turning to a consideration of the temperature
variation of C_v for solid argon, it is seen that the
scale of Fig. 9d is not large enough to distinguish
between the LJ 12:6 and EXP-6 curves in the temperature
range from 0°K to 40°K, where the value of C_v is most
rapidly varying. Similarly any discrepancy between
theory and experiment is considerably masked in this
region. Reference to Appendix 4 shows that the LJ 12:6
results are in fact slightly larger than the EXP-6
results in this range of temperature. Also, careful
examination of the figure or direct numerical comparison
of the tabulated data in the Appendices 4 and 5 reveals
that the relevant theoretical C_v values are appreciably
lower than the corresponding experimental values. Further,
the discrepancy between theory and experiment is signif-
icantly larger than the difference between the theoret-
ical results themselves.

In the temperature range from 0°K to 35°K the
disagreement between the theoretical and experimental
C_v is largest at very low temperatures (e.g. 10°K)
and becomes much less pronounced at higher temperatures.

Although not perfect, the agreement is undoubtedly
better between 20°K and 35°K than it is at lower
temperatures. Taking the value of $(\Theta)_D/4$ for argon
to be $\sim 23^{\circ}$K (as quoted by Pollack 1964), such behaviour
is a typical result of the use of an Einstein model to
represent a harmonic crystal (see the discussion for
solid neon), of which solid argon and the heavier inert
gas solids may be taken as fair examples at low temperature.

At 40°K the theoretical C_v results are once again
substantially lower than the value given by experiment
and remain so as the temperature rises to the triple
point. The theoretical curves in Fig. 9d do not remain
identical in the high temperature region, however. At
about 40°K the EXP-6 and LJ 12:6 results cross and then
diverge with increasing temperature. At temperatures
near the triple point the EXP-6 curve is significantly
higher than the LJ 12:6 curve and is closer to, though
by no means in good agreement with, the experimental
results.

Although it is not obvious in Fig. 9d, both of
the theoretical curves pass through a shallow maximum
value of about $C_v = 2.6R$ mole^{-1} at some temperature between
60°K and 83°K. Beyond this temperature the theoretical
C_v falls very slowly as the triple point is approached.
No such behaviour is shown by the experimental results,
which, in contrast, show a marked upward trend as the
triple point is approached.

This type of behaviour in the the high temperature
theoretical C_v is clearly the result of anharmonicity,
for it is known that the C_v versus T curve given by a

harmonic model is monotonically increasing and approaches $C_v = 3R$ mole^{-1} in the classical limit of high temperature. It has been pointed out in connection with solid neon that the Einstein approximation of independent molecular motion probably does not take adequate account of the effects of anharmonicity on the value of a static lattice independent property such as C_v. Nevertheless, since lattice dynamical calculations agree with ours in predicting a downward trend in the high temperature values of C_v (see for example Feldman and Horton 1967), the discrepancy between the theoretical curves and the rising experimental results at temperatures approaching the triple point cannot be entirely attributed to errors introduced by the Einstein assumption. Anomalies in the high temperature specific heats of the heavier inert gas solids are discussed later.

As mentioned earlier, any errors in the theoretical values of C_v are automatically carried over into C_p by virtue of (4.9). It is not surprising therefore, that Fig. 9.e shows both sets of theoretical results for the C_p versus T variation of solid argon to be lower than the corresponding experimental values at all temperatures. In the case of C_p, however, the influence of the $\beta^2 TV / \chi_T$ term causes the LJ 12:6 values to be higher than the EXP-6 results over the whole temperature range and not just up to 40°K as was the case with C_v. The discrepancy between theory and experiment is again seen to be most pronounced at low temperatures (0-20°K) and at temperatures approaching the triple point (70-83°K). Between these two regions the LJ 12:6 results are in fairly good agreement with experiment and the EXP-6 results somewhat too low. However, fair agreement

between theoretical and experimental values of C_v for solid argon was apparent only in a much more restricted temperature range $(20-35^\circ K)$ and, further, the agreement between experiment and both sets of theoretical results was about equally good in this region. Consequently the reasonable agreement between the LJ 12:6 and experimental C_p over such a large temperature range must be due to a concellation of errors in the theoretical values of $\beta^2 TV/\chi_T$ and C_v and is therefore regarded as somewhat fortuitous.

Fig. 9f shows that both models give an identical S versus T curve up to $40^\circ K$ but that at higher temperatures the LJ 12:6 curve is slightly higher than the EXP-6 one. As expected from the C_p results and the large model sensitivity of calculated values of S, (see discussion for solid neon), both theoretical S versus T curves are appreciably lower than the experimental results over the whole temperature range.

From. Fig.9g it is apparent that both the EXP-6 and LJ 12:6 models give predictions of V/V(0) versus p for solid argon at $77^\circ K$ within the quoted experimental uncertainty limits at pressures above 8000 kg cm^{-2}. From 4000-8000 kg cm^{-2} the LJ 12:6 results are still inside the experimental uncertainty, whereas the EXP-6 values of V/V(0) are somewhat too high. Even so, the EXP-6 results in this region are only marginally outside the appropriate error bars. At lower pressures the theoretical curves become identical and in slight disagreement with experiment (except of course at p=0, where agreement is automatic).

Solid krypton:

In contrast with the experimental lattice constant data of solid neon and solid argon, which came solely from the very accurate and systematic X-ray work of Simmons and co-workers on single crystals, those plotted in Fig. 10a for solid krypton are taken from a number of sources. Apart from the few values of a_o given by the Simmons group in their study of the isothermal compressibility of solid krypton, these data were obtained from X-ray measurements on polycrystalline samples or from bulk density measurements and do not approach the accuracy of the argon and neon results, which are quotable to six significant figures. Consequently the experimental points in Fig. 10a show some scatter. However, if the earliest X-ray data of Cheeseman and Soane and the bulk density value of Clusius and Weigand are ignored, it is clear that the EXP-6 a_o versus T curve is in better agreement with the remaining (X-ray) data than is the LJ 12:6 curve, which is appreciably too high at temperatures above 20^oK. The agreement between the EXP-6 results and the most accurate experimental values of Simmons et. al. is strikingly good. Owing to the lack of reliable experimental data no comparison can be made for temperatures above 90^oK.

Fig. 10b shows that, as in the case of solid neon and solid argon, the γ_T versus T curve given by the EXP-6 cell model is above that derived from LJ 12:6 calculations. The EXP-6 values of γ_T are within the uncertainties in the experimental data over the whole temperature range of measurement ($0-91^o$K). On the other hand, the LJ 12:6 results are within the quoted error limits only at 17^oK and 91^oK. As before, it

should be remembered that the good agreement between
the EXP-6 and the experimental results at very low
temperature is automatic by virtue of the characterisation
procedure.

For the temperature variation of the volume ex-
pansivity, Fig.10c shows the LJ 12:6 curve to be
appreciably higher than the EXP-6 curve at all temp-
eratures above 10°K. Probably the only a_o data sufficient-
ly accurate for a reliable derivation of experimental
values of β are those of the Simmons group and, for
solid neon and argon, these workers' values of β have
been used for comparison with the theoretical results.
However, for solid krypton the only experimental β data
radily available are those of Figgins and Smith and
these show considerable scatter in Fig. 10c. Con-
sequently, although the EXP-6 curve appears to show
overall better agreement with experiment, (such would
be expected from the a_o versus T results anyway), a
detailed comparison of theoretical and experimental
values of β is not possible.

Referring to Fig. 10d, it is seen that the general
features of the LJ 12:6 and EXP-6 C_v versus T curves
for solid krypton are similar to those shown by the
corresponding curves for solid argon. At 10°K the
two theoretical values of C_v are identical on the
scale of the figure, but between this temperature
and about 35°K the LJ 12:6 results are slightly larger
than the corresponding EXP-6 values. In the range
from 35°K to 60°K the two curves are again identical
on the scale of the figure. In this region the theoret-
ical results cross and beyond 60°K the two curves di-
verge. As for solid argon, the LJ 12:6 curve is

appreciably lower than the EXP-6 curve at temperatures
approaching the triple point. Also, each set of theor-
etical results again pass through a shallow maximum and,
in this case, such behaviour is immediately apparent
from the figure. The maximum value of C_v given by both
curves is about 2.7R mole^{-1} and occurs at a temperature
betwee 60°K and 100°K. As mentioned before, this type
of behaviour is a direct consequence of anharmonic
effects, the influence of which on C_v is probably not
adequately accounted for by the cell model.

On the scale of Fig. 10e, the LJ 12:6 and EXP-6
C_p versus T curves for solid krypton are identical up
to 15°K. As expected from the Einstein nature of the
cell model, the experimental C_p is higher than the
theoretical results in thes region, ($\Theta_D/4 \approx 18^\circ$K for
krypton (Pollack 1964), see discussion for solid neon).
From 15°K to the triple point the LJ 12:6 results
are slightly larger than the EXP-6 values of C_p and in
correspondingly closer agreement with experiment.
From 20°K to 80°K the agreement between the LJ 12:6
and the experimental results is particularly good.
However, in view of the indications by the theoretical
C_v curves that anharmonic effects may be appreciable
at temperatures as low as 50°K and the doubts as to the
accuracy of the Einstein anharmonic contribution to the
specific heat, this good agreement may be to some extent
fortuitous. Also, it has been noted in connection with
solid argon that cancellation of errors in the theoretical
values of C_v and $\beta^2 TV/\chi_T$ may lead to spurious good
agreement between calculated and experimental values of
C_p. Above 80°K the experimental C_p rises much more
rapidly with temperature than either of the theoretical

values. Such behaviour was also apparent in the high
temperature specific heat of solid argon and, as remark-
ed previously, will be discussed later.

In Fig. 10f, both the theoretical S veruus T curves
for solid krypton are seen to be below the experimental
values at all temperatures above 10°K. As expected from
the C_p results, of the two, the LJ 12:6 curve is the
closer to experiment. As pointed out previously, a
discrepancy between theory and experiment is expected
from the large model sensitivity of calculated values
of entropy.

Fig. 10g shows that the LJ 12:6 model predicts the
V/V(O) versus p curve of solid krypton at 77°K within
experimental error over the whole range of pressure
considered. On the other hand, the EXP-6 results for
V/V(O) become progressively larger than the experimental
values with increasing pressure. However, in the case
of solid krypton the pressure range over which measure-
ments of the variation of volume have been carried out
is considerably smaller than that for the other inert
gas solids and the scale of Fig. 10g tends to exaggerate
the relative disagreement between the EXP-6 values and
the experimental results. In fact, the discrepancy given
by the EXP-6 cell model even at 4000 kg cm^{-2} is not much
more than that for solid argon at the same pressure.

Solid xenon:

Similar to the corresponding data for solid krypton,
the experimental lattice constant data for solid xenon
plotted in Fig. 11a are drawn from a number of sources

and are of varying accuracy. None of the data approaches
the accuracy of those of Simmons and co-workers for the
lighter inert gas solids. However, if Packard's and
Swenson's bulk density values of a_o are excluded from
the comparison, the agreement between the EXP-6 curve
and the remaining (X-ray) data is seen to be good, where-
as the LJ 12:6 results are somewhat too large above 40^oK.

Fig.11b shows that both the EXP-6 and LJ 12:6 cell
models predict the experimental (in this case, bulk den-
sity) values of χ_T within the quoted accuracy limits
at all temperatures except 50^oK where the experimental
error bar spans only the LJ 12:6 curve. In contrast
with those for the other inert gases, the theoretical
χ_T versus T curves for solid xenon cross at about
120^oK. Below this temperature the EXP-6 results are
larger than the LJ 12:6 values and above it the reverse
is true. It is remembered that, in the case of xenon,
χ_T data was not used in the characterisation of the
EXP-6 function.

As expected from the a_o versus T results, it is
seen in Fig11c that the EXP-6 versus T curve is higher
than the LJ 12:6 results at all temperatures above
about 10^oK. The large scatter of the experimental
data available does not allow a detailed comparison
between theory and experiment.

In Fig.10d, the EXP-6 C_v versus T curve for solid
xenon is seen to be higher than that given by the LJ 12:6
cell model over the whole temperature range. In the low
temperature region the difference between the curves is
small but at temperatures approaching the triple point it

is appreciable. Both curves again pass through a shallow maximum in the high temperature region and then fall with temperature as the triple point is approached. In this case the maximum value of C_v given by both curves is about 2.8R mole^{-1} and occurs at a temperature between 80°K and 115°K. The position of the maximum is quite clearly shown up by the figure and the fall of specific heat beyond it appears to be linear. Anharmonic lattice dynamical calculations also give a linear fall in C_v at high temperature (see Feldman and Horton 1967). As remarked previously, however, the Einstein approximation probably does not give quantitatively correct values of C_v at high temperatures when anharmonic effects are of importance.

The scale of Fig. 11e is insufficiently large to distinguish between the LJ 12:6 and EXP-6 C_p versus T curves for solid xenon at temperatures below 40°K. Reference to Appendix 4 shows that the EXP-6 results are in fact slightly larger in this region. The theoretical values of C_p are appreciably lower than the corresponding experimental results at 10°K, but at 20°K the agreement is better, as would be expected from the Einstein nature of the cell model ($\hbar\omega_D/4 \simeq 14$°K for xenon (Pollack 1964), see discussion for solid neon). At 40°K the theoretical results cross and at temperatures above this the LJ 12:6 results become significantly larger than the EXP-6 values and in correspondingly better agreement with experiment. Between 50°K and 100°K this agreement is good, but, in view of earlier remarks, it is probably to some extent fortuitous. Once again, at temperatures approaching the triple point the experimental C_p rises much more rapidly than

both theoretical curves.

As expected from the use of the cell model, both
theoretical S versus T curves for solid xenon are lower
than the corresponding experimental results plotted in
Fig.11f. In contrast with the other inert gas solids,
however, the EXP-6 results are above the LJ 12:6 values
in this case at all temperatures above 0°K. This dem-
onstrates the already noted sensitivity of S at high
temperature to the values of C_p in the low temper-
ature region, for we have seen that, for solid xenon,
the EXP-6 value of C_p is higher than the LJ 12:6 value
only at temperatures up to 40°K.

In Fig.11g it is clear that the EXP-6 V/V(0)
versus p curve for solid xenon at 150°K is in good
agreement with the experimental results over the
whole pressure range. On the other hand the LJ 12:6
values of V/V(0) are appreciably larger than the
experimental ones for pressures above 6kbar.

****

It is clearly difficult to draw from the above
discussion any hard and fast conclusion as to whether
the EXP-6 function gives a better general represent-
ation of the inert gas pair interaction than the more
commonly used LJ 12:6 function. Not only does the
relative predictive ability of the two potential
functions vary from substance to substance, but also,
to some extent, from property to property.

However, predicted values of such properties as
specific heat and entropy are probably too sensitive
to the defects of the model to yield anything but
spurious information as to the nature of the pair
interaction and it seems sensible to make use of only
predicted values of the remaining strongly lattice
dependent properties for this purpose. When only
such properties are considered it is possible to draw
some tentative conclusions, although inevitable incon-
sistencies still exist. It should be pointed out,
however, that, even if the static lattice dependent
properties are not too sensitive to the Einstein
nature of the model, any conclusions that we make must
be viewed in the framework of the assumption of pair-
wise additivity on which the theory is based. Some
investigations of the validity of this assumption
are reported in the following chapter.

For solid neon, the overall agreement between
experiment and the EXP-6 predictions of the static
lattice dependent properties is not good. The use
of the LJ 12:6 cell model leads to considerably better
agreement in the case of all static lattice dependent
properties except isothermal compressibility, for
which the EXP-6 calculations give the better results.
However, a comparison between the LJ 12:6 and EXP-6
values of χ_T is not strictly consistent, since the
better agreement between theory and experiment in
the EXP-6 case is almost certainly due to the use of
the $T=0^{\circ}K$ value of χ_T in the original characterisation
of the potential. Where χ_T data has been used for
characterisation purposes, it seems sensible to con-
sider better prediction of χ_T as evidence in favour

of the EXP-6 function only if it is supported by other
results. With this in mind, our calculations would
appear to indicate that the EXP-6 function is not as
good a respresentation of the neon-neon interaction
as the more commonly used and mathematically simpler
LJ 12:6 function.

In the case of solid argon, the EXP-6 calculations
do lead to results in reasonable agreement with experi-
mental values of the static lattice dependent properties.
The good prediction of the a_o versus T variation up to
the triple point and the related β versus T dependence
up to $70^{\circ}K$ argues especially strongly in favour of the
use of the EXP-6 function to represent the argon-argon
interaction. This is supported by the good agreement
by the EXP-6 χ_T versus T curve with experiment, but
it is remembered that the LJ 12:6 model also determines
this property within experimental error, even though
the characterisation of the LJ 12:6 function required
the use of no χ_T data. The EXP-6 model also predicts
the $V/V(O)$ versus p curve for solid argon at $77^{\circ}K$
reasonably well, although not quite as well as the
LJ 12:6 model.

Where the available experimental data are accu-
rate enough for a comparison to be made, the use of
the EXP-6 function is in better accord with the
experimental results for solid krypton as far as the
temperature dependent properties are concerned. In
the case of the solid krypton $V/V(O)$ versus p variation
at $77^{\circ}K$ the EXP-6 predictions are not as good as those
given by the LJ 12:6 model, but even so, are still in
fair agreement with experiment.

Where a comparison can be made, our results for the static lattice dependent properties of solid xenon unquestionably favour the EXP-6 representation of the pair interaction.

Thermal vacancies in the heavier inert gas solids

It has been noted that, for solid argon, krypton and xenon, the experimental C_p shows a marked upward trend at temperatures approaching the triple point and, in this region, the discrepancy between the experimental points and the cell model curves is much more marked than at lower temperatures, (see Figs. 9d, 10d, 11d).

Such behaviour in the experimental high temperature specific heat has been taken by several workers (e.g. Lidiard 1957, Beaumont, Chihara and Morrison 1961, Foreman and Lidiard 1963, Hillier and Walkley 1965, Kuebler and Tosi 1965) to be the result of the formation of thermal vacancies in the solid lattice and, by considering the temperature dependence of the difference, ΔC_p, between the experimental specific heat and that of an assumed "no vacancy" system, various estimates of h_s, the enthalpy of vacancy formation, have been derived.

Now, while the vacancy theory cannot be dismissed out of hand, some of the methods used to calculate h_s are decidedly open to question. In particular, Hillier and Walkley, in their calculations for solid argon, took the "no vacancy" values of C_p to be the LJ 12:6 cell model ones, the accuracy of which, even if we

assume the LJ 12:6 function to be a good representation
of the inert gas pair interaction, must be open to
question (see previous section). Further, any errors
in the no vacancy values of C_p are greatly magnified in
ΔC_p, which is a small difference between two relatively
large quantities. It is true that Beaumont and co-
workers (see below) have pointed out that h_s is not
too sensitive to ΔC_p, but there is clearly something
dubious about Hillier's and Walkley's approach, in that
further calculations using their results lead to the
anomaly of an entropy of vacancy formation, S_s, of
opposite sign to h_s.

More consistent results are obtained from the
earlier approach of Beaumont, Chihara and Morrison,
who derived "no vacancy" values of C_p for solid argon
and krypton by extrapolating low temperature experi-
mental data. Having calculated h_s these workers then
derived a value of s_s of the same sign as h_s and
finally an expression for n_s, the concentration of
vacancies as a function of temperature. For argon,
the value of n_s at the triple point given by these
results is of the order of 1% mole fraction. Later
analyses of the specific heat by Foreman and Lidiard
and Kuebler and Tosi lead to a similar result. How-
ever, as well as being inconsistent with theoretical
estimates of vacancy free energy (Nardelli and
Chiarotti 1960), such a vacancy content in solid
argon requires a large relaxation around the vacancy -
Beaumont and co-workers estimate that a vacancy of
23% of the atomic volume is necessary - to be con-
sistent with the observed thermal expansion of solid
argon. On the other hand, calculations by Hall (1957),

Kanzaki (1957) and Gallina and Omini (1964) indicate
only small relaxation effects.

Recently other objections have been lodged against
the appreciable formation of lattice vacancies in solid
argon. McGlashan (1965) using the Guggenheim-McGlashan
piecewise potential (Guggenheim and McGlashan 1960, see
Chapter 1 of this thesis) has shown that it is possible
to reproduce the experimental values of C_p for solid
argon without invoking vacancy phenomena. However,
these results must be viewed with suspicion since
McGlashan relied heavily upon specific heat data
together with an Einstein model of the crystal to
characterise his potential function. This forces
correct values of specific heat on a model which
cannot really cope with them (see the previous
section of this thesis).

A much more convincing objection to the vacancy
theory for argon is that of Batchelder, Peterson and
Simmons (1965) who, by comparing the results of their
experimental X-ray measurements of the interatomic
distances in a rather perfect single crystal with
those given by bulk density measurements, conclude
that, if vacancies are present at all in solid argon,
their concentration even at the triple point is less
than 0.2% of a mole fraction. This concentration is
much less than that given by specific heat analysis.

More recently, Losee and Simmons (1967) have
crystallographically measured the concentration of
vacancies in solid krypton. While their results
lead to a value of h_s in good agreement with that

obtained by Beaumont and co-workers from a consideration of the specific heat, they again give a much smaller value of n_s (0.3% compared with 1.5% of a mole fraction at the triple point) than that given by a specific heat analysis.

The purely experimental evidence of Simmons and co-workers cannot be disregarded and casts considerable doubt on the wisdom of estimating vacancy effects from the high temperature specific heat of the inert gas solids. In view of this and the fundamental inconsistency given by the assumption of Hillier and Walkley that a cell model system can be taken as a "no vacancy" system, it was felt that our specific heat calculations can throw no real light on the importance of vacancy effects and no such investigations were attempted in the present work.

<u>Chapter 5</u>

<u>Triplet Interactions in the Inert Gas Solids and Some
Considerations of the Second Virial Coefficient</u>

<u>Triplet interactions in the solid state of the inert gases</u>

All the calculations described to date were per-
formed under the commonly made assumption of pairwise
additivity in the solid state. We now describe EXP-6
solid state calculations which make some attempt to
allow for non-central many-body interactions - in par-
ticular triplet interactions.

The first calculation of many-body interactions
was by Axilrod and Teller (1943) who, by means of
third order perturbation theory, considered the inter-
action of three instantaneous dipoles. Their approach
was analogous with London's use of second order per-
turbation theory to give the r^{-6} attraction between
two instantaneous dipoles (see Chapter 1) and, in
addition to the three pair interactions, led to an
expression for the triplet energy of the three particles.
This was:

$$\phi^{ABC} = \frac{C^{ABC}(3\cos\Theta_A\cos\Theta_B\cos\Theta_C + 1)}{r_{AB}^3 r_{BC}^3 r_{CA}^3} \qquad (5.1)$$

where Θ_A, Θ_B, Θ_C are the interior angles and r_{AB}, r_{BC},
r_{CA} the sides of the triangle formed by the three
particles A, B and C. Axilrod (1949) later estimated
the proportionality constant C^{ABC} in terms of the

ionisation energies and polarisabilities of A, B and C.
For three identical atoms, A, the appropriate expression
is:

$$C^{AAA} = (9/16)I_A \alpha_A^3 \qquad\qquad (5.2)$$

where I_A is the ionisation energy and α_A' the polaris-
ability of A. C^{ABC} may also be evaluated from quantum
mechanical first principles and such calculations have
been performed for the inert gases by Kihara (1958) and,
more recently, by Bell and Kingston (1966). The values
of C^{ABC} given by Bell and Kingston are quoted to an
accuracy of 10% and agree with those given by Axilrod's
expression, but are in disagreement with those of
Kihara.

Similar to London's dipole-dipole pair interaction
energy, the energy given by (5.1) is in fact the first
of a series of terms constituting the triplet dispersion
energy of the three particles. Higher terms in the
series, such as the dipole-dipole-quadrupole interaction,
have been derived by Ayres and Tredgold (1956). However,
such terms are small and, in the present work, the use
of the expression "triplet dispersion energy" refers
only to the triple dipole interaction given by (5.1).

The triplet dispersion energy takes no account of
electron overlap and represents only the long range
interaction. Jansen and co-workers (see Jansen and
Lombardi 1965 and the references quoted therein) have
made several investigations of the short range exchange
triplet interaction, using a Gaussian effective electron
model. However, such an approach does not lead to

explicit expressions and, moreover, Swenberg (1967) has
recently cast doubt on the validity of one of the
approximations made in Jansen's calculations. Con-
sequently, the detailed nature of short range triplet
effects must, as yet, be considered uncertain. As was
pointed out in Chapter 1, such is also the case with
the short range pair interaction.

Recent investigations of triplet interactions in
the solid state of the inert gases have been concerned
with their effect on such properties as stacking fault
energy (Pliskin and Greenberg 1965, Bullough, Glyde
and Venables 1966), elastic constant (Götze and Schmidt
1966), vacancy formation energy (Jansen 1965) and
lattice relaxation around a vacancy (Foreman 1963).
However, such interactions have been of interest
mainly because of the possibility of their explaining
why neon, argon, krypton and xenon crystallise with a
face centred cubic (f.c.c.) rather than a hexagonal
close packed (h.c.p.) structure.

Kihara and Koba (1952) and Kihara (1953) showed
that pairwise additive LJ m:6 and EXP-6 calculations of
the static energies of f.c.c. and h.c.p. lattices
invariably favour the h.c.p. structure. The relative
difference in pair energy is only small - of the order
of 0.01% - but is nevertheless constant for different
pair potentials. This conclusion is unaltered by the
consideration of zero point energy (Barron and Domb
1955, Jansen and Dawson 1955, Wallace 1964). Axilrod
(1951) had previously calculated the static triplet
dispersion energy in the f.c.c. and h.c.p. structures
by summing over a large (but finite) cylindrical lattice.

In both cases he found the energy to be repulsive
(i.e. of positive sign) and such that the f.c.c.
structure is favoured. The difference, however, is
not enough to overcome the stability of the h.c.p.
lattice predicted by pairwise additive calculations.
The work of Jansen and co-workers on the short range
interaction predicts the correct f.c.c. structure,
but, as mentioned previously, this work has been
questioned.

Although many-body interactions have been gener-
ally recognised as probably decisive in determining
the stable structure of the inert gas solids, the very
small difference between the energies of the two poss-
ible lattices has been taken by some (e.g. Pollack
1964) to show that many-body effects may be neglected
in the calculation of thermodynamic properties. Such
a conclusion, however, ignores an important result of
Axilrod's work. Taking the f.c.c. structure as read,
the expression derived by Axilrod for the contribution
of triplets to the static energy of a lattice of N atoms
of type A may be written:

$$W(0)^{triplets} = (N/3)56.7C^{AAA}/a_1^9 \qquad (5.3)$$

and, using (5.2) to evaluate C^{AAA}, Axilrod showed
that this energy is by no means negligible, at least
in the case of the heavier inert gas solids. For
solid xenon, he found the magnitude of $W(0)^{triplets}$
given by (5.3) to be of the order of 10% of the total
energy of the crystal at $0^{\circ}K$. Bell and Kingston's
values of C^{AAA} lead to similar results.

The values of $W(O)^{triplets}$ for solid neon, argon, krypton and xenon at $O^{O}K$ and zero pressure, calculated from (5.3) using the values of Bell and Kingston for C^{AAA} and the values of a_1 corresponding to those of $a_{oo}(O)$ given in Table 1 (p.70), are given in Table 4. They are compared with the corresponding $O^{O}K$, zero pressure values of the sublimation energy, $L_o(O)$ (which is the negative of the free energy of the crystal at $O^{O}K$ and zero pressure), given in Table 1.

<u>Table 4</u>

<u>The static lattice triplet dispersion energy of the inert gas solids at $O^{O}K$ and zero pressure</u>

Substance (A)	C^{AAA} (erg $\mathring{A}^{9}$)x10^{12}	$W(O)^{triplets}$ (cal mole^{-1})	$L_o(O)$ (cal mole^{-1})
Neon	1.68	15	448
Argon	74.5	136	1846
Krypton	224	236	2666
Xenon	750	377	3828

(5.3) may be written in a reduced form analogous to that corresponding to the pair static lattice energy, thus:

$$W*(O)^{triplets}=\tfrac{1}{3}w*(o)^{triplets}=\tfrac{1}{3}(56.7C*^{AAA}/a_1^{*9})$$

$$(5.4)$$

where $W*(O)^{triplets}=W(O)^{triplets}/(N\epsilon)$

$w*(o)^{triplets}=w(o)^{triplets}/\epsilon$

$C*^{AAA}=C^{AAA}/(\epsilon d^{9})$

$a_1^{*}=a_1/d$

ξ and d being the characteristic energy and length
parameters in the pair potential function and w(o) the
potential energy experienced by a representative particle
in the lattice due to all pairs of other particles in
the lattice.

The direct experimental measurement of many-body
contributions to the potential energy of a crystal is
very difficult, since it is difficult to isolate many-
body from two-body effects. From their measurements of
of vacancy concentrations, Losee and Simmons (1967)
have obtained a rather imprecise value of 650 ± 300 cal
mole^{-1} for the many-body interactions in solid krypton,
but, to the author's knowledge, this is the only ex-
perimental result as yet available. The result of
Losee and Simmons does not distinguish between triplet
and higher order interactions, but it does lend support
to the importance of many-body effects in the inert
gas solids and it is reasonable to assume that triplet
effects are by far the largest of these.

In view of the above, it seemed worthwhile to in-
vestigate how the results of our solid state calculations
would be affected by allowing for triplet interactions.
The approach taken was that of Zucker (1968 - but
communicated to the author prior to publication), who
made use of (5.3), together with Bell and Kingston's
values of C^{AAA}, to evaluate the contribution of triplets
to the total energy of the crystal.

This approach involves two major approximations.
The first is that triplet effects in the vibrational
energy of the crystal are ignored. At the time that

that the work described here was undertaken there was little information as to the nature of such effects. More recently, however, Chell and Zucker (1968) have explicitly evaluated the harmonic contribution of triplet dispersion interactions to the zero point energy of the inert gas solids using an Einstein model of the crystal. They found that triplet interactions lowered the zero point energy by amounts ranging from less than 1% in the case of neon to about 2% in the case of xenon. Such changes in the zero point energy lead to changes in the total crystal free energy which are minimal in comparison with the effect of the triplet dispersion energy in the static lattice.

The second approximation is that short range triplet effects are completely neglected and this is undoubtedly more serious. However, until more detailed information as to the nature of such effects is available, there seems no alternative but to ignore them and trust that their inclusion would not drastically alter any conslusions which we might draw. In any case the use of (5.3) should serve as a first approximation for the evaluation of triplet effects.

Zucker investigated the effect of the triplet dispersion interactions in the static lattice on LJ pair potentials characterised from 0°K solid state data, which gave the best fit with experimental solid state isotherms, and also the effect on the predicted isotherms thermselves. The appropriate LJ functions were the 12:6 for neon, argon and krypton and the 11:6 for xenon. He found that the pair parameters for

neon were only slightly affected by the inclusion of $W(0)$ ^{triplets} but that those of the heavier gases were substantially changed. On the other hand, none of the predicted isotherms was appreciably affected.

In our work we investigated the influence of $W(0)^{triplets}$ given by (5.3) on the EXP-6 pair potential parameters determined from solid state data at $0^{O}K$ and the subsequent EXP-6 prediction of all the solid state properties calculated in the previous chapter. The experimental data used for the characterisation were those used in the pairwise additive calculations (see Table 1). The numerical precedure employed in the characterisation and the subsequent calculation of the thermodynamic properties was also the same as before except that $\frac{1}{2}w^*(o) + \frac{1}{3}w^*(o)^{triplets}$ was used in place of $\frac{1}{2}w^*(o)$.

The parameters obtained are given in Table 5 below and the corresponding potential functions are plotted as the dashed-dotted curves in Figs.4, 5, 6 and 7 (pp. 75-78) for neon, argon, krypton and xenon respectively. The results of the calculations of the thermodynamic properties are tabulated in Appendix 6 and plotted as the dashed-dotted curves in Figs.8a-11g (pp.90-117). (The reader is asked to note that, on the scale of Fig.11a, the a_o versus T curve for xenon derived by including triplet dispersion interactions in the static lattice is identical to the corresponding "pairwise additive" LJ 12:6 curve over the whole temperature range.)

Table 5

EXP-6 parameters derived from solid state data at $0°K$ with triplet dispersion energy included in the static lattice

Substance	$\mathcal{E}(erg) \times 10^{15}$	$r_m(\mathring{A})$	α	$\Lambda^* = h/[(m\mathcal{E})^{\frac{1}{2}}r_m]$
Neon	5.642	3.077	16.27	0.4952
Argon	18.37	3.774	14.13	0.1590
Krypton	26.07	4.020	14.87	0.08654
Xenon	36.10	4.387	13.47	0.05384

Comparison of the values of the parameters in Table 5 with those in Table 2 (p. 74), or of the full curves with the dashed-dotted ones in Figs.4,5, 6 and 7, shows that the inclusion of triplet dispersion interactions in the static lattice lowers the depth of the EXP-6 well (i.e. increases $\mathcal{E}$) and moves it to a slightly smaller intermolecular separation (i.e. decreases r_m). Such is in agreement with Zucker's results for the best fit LJ potentials. Similarly the effect on $\mathcal{E}$ and r_m is only small for neon, but is appreciable for argon, krypton and xenon. In all cases the value of α is not significantly altered.

From comparison of the full and dashed-dotted curves in Figs.8a-c, 9a-c, 10a-c and 11a-c, it is clear that the effect of the inclusion of $W(0)^{triplets}$, evaluated from (5.3), on the EXP-6 prediction of the temperature variation of lattice constant, isothermal compressibility and volume expansivity of the inert

gas solids, is to increase the values of these properties at temperatures above $0^{\circ}K$.

In the case of solid neon this has the effect of bringing the predicted values of a_0 and β (see Figs. 8a, 8c) marginally closer to the corresponding experimental values, but by no means into good agreement with them. The EXP-6 values of χ_T for solid neon (see Fig.8b) predicted by the inclusion of $W(0)^{triplets}$ in the static lattice energy are, like the corresponding pairwise additive values, in agreement with experiment within the quoted error limits over the whole temperature range.

For the heavier inert gas solids the inclusion of $W(0)^{triplets}$ given by (5.3) removes the good agreement between the EXP-6 and experimental a_0 versus T curves (see Figs. 9a, 10a, 11a). In these cases the discrepancy between the EXP-6+$W(0)^{triplets}$ curves and the experimental results is approximately the same as that between the pairwise additive LJ 12:6 curves and experiment. A similar discrepancy is also shown by the β versus T plot for solid argon up to $70^{\circ}K$ (see Fig. 9c). As mentioned in Chapter 4, the volume expansivity data for solid krypton and xenon is not accurate enough for a detailed comparison between theoretical and experimental values of this property to be carried out, but for these substances too the EXP-6+$W(0)^{triplets}$ β versus T curves are similar to the corresponding pairwise additive LJ 12:6 curves (see Figs. 10c, 11c). Both the EXP-6 pairwise additive and EXP-6+$W(0)^{triplets}$ models predict the available χ_T versus T data for solid argon, krypton and xenon within the experimental uncertainties

quoted (see Figs. 9b, 10b, 11b).

Owing to the independence of C_v of the static lattice energy, the new EXP-6 C_v versus T curves differ from the old only by virtue of the difference between the two sets of parameters in Tables 2 and 5. The small difference between these sets of parameters in the case of neon leads to a small increase in the predicted C_v at the higher temperatures, but does not significantly improve agreement with experiment (see Fig. 8d). The new C_v versus T curves for the heavier inert gas solids show the same general features as those derived from the "pairwise additive" parameters, but are considerably different from a quantitative point of view (see Figs. 9d, 10d, 11d). It appears that the use of the new parameters leads to an increase in C_v in the low temperature region and a decrease at temperatures approaching the triple point. Also the fall of the C_v versus T curves in the high temperature region appears to be slightly more rapid. In the case of solid argon, which is the only one of the heavier inert gas solids for which experimental C_v data are given, Fig. 9d shows that the new EXP-6 C_v versus T curve is in better agreement with experiment at the lower temperatures and in worse agreement at the higher temperatures than is the corresponding "pairwise additive" curve. However, for reasons given in Chapter 4, a detailed comparison between experimental and cell model values of C_v is probably not meaningful.

In analogy with the corresponding C_v versus T results, the EXP-6+W(0)^{triplets} C_p versus T curve for solid neon is slightly above that given by pairwise

additive calculations and, therefore, slightly closer to
(but by no means in agreement with) the experimental
results (see Fig. 8e).   The new EXP-6 C_p versus T
curves for the heavier inert gas solids are considerably
higher than the corresponding pairwise additive ones at
all appreciable temperatures (see Figs.9e, 10e, 11e).
In all cases the agreement between theory and experiment
is better over the whole temperature range, and is
remarkably good at the lower temperatures. However,
in view of remarks made in Chapter 4, such agreement
is probably to some extent fortuitous.

The increased values of C_p given by the inclusion
of $W(0)^{triplets}$ automatically lead to increased values
of the entropy and, consequently, the appropriate S
versus T curves in Figs. 8f, 9f, 10f and 11f are closer
to the experimental results than those derived from
pairwise additive calculations. In the case of solid
xenon the agreement between the new S values and ex-
periment is reasonably good, but, once again, owing to
the previously mentioned (see Chapter 4) model sensitivity
of the entropy, this is almost certainly fortuitous.

The effect of the static lattice triplet dispersion
energy on the predicted V/V(0) versus p curves is once
again small in the case of solid neon (see Fig. 8g),
but more marked in the case of argon, krypton and
xenon (see Figs. 9g, 10g, 11g). For solid neon the
effect of $W(0)^{triplets}$ is to slightly increase the
values of V/V(0) at high pressure. On the other hand,
the values of V/V(0) predicted for the heavier inert
gas solids are lowered. The agreement with experiment
is somewhat improved in the case of solid argon and solid

krypton. For solid xenon both EXP-6 models predict the experimental V/V(0) versus p data within the appropriate experimental uncertainties.

It is clear then that the inclusion of $W(0)^{triplets}$ given by (5.3) does lead to changes both in the pair potentials and in the predicted values of the thermo-dynamic properties of the inert gas solids.

For solid neon these changes are not large enough either to seriously question the assumption of pairwise additivity or to alter the conclusion arrived at in Chapter 4 that the EXP-6 function does not give a good representation of the pair interaction, which appears to be better described by the LJ 12:6 function.

In the case of solid argon, krypton and xenon, however, the effect of $W(0)^{triplets}$ is significant and, for these substances, the speculation in Chapter 4, that solid state, "pairwise additive" parameters can be regarded as defining an "effective" pair inter-action, which, in turn, may be used in the pairwise additive calculation of the thermodynamic properties, appears to be contradicted.

Once again we draw no conclusions from a consid-eration of C_v, C_p and S versus T plots, since, as pointed out in Chapter 4, the calculated values of these prop-erties are probably too sensitive to the Einstein nature of the cell model for a meaningful comparison with experiment to be made. Leaving such properties aside then, we have seen that the inclusion of $W(0)^{triplets}$ in the EXP-6 cell model does lead to somewhat better

predictions of the V/V(0) versus p data of solid argon
and krypton. However, taking account of experimental
error, this improvement is not substantial. For solid
xenon the two EXP-6 models predict the V/V(0) versus
p data equally well within the quoted experimental
error limits. The rather imprecise χ_T data for all the
heavier inert gas solids is also predicted within ex-
perimental error by both models. On the other hand,
the good agreement between the EXP-6 a_o versus T curves
and experiment, which was taken to argue so strongly
for the use of the EXP-6 function for argon, krypton
and xenon in the pairwise additive case, is destroyed
by the inclusion of $W(0)^{triplets}$. This, in turn, is
also the case for the β versus T curve of solid argon,
which is the only one of the heavier inert gas solids
for which the volume expansivity data is accurate enough
for a reliable comparison between theory and experiment
to be made. Such a_o versus T and β versus T results,
however, do not alter the conclusion drawn in Chapter
4 that the EXP-6 function gives a better description
of these properties of the heavier inert gases than does
the LJ 12:6 function, for the inclusion of the value of
$W(0)^{triplets}$ given by (5.3) in the LJ 12:6 calculations
would lead to results even further removed from ex-
periment. Nevertheless, if the use of (5.3) is a valid
way of allowing for the effect of triplet interactions,
these results would appear to indicate that the EXP-6
function is not such a good representation of the
argon-argon, krypton-krypton and xenon-xenon interactions
as would be supposed from pairwise additive calculations.

Some considerations of the second virial coefficient

It is well known that the equation of state of a
non-ideal gas may be written as the virial expansion:

$$\frac{pV}{NkT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} \ldots \ldots \quad (5.4)$$

where p, V, N, k and T have their usual significance
and B(T), C(T), D(T) ... are called the second, third,
fourth ... virial coefficients of the gas. The term
B(T)/V represents the contribution of interacting
pairs of molecules, outside the perturbing field of
others in the system, to the compressibility factor
of the gas. Higher terms represent contributions
from groups of three, four ... molecules and involve
triplet, quadruplet ... interactions as well as the
pair interaction. The study of B(T), therefore,
provides a means of obtaining information as to the
nature of the pair interaction itself, without having
to consider many-body effects. In consequence, it is
of interest to compare pair potentials derived from a
consideration of B(T) with those given by a consider-
ation of a multiparticle system such as the solid state.

The second virial coefficient, B(T), in quantum
statistical mechanics may be written as:

$$B(T) = \frac{-N}{2V} \int\int \left[W_2(r_1, r_2) - 1 \right] dr_1 dr_2 \quad (5.4)$$

where $W_2(r_1, r_2)$ is the Slater sum for two molecules
with position vectors r_1 and r_2 and is given by:

$$\mathcal{N}_2(r_1, r_2) = 2! \left(\frac{h^2}{2\pi mkT} \right)^3 \sum_i \psi_i^*(r_1, r_2) \exp\left(\frac{-H}{kT} \right) \psi_i(r_1, r_2)$$

$$(5.4a)$$

In (5.4a) ψ_i (i=1,2,3,...) is a complete set of orthonormal wave functions, ψ_i^* (i=1,2,3,...) is the corresponding complex conjugate set and H is the quantum mechanical Hamiltonian operator for the two particles. On choosing ψ_i (i=1,2,3,...) to be the momentum wave functions, (5.4) may be expanded in even powers of (h^2/m) to give:

$$B(T) = B_{Cl}(T) + \left(\frac{h^2}{m} \right) B_I(T) + \left(\frac{h^2}{m} \right)^4 B_{II}(T) + \dots \qquad (5.5)$$

where $B_{Cl}(T)$ is the classical value of the second virial coefficient and is given in terms of the pair interaction, $\phi(r)$, by:

$$B_{Cl}(T) = -2\pi N \int_0^\infty \left[\exp\left(\frac{-\phi(r)}{kT} \right) - 1 \right] r^2 dr \qquad (5.5a)$$

Higher terms in the series represent quantum corrections, $B_I(T)$ and $B_{II}(T)$ being given by:

$$B_I(T) = \frac{2\pi N}{48\pi^2 k^3 T^3} \int_0^\infty \left[\exp\left(\frac{-\phi(r)}{kT} \right) \right] \left[\frac{d\phi(r)}{dr} \right]^2 r^2 dr \qquad (5.5b)$$

and

$$B_{II}(T) = \frac{-2\pi N}{1920\pi^4 k^4 T^4} \int_0^\infty \exp\left(\frac{-\phi(r)}{kT} \right) \left\{ \left[\frac{d^2\phi(r)}{dr^2} \right]^2 + \frac{2}{r^2} \left[\frac{d\phi(r)}{dr} \right]^2 \right.$$

$$+ \frac{10}{9kTr} \left[\frac{d\phi(r)}{dr} \right]^3 - \frac{5}{36k^2 T^2} \left[\frac{d\phi(r)}{dr} \right]^4 \right\} r^2 dr$$

$$(5.5c)$$

(see Hirschfelder, Curtiss and Bird 1954, p.420).

A further term $(h^2/m)^{3/2} B_o(T)$ $(B_o(T) = {}^{-5/2}(2\pi kT)^{-3/2})$ must be included in this series to account for Bose-Einstein (B.E.) or Fermi-Dirac (F.D.) statistics (de Boer and Michels 1938). The sign of this term is negative for B.E. statistics (i.e. for systems of molecules consisting of an even number of nucleons and electrons) and positive for F.D. statistics (i.e. for systems of molecules consisting of an odd number of nucleons and electrons). The final expression may be written in reduced form as an expansion in powers of the quantum parameter, Λ^* (see (2.28) in Chapter 2), thus (Hirschfelder, Curtiss and Bird 1954, p.420):

$$B^*(T^*) = \left[B^*_{C1}(T^*) + \Lambda^{*2} B^*_I(T^*) + \Lambda^{*4} B^*_{II}(T^*) + \cdots \right]$$
$$\mp \Lambda^{*3} B^*_o(T^*) \qquad (5.6)$$

where $B^*(T^*) = B(T)/(\tfrac{2}{3}\pi N d^3)$, d being the characteristic length parameter of the pair potential. $B^*_{C1}(T^*)$, $B^*_I(T^*)$, $B^*_{II}(T^*)$, $B^*_o(T^*)$ are given by:

$$B^*_{C1}(T^*) = -3 \int_0^\infty \left[\exp\left(\frac{-\phi^*(r^*)}{T^*}\right) - 1 \right] r^{*2} dr^* \qquad (5.6a)$$

$$B^*_I(T^*) = \frac{1}{16\pi^2 T^{*3}} \int_0^\infty \exp\left(\frac{-\phi^*(r^*)}{T^*}\right) \left[\frac{d\phi^*(r^*)}{dr^*}\right]^2 r^{*2} dr^* \qquad (5.6b)$$

$$B^*_{II}(T^*) = -\frac{1}{640\pi^4 T^{*4}} \int_0^\infty \exp\left(\frac{-\phi^*(r^*)}{T^*}\right) \left\{ \left[\frac{d^2\phi^*(r^*)}{dr^{*2}}\right]^2 \right.$$
$$+ \frac{2}{r^{*2}} \left[\frac{d\phi^*(r^*)}{dr^*}\right]^2 + \frac{10}{9T^*r^*} \left[\frac{d\phi^*(r^*)}{dr^*}\right]^3$$
$$\left. - \frac{5}{36T^{*2}} \left[\frac{d\phi^*(r^*)}{dr^*}\right]^4 \right\} r^{*2} dr^* \qquad (5.6c)$$

$$B_o^*(T^*) = \left(\frac{3}{32\pi^{5/2}}\right) T^{*-3/2} \qquad (5.6d)$$

For fuller details of the formulation and the range of
its validity the reader is referred to Hirschfelder,
Curtiss and Bird (1954, p.419 et.seq.) and de Boer and
Michels (1938). For the calculation of high temper-
ature values of the second virial coefficient, terms
beyond the classical one may be neglected, but at low
temperatures higher terms may become significant,
especially for light substances. In our work we took
account of terms up to and including that in Λ^{*4},
using the expressions given below.

Experimental measurements of the second virial
coefficient have been widely used in the character-
isation of empirical pair potential functions. Typical
of such work is that of Nicholson and Schneider (1955),
Sherwood and Prausnitz (1964), Dymond, Rigby and Smith
(1965) and Weir, Wynne Jones, Rowlinson and Saville
(1967). Nicholson and Schneider characterised the
LJ 12:6 and EXP-6 potentials for neon by calculating
the parameters which gave the best fit with their own
and earlier B(T) data. They found that each function
predicted the B(T) data equally well, but that the
EXP-6 function gave a slightly deeper potential well.
Sherwood and Prausnitz made use of all the relevant
B(T) data available at the time to determine the best
fit parameters of, among others, the LJ12:6, EXP-6
and Kihara 12:6 potential functions for argon, krypton
and xenon. They found that, in each case, the EXP-6
and Kihara 12:6 potentials gave a better overall fit
with experiment, a deeper well and smaller equilibrium

separation than the LJ 12:6 function. The use of
the five term empirical function proposed by Dymond,
Rigby and Smith leads to results similar to those
given by the EXP-6 and Kihara 12:6 functions. The
results of Weir, Wynne Jones, Rowlinson and Saville,
who used their own recent measurements of $B(T)$ and
those of others to characterise the LJ 12:6 and Kihara
12:6 functions for argon and krypton, are in agreement
with those given by the corresponding calculations of
Sherwood and Prausnitz, but give a deeper well for
the Kihara potential.

In our work we decided to recharacterise the
EXP-6 function for neon, argon, krypton and xenon
using the most modern $B(T)$ data available and to
compare the pair interactions obtained with those
given by solid state data with and without $W(0)^{triplets}$
included. In contrast to the second virial coeff-
icients corresponding to the LJ 12:6 and Kihara 12:6
potentials, which may be evaluated analytically in
terms of gamma functions, the calculation of those
corresponding to the EXP-6 potential requires the
use of numerical integration. In view of this, it
seemed sensible to study the nature of the integrals
in (5.6a), (5.6b) and (5.6c) as a preliminary to more
detailed calculations.

First it should be remembered that the spurious
maximum in the EXP-6 pair potential requires the
imposition of an infinite cutoff at a reduced inter-
molecular separation of r^*_{max}. For distances between
$r^*=0$ and $r^*=r^*_{max}$, therefore, the value of $\exp(-\phi^*(r^*)/T^*)$

is zero and the contribution to $B_{Cl}^*(T^*)$ in this region is:

$$-3 \int_0^{r^*_{max}} (-r^{*2})dr^* = r^{*3}_{max} \tag{5.7}$$

The corresponding contributions to $B_I^*(T^*)$ and $B_{II}^*(T^*)$ are zero. The value of r^*_{max} is easily obtained for any value of α by the numerical solution of the transcendental equation (4.5) in Chapter 4.

It is relevant to note the r^* dependence of the integrands, I_{Cl}^*, I_I^* and I_{II}^* appearing in the expressions (5.6a), (5.6b) and (5.6c). The r^* dependence of I_{Cl}^* is such that this quantity passes through a negative minimum followed by a positive maximum in the region of $r^*=1$. The behaviour of I_I^* with r^* is such that I_I^* is always positive and passes through two positive maxima on either side of a minimum value of zero at $r^*=1$. The r^* dependence of I_{II}^* is of a similar form to that of I_{Cl}^*. All three functions approach zero at small and large values of r^*. The values of r^* at which the various maxima and minima appear are virtually independent of the values of α and T^*, both of which affect only the values of I_{Cl}^*, I_I^* and I_{II}^* at these points. The values of r^* corresponding to the minimum and maximum in I_{Cl}^* are about 0.8 and 1 respectively, those corresponding to the two maxima in I_I^* are about 0.9 and 1.1 and those corresponding to the minimum and maximum values of I_{II}^* are about 0.85 and 0.9 respectively.

The major contributions to the various integrals clearly come from the restricted regions around the

various maxima and minima in I^*_{Cl}, I^*_I and I^*_{II}, and it is wise to consider these regions separately from those where the integrands are approaching zero. This is especially the case in the evaluation of $B^*_I(T^*)$ and $B^*_{II}(T^*)$ for which the relevant maxima and minima are so sharp that, if the range of integration is divided without regard to the behaviour of the integrands, the major contributions may be missed altogether. With this in mind, we divided the range of integration for $r^* \geqslant r^*_{max}$ into five separate sub-ranges for each integral. In each case the first four of these sub-ranges covered intermolecular distances from $r^*=r^*_{max}$ to $r^*=3$. For $B^*_{Cl}(T^*)$ they were $r^*_{max} \leqslant r^* \leqslant 0.6$; $0.6 \leqslant r^* \leqslant 0.9$; $0.9 \leqslant r^* \leqslant 1.2$; $1.2 \leqslant r^* \leqslant 3$: for $B^*_I(T^*)$, $r^*_{max} \leqslant r^* \leqslant 0.7$; $0.7 \leqslant r^* \leqslant 1$; $1 \leqslant r^* \leqslant 1.3$; $1.3 \leqslant r^* \leqslant 3$: and for $B^*_{II}(T^*)$, $r^*_{max} \leqslant r^* \leqslant 0.6$; $0.6 \leqslant r^* \leqslant 0.9$; $0.9 \leqslant r^* \leqslant 1.1$; $1.1 \leqslant r^* \leqslant 3$. In each case the integration in the four sub-ranges was by 8, 12, 12 and 8 point Gaussian quadrature formulae, (see Kopal 1955 p.367 et seq.), respectively. For all three integrals the fifth sub-range of integration was from $r^*=3$ to $r^*=\infty$. For $r^* \geqslant 3$, the repulsive energy in the pair interaction was found to be negligible and, retaining only the r^{*-6} attractive term, the contributions of this region to the three integrals were simply evaluated by expanding the integrands as series in inverse powers of r^* and integrating term by term.

The EXP-6 potential parameters for neon, argon, krypton and xenon giving the optimum fit with the experimental $B(T)$ data were calculated using the least squares refinement technique described in

Appendix 7. The relevant experimental data are given
in Appendix 8, together with sources. All experimental
data were given equal weight in the calculations, but
the very accurate results of Michels and co-workers and
of Weir, Wynne Jones, Rowlinson and Saville were taken
in preference to those measured by other workers in
corresponding temperature ranges.

The parameters obtained are shown in Table 6,
together with the root mean square deviation of the
experimental B(T) values from the calculated values.
The experimental and calculated values of B(T) are
compared in Appendix 8.

Table 6

**EXP-6 parameters derived from a consideration of the
second virial coefficient**

Substance	$\varepsilon(erg) \times 10^{15}$	$r_m(\text{Å})$	α	rms devn. $(cm^3\ mole^{-1})$
Neon	5.800	2.980	17.00	0.13
Argon	23.29	3.539	20.68	1.23
Krypton	32.42	3.787	20.49	1.95
Xenon	43.70	4.203	20.87	0.93

The potential curves corresponding to the parameters
in Table 6 are plotted as the dashed-double dotted
curves in Figs.4,5,6 and 7 (pp.75-78).

From Tables 2 (p.74), 5 (p.148) and 6 and Figs.
4,5,6 and 7 it is seen that the use of second virial
data leads to EXP-6 potential functions for neon,

argon, krypton and xenon which have deeper wells
(i.e. larger ε values) and smaller equilibrium
separations (i.e. smaller r_m values) than those
given by solid state calculations either with or
without $W(0)^{triplets}$ included. The values of α
given by second virial calculations are larger
than those given by the solid state calculations
and this leads to narrower potential wells. The
differences between the solid state and second
virial potential functions is small in the case of
neon but considerable in the case of argon, krypton
and xenon. Of the two sets of potential functions
derived from solid state data, the well depths and
equilibrium separations of those calculated by
including $W(0)^{triplets}$ are, in all cases, more
in line with the results of the second virial
calculations. As pointed out earlier, both sets
of α values given by solid state calculations are
virtually the same and, therefore, neither set is
nearer the second virial values.

We have pointed out earlier that the LJ 12:6
potential leads to worse predictions of the second
virial coefficients of argon, krypton and xenon
than the EXP-6 function. There is also another
point worth noting in connection with the appli-
cation of the LJ 12:6 function to these substances.
This is that, in contrast to the EXP-6 case, the
LJ 12:6 parameters derived from pairwise additive
solid state calculations are similar to those given
by second virial data (compare the LJ 12:6 values of
ε and σ obtained by Sherwood and Prausnitz with
those in Table 3, p. 74). In the absence of many-

body effects in the solid state this could be taken
to indicate the LJ 12:6 function to be a good rep-
resentation of the pair interaction of these sub-
stances. However, if triplet effects are adequately
evaluated by (5.3), this is not so, because the
inclusion of $W(0)^{triplets}$, by increasing ξ and de-
creasing σ , pushes the solid state parameters away
from the second virial ones. The contrasting behaviour
of the EXP-6 solid state parameters of argon, krypton
and xenon is another indication that the EXP-6
function is a better representation of the pair
interactions of the heavier inert gases.

Since the use of second virial coefficient data
does not always determine a unique pair interaction
(Keller and Zumino 1959), we also tested how well
the two sets of EXP-6 solid state parameters them-
selves (see Table 2, p.74, and Table 5, p.148) pre-
dicted the experimental values of B(T) for neon,
argon, krypton and xenon. The evaluation of B(T)
was carried out in precisely the same way as in the
characterisation procedure. For neon, argon and
krypton it was found that the parameters obtained
by the inclusion of $W(0)^{triplets}$ lead to values of
B(T) in better overall agreement with experiment
than do those given by pairwise additive solid state
calculations. For xenon, on the other hand, it is
the pairwise additive solid state parameters which
lead to the better predictions of B(T). The rms
deviations from experiment given by the pairwise
additive solid state parameters for neon, argon,
krypton and xenon are 0.94, 10.31, 25.5 and 2.52
cm^3 $mole^{-1}$ respectively, whereas those given by the

"W(O) $^{\text{triplets}}$" parameters are 0.76, 3.42, 8.19, 2.52 cm^3 $mole^{-1}$ respectively. The values of B(T) calculated using both sets of solid state parameters are compared with the corresponding experimental values in Appendix 8. In no case, does either set of solid state parameters predict the experimental B(T) data with an accuracy even approaching that given by the second virial parameters themselves.

Chapter 6

Conclusion

The solid state calculations described in this thesis are rather crude and any conclusion drawn from their results must be viewed in this light.

The approximation common to them all is the Einstein assumption of independent motion and we have taken some regard of this by not putting any weight at all on how well calculated values of specific heat and entropy agree with experiment. Instead, we have drawn definite conclusions only from predictions of solid state properties, such as lattice constant, which, in contrast to the specific heat and entropy, are strongly dependent on the static lattice energy and, therefore, should be less sensitive to the vibrational motion of the crystal. It is possible that even these properties are not adequately predicted by an Einstein model of the solid, but, in view of the fact that we used potential parameters calculated from solid state data using the same assumption as that used in the subsequent calculation of the thermodynamic properties, we felt that such an approach is justified.

However, to be sure of the results of solid state calculations it is necessary to make use of lattice dynamical techniques, in spite of the considerable computational difficulties involved. We have mentioned that, to date, only first order anharmonic effects have

been taken into account in lattice dynamical calcul-
ations and, usually, only nearest neighbour inter-
actions are considered. Nevertheless, this is in
spite of the widely held opinion of only a few years
ago, that the difficulties in taking account of even
low order anharmonic effects by lattice dynamical
methods were formidable. With the continual develop-
ment of the theory and the advent of ever larger and
faster electronic computers it is well within the
bounds of possibility that many of the remaining
problems will be overcome in the not too far distant
future. In view of the rigour of lattice dynamics
it would seem more sensible to concentrate on this
approach to the solid state rather than persevering
with models based on the Einstein assumption. On
the other hand, the mastery of lattice dynamical
techniques requires considerable mathematical fac-
ility on the part of the researcher, whereas use of
an Einstein approach involves comparatively easy and
rapid calculations. In view of this, such an approach
has much to recommend it in situations where the
absolute accuracy of the results is not critical.

Another approximation that is commonly made in
solid state calculations is that of assuming pair-
wise additivity of the potential. We have attempted
to overcome this in our later EXP-6 solid state calcul-
ations by making some allowance for triplet effects.
This does not substantially alter the indications of
the pairwise additive calculations as to the relative
ability of the EXP-6 and LJ 12:6 functions to describe
the solid state of neon, argon, krypton and xenon, but
it does lead to appreciably different quantitative

results in the case of the heavier inert gases. It is
interesting that the values of the EXP-6 pair parameters
obtained by allowing for triplet effects in the solid
state are more in line with those given by a consider-
ation of the second virial coefficient than are the
corresponding values derived from pairwise additive
solid state calculations. However, the method by which
we allowed for triplet effects was, of necessity, app-
roximate and took account of only dispersion inter-
actions in the static lattice energy. To be sure of
the precise effect of triplets in the solid state,
more information is required as to the nature of the
short range triplet interaction.

Finally we come to the pair potential itself.
We have pointed out in Chapter 1 that the r^{-6} depend-
ence of the long range part of the pair interaction
of the inert gases is well established, but that the
nature of the short range interaction is still subject
to considerable uncertainty. Our reason for investi-
gating the EXP-6 potential was that the use of an
exponential repulsion of some sort seemed more in
accord with the results of fundamental quantum mech-
anical considerations of simple systems, than did the
use of the inverse power repulsions typical of Lennard-
Jones functions. The calculations in this thesis do in
fact indicate, to some extent, a superiority of the
EXP-6 function over the LJ 12:6 function in the overall
description of the solid state of at least the heavier
inert gases. It should be remembered, however, that
the EXP-6 function is still empirical in nature and the
use of the LJ 12:6 potential can lead to better predict-
ions of some properties even of systems for which the

EXP-6 gives an overall better description. To obtain a truly rigorous picture of the nature of the inert gas pair interaction it is necessary to undertake a fundamental study of a pair of isolated molecules, but, as we have pointed out, the mathematical obstacles to such an approach are formidable except for the simplest systems. Nevertheless, with the large electronic computers at present available, some progress could probably be made in this direction.

References

Alder, B.J., 1962, Phys.Rev., 127, 359.

Amdur,I., & Mason,E.A., 1958, Phys.Fluids, 1,370.

Axilrod,B.M., 1949, J.Chem.Phys., 17,1349.

Axilrod,B.M., 1951, J.Chem.Phys. 19,724.

Axilrod,B.M., & Teller,E., 1943, J.Chem.Phys., 11,299.

Ayres, R.U., & Tredgold,R.H.,1956, Proc.Phys.Soc.,
          69B,840

Barker,J.A.,1955, Proc.Roy.Soc.A, 230,390.

Barker,J.A., 1956, Proc.Roy.Soc.A, 237,63.

Barker,J.A., 1963, "Lattice Theories of the Liquid State"
          (Pergamon Press; Oxford, London, New York,
          Paris).

Barron,T.H.K., 1965, Disc.Faraday Soc., 40,119.

Barron,T.H.K., & Domb,C., 1955, Proc.Roy.Soc A, 227,447

Batchelder,D.N., Losee,D.L., & Simmons,R.O., 1967
          Phys.Rev.,162,767.

Batchelder,D.N., Peterson,O.G., & Simmons,R.O., 1965
          Phil.Mag., 12,1193.

Beattie,J.A., Barriault,R.J., & Brierly,J.S., 1951,
          J.Chem.Phys.,19,1219,1222.

Beattie,J.A., Barriault,R.J.,& Brierly,J.S., 1952,
          J.Chem.Phys.,10,1615.

Beaumont,R.H., Chihara,H., Morrison,J.A., 1961
          Proc.Phys.Soc., 78,1462.

Bell,R.J., & Kingston,A.E., 1966, Proc.Phys.Soc.,88,901.

Bernardes,N., 1960, Phys.Rev., 120,807.

Born,M., & von Karman,T., 1912, Z.Phys.,13,297.

Born,M., & von Karman,T., 1913, Z.Phys., 14,15.

Brown,W.B., & Rowlinson,J.S., 1960, Mol.Phys., 3,35.

Buckingham,R.A., & Corner,J., 1947, Proc.Roy.Soc.A,
          189,118.

Bullough,R., Glyde,H.R., & Venables,J.A., 1966,
          Phys.Rev.Letters, 17,249.

References (Cont.)

Casimir,H.B.G., & Polder,D., 1948, Phys.Rev., 73,360.

Cheeseman,G.H., & Soane,C.M., 1957, Proc.Phys.Soc.,
70B, 700.

Chell,G.G., & Zucker,I.J., 1968, Proc.Phys.Soc.C,
(Solid State Physics), 1,35.

Clusius,K., Flubacher,P., Piesbergen,U., Schleich,K.,
& Sperandio,A., 1960, Z.Naturforsch,
15,1.

Clusius,K., & Riccoboni,L., 1938, Z.Phys.Chem.,B38,81

Clusius,K., & Weigand,K., 1960, Z.Phys.Chem., B46,1.

Cohen.E.G.D., de Boer,J., & Salsburg,Z.W., 1955,
Physica, 21,137.

Cohen,E.G.D., de Boer,J., & Salsburg,Z.W., 1957,
Physica, 23,389.

Cohen,E.G.D. & Reithmeyer,B.C., 1958, Physica, 24,959.

Corner,J., 1948, Trans.Faraday Soc., 44,914.

Corner,J., & Lennard-Jones,J.E., 1941, Proc.Roy.Soc.,
178,401.

Cowley,R.A., 1963, Adv.Phys., 12,421.

Dalgarno,A., & Kingston,A.E., 1961, Proc.Phys.Soc.,
78,607.

Danon,F., & Pitzer,K., 1962, J.Chem.Phys., 36,425.

de Boer,J., 1948, Physica, 14,139.

de Boer,J., 1954, Physica, 20,655.

de Boer,J., & Blaisse,B.S., 1948, Physica, 14.149.

de Boer,J.L & Michels,A., 1938, Physica, 5,945.

Debye,P., 1912, Ann.Phys., 39,789.

Devonshire,A.F., 1940, Proc.Roy.Soc.A, 174,102.

Dugdale,J.S., & MacDonald,D.K.C., 1954, Phil.Mag.,45,811.

Dymond,J.H., Rigby,M., & Smith,E.B., 1965, J.Chem.Phys.
42,2801.

References (Cont.)

Eatwell,A.J., & Smith,B.L., 1961, Phil.Mag., 6,461.

Einstein,A., 1907, Ann.Phys., 22,180.

Einstein,A., 1911a, Ann.Phys., 34,170.

Einstein,A., 1911b, Ann.Phys., 35,679.

Eyring,H., 1936, J.Chem.Phys., 4,283.

Fagerstroem,C.H., & Hallet,A.C.H., 1964, "Low Temperature
        Physics - LT9", (Plenum Press,NewYork) p.1092.

Feldman,J.L., & Horton,G.K., 1967, Proc.Phys.Soc.,92,227.

Fenichel,H., & Serin,B., 1966, Phys.Rev., 142,490.

Figgins,B.F., & Smith,B.L., 1960, Phil.Mag., 5,186.

Flubacher,P., Leadbetter,A.J., & Morrison,J.A., 1961,
        Proc.Phys.Soc., 78,1449.

Foreman,A.J.E., 1963, Phil.Mag., 8,1211.

Foreman,A.J.E., & Lidiard,A.B., 1963, Phil.Mag., 8,97.

Fröman,N., & Fröman,P.O., 1965, "JWKB Approximation,
        Contributions to the Theory",
        (North Holland Publishing Company, Amsterdam).

Gallina,V., & Omini,M., 1964, Phys.Stat.Sol., 6, 391,627.

Götze,W., & Schmidt,H., 1966, Z.Phys., 192,409.

Griffing,V., & Wehner,J.F., 1955, J.Chem.Phys., 23,1024.

Guggenheim,E.A., & McGlashan,M.L., 1960, Proc.Roy.Soc.A,
        255,456.

Hall,G.L., 1957, J.Phys.Chem.Solids, 3,210.

Henderson,D., & Reed,R.D., 1964, J.Chem.Phys., 40,975.

Henkel,J.H., 1955, J.Chem.Phys., 23,681.

Hillier,I.H., Islam,M.S., & Walkley,J., 1965, J.Chem.Phys.,
        43,3705.

Hillier,I.H., & Walkley,J., 1964, J.Chem.Phys., 41,2168.

Hillier,I.H., & Walkley,J., 1965, J.Chem.Phys., 43,3713.

Hirschfelder,J.O., Curtiss,C.F., & Bird,R.B., 1954,
        "Molecular Theory of Gases and Liquids"
        (John Wiley & Sons,Inc.,New York;
        Chapman & Hall Limited, London.)

Holborn,L., & Otto,J., 1925, Z.Phys., 33,1.

Horton,G.K., & Leech,J.W., 1963, Proc.Phys.Soc., 82,816.

Hurst,R.P., & Levelt,J.M.H., 1961, J.Chem.Phys., 34,54.

References (Cont.)

Jansen,J., & Dawson,L.M., 1955, J.Chem.Phys., 23,482.

Jansen,L., 1965, Phil.Mag. 8,1305.

Jansen,L., & Lombardi,E., 1965, Disc.Faraday Soc., 40,78.

Janssens,P., & Prigogine,I., 1950, Physica, 16,895.

Jenkins,W.I., 1966, Ph.D Thesis, University of London.

Jenkins,W.I., & Walkley,J., 1965, Chem.Phys., 43,3721.

Kamerlingh Onnes,H., & Crommelin,C.A., 1915, Leiden Comm.
147d.

Kamerling Onnes,H., Crommelin,C.A., & Martinez, 1919,
Leiden Comm., 154a.

Kanzaki,H., 1957, J.Phys.Chem.Solids, 2,24.

Keller,J.B., & Zumino,B., 1959, J.Chem.Phys. 30,1351.

Kestner,N.R. & Sinanoglu,O., 1966, J.Chem.Phys. 45, 194.

Kihara,T., 1951, Proc.Phys.Soc.Japan, 6,289.

Kihara,T., 1953, Rev.Mod.Phys., 25,831.

Kihara,T., 1955, Rev.Mod.Phys., 27,412.

Kihara,T., 1958, Adv.Chem.Phys., 1,267.

Kihara,T., & Koba,S., 1952, J.Phys.Soc.Japan, 7,348.

Kopal,Z., 1955, "Numerical Analysis", (Chapman & Hall
Ltd., London.)

Kuebler,J., & Tosi,M.P., 1965, Phys.Rev., 137,A1617.

Langer,R.E., 1937, Phys.Rev., 51,669.

Lecocq,A., 1960, J. de Recherche CNRS,11,55.

Leibfried,G., & Ludwig,W., 1961, Solid St.Phys., 12,275.
(Academic Press, New York.).

Lennard-Jones,J.E., 1924, Proc.Roy.Soc.A, 106,463.

Lennard-Jones,J.E., & Devonshire,A.F., 1937, Proc.Roy.
Soc.A, 163,53.

Lennard-Jones,J.E., & Devonshire,A.F., 1938, Proc.Roy.
Soc.A, 165,1.

Lennard-Jones,J.E.,& Devonshire,A.F., 1939a, Proc.Roy.
Soc.A, 169,317.

Lennard-Jones,J.E.,& Devonshire,A.F., 1939b, Proc.Roy.
Soc.A, 170,469.

Lennard-Jones,J.E., & Ingham,A.E., 1925, Proc.Roy.Soc.A,
107,636.

References (Cont.)

Levelt,J.M.H., & Hurst,R.P., 1960, J.Chem.Phys., 32,96.

Lidiard,A.B., 1957, Handbook of Physics, 20,246,
(Springer-Verlag, Berlin).

London,F., 1930, Z.Physik Chem. B11,222.

Losee,D.L., & Simmons,R.O., 1967, Phys.Rev.Letters,
18,451.

McGlashan,M.L., 1965, Disc.Faraday Soc., 40,59.

McWeeny,R., 1959, Proc.Roy.Soc.A, 253,242.

McWeeny,R., 1960, Rev.Mod.Phys., 32,335.

Margenau,H., 1939a, Rev.Mod.Phys., 11,1.

Margenau,H., 1939b, Phys.Rev., 56,1000.

Mason,E.A., & Rice,W.E., 1954, J.Chem.Phys., 22,843.

Michels,A., Levelt,J.M., & de Graaf,W., 1958, Physica,
24,659.

Michels,A., Wassenaar,T., & Louwerse,P., 1954,Physica,
20,99.

Michels,A., Wassenaar,T., & Louwerse,P., 1960,Physica,
26,539.

Michels,A., Wijker,H., & Wijker,H., 1949, Physica,15,627.

Mie,G., 1903, Ann.Phys.(Leipzig), 11,657.

Montroll,E.W., 1942, J.Chem.Phys., 10,218.

Montroll,E.W., 1943, J.Chem.Phys., 11,481.

Montroll,E.W., & Peaslee,D.C., 1944, J.Chem.Phys.,12,98.

Murrell,J.N., Randic,M., & Williams,D.R., 1965, Proc.
Roy.Soc.A, 284,566.

Nardelli,G.F., & Chiarotti,A., 1960, Nuovo Cim, 18,1053.

Nicholson,G.A., & Schneider,W.G., 1955, Can.J.Chem,33,589.

Peterson,O.G., Batchelder,D.N., & Simmons,R.O., 1966,
Phys.Rev., 150,703.

Packard,J.R. & Swenson,C.A., 1963, J.Phys.Chem.Solids,
24,1405.

Phillipson.P.E., 1962, Phys.Rev., 125,1981.

Pliskin,Yu.M., & Greenberg,B.A., 1965, Phys.Letters,
19,375.

Pollack,G.L., 1964, Rev.Mod.Phys., 36,748.

Pople,J.A., 1951, Phil.Mag., 42,459.

Reissland,J.A., 1965, Disc.Faraday Soc., 40,123.

Rosen,P., 1950,J.Chem.Phys., 18,1182.

Rossi,J.C. & Danon,F., 1965, Disc.Faraday Soc., 40,97.

Sakamoto,M., & Ishiguiro,E., 1956, Progr.Theoret.Phys.
            (Japan), 15,37.

Salem,L., 1965, Disc.Faraday Soc., 40,140.

Salsburg,Z.W., Cohen,E.G.D., Reithmeyer,B.C. & de Boer,J.,
            1957, Physica,23,400.

Salter,L., 1954, Phil.Mag., 45,360.

Schiff,L.I., 1955, "Quantum Mechanics" (McGraw-Hill Book
            Company Inc., New York, Toronto, London;
            Kogakusha Company Ltd., Tokyo).

Sears,D.R., & Klug,H.P., 1962, J.Chem.Phys., 37,3002.

Sherwood,A.E., & Prausnitz,J.M., 1964, J.Chem.Phys.,
            41,429.

Slater,J.C., 1928, Phys.Rev., 32,349.

Slater,J.C. & Kirkwood,J.G., 1931, Phys.Rev., 37,682.

Stewart,J.W., 1955, Phys.Rev., 97,578.

Stewart,J.W., 1956, J.Phys.Chem.Solids, 1,146,

Swenberg,C.E., 1967, Phys.Letters, 24A,163.

Urvas,A.O., Losee,D.L., & Simmons,R.O., 1967,
            J.Phys.Chem.Solids, 28,2269.

Wallace,D.C., 1963, Phys.Rev., 131,2046.

Wallace,D.C., 1964, Phys.Rev., 133,153.

Weir,R.D., Wynne Jones,I., Rowlinson,J.S., & Saville,G.,
            1967, Trans.Faraday Soc., 63,1320.

Whalley,E., Lupien,Y., & Schneider,W.G., 1955, Can.
            J.Chem., 33,633.

Whalley,E., & Schneider,W.G., 1955, J.Chem.Phys.,
            23,1644.

Zucker,I.J., 1956, J.Chem.Phys., 25,915.

Zucker,I.J., 1961, Proc.Phys.Soc., 77,889.

Zucker,I.J., 1964, Proc.Camb.Hil.Soc., 60,273.

Zucker,I.H., 1968, Nuovo Cim., 54,177.

Appendix 1

The Derivation of the Spherically Symmetric Cell Potential for the EXP-6 Potential

The reduced spherically symmetric cell potential is given by:

$$\overline{w^*(R^*)} = \sum_i z_i \left\{ \tfrac{1}{2} \int_0^\pi \left[\phi^*\left(\sqrt{a_i^{*2} + R^{*2} - 2R^* a_i^* \cos\theta}\right) \sin\theta \, d\theta \right] - \phi^*(a_i^*) \right\} \quad (A.1.1.)$$

If we make the transformation, $x = (a_i^{*2} + R^{*2} - 2R^* a_i^* \cos\theta)^{\frac{1}{2}}$, expression (A.1.1.) becomes:

$$\overline{w^*(R^*)} = \sum_i z_i \left[\frac{1}{2R^* a_i^*} \int_{(a_i^* - R^*)}^{(a_i^* + R^*)} x\, \phi^*(x)\, dx - \phi^*(a_i^*) \right] \quad (A.1.2)$$

For the EXP-6 pair potential, which may be written in reduced form as:

$$\phi^*(r^*) = \frac{\alpha}{\alpha - 6} \left[\frac{6 e^\alpha}{\alpha} \exp(-\alpha r^*) - r^{*-6} \right]$$

$\overline{w^*(R^*)}$ becomes:

$$\overline{w^*(R^*)} = \frac{\alpha}{\alpha - 6} \sum_i z_i \left\{ \frac{1}{2R^* a_i^*} \left[\frac{6 e^\alpha}{\alpha} \int_{(a_i^* - R^*)}^{(a_i^* + R^*)} x \exp(-\alpha x)\, dx \right. \right.$$

$$\left. \left. - \int_{(a_i^* - R^*)}^{(a_i^* + R^*)} x^{-5}\, dx \right] - \frac{6 e^\alpha}{\alpha} \exp(-\alpha a_i^*) + \frac{1}{a_i^{*6}} \right\}$$

$$(A.1.3)$$

Now:

$$\int_{(a_i^*-R^*)}^{(a_i^*+R^*)} x^{-5}dx = \left[\frac{-x^{-4}}{4}\right]_{(a_i^*-R^*)}^{(a_i^*+R^*)}$$

$$= \frac{1}{4}\left[(a_i^*-R^*)^{-4} - (a_i^*+R^*)^{-4}\right] \qquad (A.1.4)$$

and the integration

$$\int_{(a_i^*-R^*)}^{(a_i^*+R^*)} x\exp(-\alpha x)dx$$

may be performed by parts, thus:

$$\int_{(a_i^*-R^*)}^{(a_i^*+R^*)} x\exp(-\alpha x)dx = \left[\frac{-x\exp(-\alpha x)}{\alpha}\right]_{(a_i^*-R^*)}^{(a_i^*+R^*)} + \frac{1}{\alpha}\int_{(a_i^*-R^*)}^{(a_i^*+R^*)}\exp(-\alpha x)dx$$

$$= \left[\frac{-x\exp(-\alpha x)}{\alpha}\right]_{(a_i^*-R^*)}^{(a_i^*+R^*)} + \frac{1}{\alpha^2}\left[\exp(-\alpha x)\right]_{(a_i^*-R^*)}^{(a_i^*+R^*)}$$

On substitution of the limits and suitable grouping of terms, this expression becomes:

$$\int_{(a_i^*-R^*)}^{(a_i^*+R^*)} x\exp(-\alpha x)dx = \frac{2\exp(-\alpha a_i^*)}{\alpha}\left[(a_i^*+\frac{2}{\alpha})\sinh(\alpha R^*) - r^*\cosh(\alpha R^*)\right]$$

$$(A.1.5)$$

Substitution of (A.1.5) and (A.1.3) and again suitable grouping of terms, gives:

$$\overline{w^*(R^*)} = \frac{\alpha}{\alpha-6}\left\{\frac{6e^{\alpha}}{\alpha^2}\left[\frac{A\,\sinh(\alpha R^*)}{R^*} - \frac{R(-1)\cosh(\alpha R^*)}{a_1^*}\right] - \frac{T(4)_6}{8\bar{J}_1 R^*}\right.$$

$$\left. - \frac{6e^{\alpha}}{\alpha}R(0) + \frac{S(6)}{a_1^{*6}}\right.$$

where

$$R(n) = \sum_i z_i(a_i^*/a_1^*)^n \exp(-\alpha a_i^*)$$

$$S(n) = \sum_i z_i(a_i^*/a_1^*)^{-n}$$

$$T(n)_m = \sum_i z_i(a_i^*/a_1^*)^{(n-m+1)}\left[(a_i^*-R^*)^{-n} - (a_i^*+R^*)^{-n}\right]$$

$$A = R(0) + \frac{R(-1)}{\alpha a_1^*}$$

Appendix 2

The "Exact" Finite Difference Solution of the Radial Wave Equation, (Hillier, Islam and Walkley 1965)

The radial Schroedinger equation corresponding to the cell potential, $\overline{w^*(R^*)}$, may be written in reduced variables as:

$$S^{*''}_{l,n} + f(\lambda^*_{l,n}, R^*) S^*_{l,n} = 0 \qquad (A.2.1)$$

where

$$f(\lambda^*_{l,n}, R^*) = \frac{8\pi^2}{\Lambda^{*2}} \lambda^*_{l,n} - \frac{l(l+1)}{R^{*2}} - \frac{8\pi^2}{\Lambda^{*2}} \overline{w^*(R^*)}$$

and primes denote differentiation with respect to R^*. Assuming a first approximation to $\lambda^*_{l,n}$ to be $(\lambda^*_{l,n})_o$ and a better approximation to be $(\lambda^*_{l,n})_o + \delta\lambda^*_{l,n}$, the boundary condition at $R^* = R^*_c$ is written:

$$S^*_{l,n}[(\lambda^*_{l,n})_o + \delta\lambda^*_{l,n}, R^*_c] = 0$$

which gives:

$$\delta\lambda^*_{l,n} \simeq \frac{-S^*_{l,n}[(\lambda^*_{l,n})_o, R^*_c]}{\left(\dfrac{\partial S^*_{l,n}}{\partial \lambda^*_{l,n}}\right)_{\lambda^*_{l,n}=(\lambda^*_{l,n})_o, R^*=R^*_c}}$$

$$(A.2.2)$$

Putting:

$$Y_1 = S^*_{l,n}$$

$$Y_2 = S^{*''}_{l,n}$$

$$Y_3 = \partial S^*_{l,n} / \partial \lambda^*_{l,n} \qquad (A.2.3)$$

(A.2.1) and (A.2.2) become:

$$Y_2' + \int(\lambda_{i,n}^*, R^*)Y_1 = 0 \qquad (A.2.4)$$

$$\delta\lambda_{i,n}^* \simeq (-Y_1/Y_3)_{\lambda_{i,n}^* = (\lambda_{i,n}^*)_o, R^* = R_c^*} \qquad (A.2.5)$$

Differentiation of (A.2.4) with respect to $\lambda_{1,n}^*$ and putting:

$$Y_4 = Y_3' \qquad (A.2.6)$$

gives:

$$Y_4' + \int(\lambda_{i,n}^*, R^*)Y_3 - Y_1 = 0 \qquad (A.27)$$

(A.2.3), (A.2.4), (A.2.5), (A.2.6) and (A.2.7) provide the basis for the determination of $\lambda_{1,n}^*$ to any desired degree of accuracy. For any value of $\lambda_{1,n}^*$, (A.2.3), (A.2.4), (A.2.6) and (A.2.7) may be integrated in a stepwise manner using the Runge-Kutta technique. Due to the singularity in the radial equation at R*=0, the integration has to be started at some value of $R^* = R_o^*$ close to R*=0, rather than at R*=0 itself. The initial values of Y_1, Y_2, Y_3 and Y_4 are calculated from the Levelt and Hurst (1960) series expansion:

$$S_{i,n}^* = \sum_i a_{2i+1}(\lambda_{i,n}^*)R^{*2i+L+1}$$

where a_1 has an arbitrary value determined by normal-

isation, a_3 is given by:

$$a_3 = \frac{8\pi^2}{\Lambda^{*2}}\left[\frac{-\lambda^{*}_{l,n}a_1}{(l+3)(l+2)-l(l+1)}\right]$$

and the other coefficients by the recursion relations

$$a_{2m+1} = \frac{8\pi^2}{R^{*2}}\left[\frac{\sum_{j=1}^{m-1} c^{*}_{2m-2j}\,a_{2j-1} - \lambda^{*}_{l,n}a_{2m-1}}{(l+2m+1)(l+2m)-l(l+1)}\right]$$

$$(m = 2, 3, 4, \ldots)$$

where c^{*}_{2k} (k=1,2,3,...) are the coefficients in the
series expansion of $\overline{w^{*}(R^{*})}$:

$$\overline{w^{*}(R^{*})} = \sum_{k} c^{*}_{2k} R^{*2k}$$

Using the initial values of Y_1, Y_2, Y_3, Y_4 calculated
in this manner for $\lambda^{*}_{1,n} = (\lambda^{*}_{1,n})_o$ the equations
(A.2.3), (A.2.4), (A.2.6) and (A.2.7) are integrable
step by step from $R^{*}=R^{*}_o$ to $R^{*}=R^{*}_c$. By correcting the
eigenvalue by the amount $\delta^{*}_{1,n}$ given by (A.2.5) and
repeating the procedure, $\lambda^{*}_{1,n}$ can be calculated to
any desired accuracy.

Appendix 3

The Numerical Characterisation of an n Parameter
Potential Function from Zero Point Solid State Data

Let the n parameters appearing in the potential function be P_j (j=1,2,...,n) and the n appropriate zero point equations be:

$$F_i(P_1, \cdots, P_n) = 0 \quad (i=1,\ldots,n) \qquad (A.3.1)$$

Taking a first approximation to the solution of these equations to be P_{jo} (j=1,...,n) and a better solution to be $(P_{jo} + \delta P_j)$ (j=1,...,n) we write:

$$F_i(P_{1o} + \delta P_{1o}, \ldots, P_{no} + \delta P_{no}) = 0 \quad (i=1,\ldots,n) \quad (A.3.2)$$

Expanding the equations (A.3.2) as Taylor series and truncating after terms linear in δP_j (j=1,...,n), we obtain:

$$F_i(P_{1o}, \ldots, P_{no}) + \sum_{j=1}^{n} P_j (\partial F_i / \partial P_j)_o = 0 \quad (i=1,\ldots,n) \quad (A.3.3)$$

which rewritten in terms of difference quotients become:

$$F_i(P_{1o}, \ldots, P_{no}) + \sum_{j=1}^{n} P_j (\Delta F_i / \Delta P_j)_\delta = 0 \quad (i=1,\ldots,n)(A.3.4)$$

where

$$\left(\frac{\Delta F_i}{\Delta P_j}\right)_o = \frac{F_i(P_{1o}, \ldots, P_{jo}+\Delta P_{jo}, \ldots, P_{no}) - F_i(P_{1o}, \ldots, P_{jo}, \ldots, P_{no})}{\Delta P_{jo}}$$

and ΔP_{jo} is chosen to be some small increment in P_{jo}, e.g. $\Delta P_{jo} = 0.01 P_{jo}$.

Calculation of $F_i(P_{10}, \ldots, P_{no})$ $(i=1, \ldots, n)$ and $(\Delta F_i / \Delta P_j)_o$ $(i=1, \ldots, n; \; j=1, \ldots, n)$ allows the equations (A.3.4) to be solved for $\delta P_j (j=1, \ldots, n)$. Addition of $\delta P_j (j=1, \ldots, n)$ to the first approximation $P_{jo} (j=1, \ldots, n)$ then gives a better approximation. Continued application of this procedure gives the parameters to any specified degree of accuracy.

(iii) Zero pressure LJ 12:6 values of a_o, χ_T, β, c_v, c_p and S as functions of T.

T	a_o	χ_T	β	c_v	c_p	S
0	4.4637	10.32	0	0	0	0
8	4.4642	10.42	3.48	1.60	1.61	0.29
12	4.4694	11.02	14.55	6.36	6.67	1.83
16	4.4820	12.28	27.91	11.06	12.44	4.54
20	4.5029	14.34	41.64	14.42	17.75	7.89
23.5	4.5281	17.04	54.70	16.33	22.10	11.10

(iv) LJ 12:6 values of V/V(0) as a function of p at $4^{\circ}K$.

p	2043	4000	6000	8000	10000	12000	16000	20000
V/V(0)	0.882	0.828	0.790	0.762	0.740	0.722	0.693	0.670

Solid argon

(i) Zero pressure EXP-6 values of a_o, χ_T, β, c_v, c_p and S as functions of T.

T	a_o	χ_T	β	c_v	c_p	S
0	5.3111	3.75	0	0	0	0
10	5.3113	3.76	0.76	1.63	1.63	0.30
20	5.3167	3.92	5.41	11.13	11.47	4.39
30	5.3296	4.24	8.85	17.01	18.28	10.47
40	5.3473	4.65	11.11	19.72	22.16	16.30
50	5.3689	5.17	12.95	20.98	24.75	21.54
59.88	5.3934	5.82	14.71	21.54	26.79	26.19
70	5.4220	6.68	16.68	21.74	28.74	30.51
83	5.4650	8.22	19.86	21.69	31.48	35.64

(ii) EXP-6 values of V/V(0) as a function of p at $77^{o}K$.

p	2043	6000	8000	12000	16000	19000
V/V(0)	0.909	0.830	0.804	0.766	0.738	0.721

(iii) Zero pressure LJ 12:6 values of a_o, χ_T, β, c_v C_p and S as functions of T.

T	a_o	χ_T	β	c_v	C_p	S
0	5.3111	3.81	0	0	0	0
10	5.3113	3.82	0.83	1.68	1.68	0.31
20	5.3171	4.00	5.83	11.23	11.62	4.47
30	5.3310	4.35	9.50	17.03	18.45	10.61
40	5.3502	4.81	11.93	19.65	22.38	16.50
50	5.3732	5.39	13.90	20.83	25.02	21.80
60	5.3998	6.12	15.81	21.33	27.15	26.55
70	5.4304	7.07	17.94	21.47	29.15	30.88
83	5.4765	8.79	21.36	21.34	32.00	36.08

(iv) LJ 12:6 values of V/V(0) as a function of p at $77^{o}K$.

p	2043	6000	8000	12000	16000	19000
V/V(0)	0.906	0.827	0.802	0.765	0.738	0.722

Solid krypton

(i) Zero pressure EXP-6 values of a_o, χ_T, β, c_p, C_v and S as functions of T.

T	a_o	χ_T	β	C_v	c_p	S
0	5.6459	2.91	0	0	0	0
10	5.6463	2.92	1.21	0.913	0.916	0.21
20	5.6522	3.04	4.81	3.498	3.597	1.74
40	5.6770	3.44	7.78	5.089	5.551	4.99
60	5.7096	3.99	9.32	5.381	6.255	7.39
80	5.7480	4.75	10.85	5.410	6.765	9.26
100	5.7932	5.82	12.75	5.353	7.308	10.83
115.78	5.8352	7.06	14.81	5.275	7.846	11.94

(ii) EXP-6 values of V/V(0) as a function of p at 77^oK

p	200	400	600	1000	2000	3000	4000
V/V(0)	0.991	0.983	0.976	0.963	0.935	0.914	0.895

(iii) Zero pressure LJ 12:6 values of a_o, χ_T, β, C_v, c_p and S as functions of T.

T	a_o	χ_T	β	C_v	c_p	S
0	5.6459	3.11	0	0	0	0
10	5.6464	3.12	1.43	0.998	1.002	0.24
20	5.6531	3.26	5.34	3.592	3.705	1.85
40	5.6803	3.72	8.48	5.104	5.613	5.15
60	5.7157	4.35	10.12	5.361	6.310	7.57
80	5.7573	5.20	11.74	5.370	6.824	9.46
100	5.8063	6.42	13.76	5.296	7.375	11.04
115.78	5.8518	7.81	15.93	5.208	7.918	12.16

(iv) LJ 12:6 values of V/V(0) as a function of p at 77°K

p	200	400	600	1000	2000	3000	4000
V/V(0)	0.991	0.982	0.974	0.960	0.931	0.908	0.889

Solid xenon

(i) Zero pressure EXP-6 values of a_o, χ_T, β, C_v, C_p and S as functions of T.

T	a_o	χ_T	β	C_v	C_p	S
0	6.1310	2.89	0	0	0	0
10	6.1316	2.91	1.42	1.504	1.510	0.42
20	6.1374	3.00	3.95	4.073	4.160	2.42
40	6.1576	3.25	5.55	5.330	5.648	5.89
80	6.2091	3.95	6.85	5.589	6.408	10.08
115	6.2630	4.85	8.05	5.529	6.888	12.49
150	6.3280	6.23	9.74	5.412	7.495	14.39
160	6.3492	6.77	10.38	5.371	7.715	14.88

(ii) EXP-6 values of V/V(0) as a function of p at 150°K

p	2	5	8	14	20
V/V(0)	0.918	0.855	0.815	0.762	0.726

(iii) Zero pressure LJ 12:6 values of a_o, χ_T, β, C_v, C_p and S as functions of T.

T	a_o	χ_T	β	C_v	C_p	S
0	6.1310	2.75	0	0	0	0
10	6.1316	2.76	1.41	1.417	1.423	0.39
20	6.1375	2.85	4.08	3.996	4.093	2.32
40	6.1585	3.13	5.82	5.282	5.647	5.77
80	6.2129	3.87	7.25	5.526	6.463	9.98
115	6.2703	4.84	8.57	5.442	6.991	12.41
150	6.3397	6.36	10.44	5.300	7.658	14.32
160	6.3625	6.96	11.15	5.252	7.901	14.81

(iv) LJ 12:6 values of V/V(0) as a function of p at 150°K

p	2	5	8	14	20
V/V(0)	0.919	0.857	0.819	0.769	0.735

Appendix 5

Experimental Data for Solid Neon, Argon, Krypton and Xenon

The symbols used in this appendix represent the same properties as they do in Appendix 4. The properties are expressed in the same units as are the corresponding ones in Appendix 4.

Solid neon

(i) Zero pressure values of a_o, χ_T, β, C_v, C_p and S as functions of T.

T	a_o a)	χ_T a)	β a)	C_v b)	C_p c)	S d)
4	4.4637	9.0±0.2	0.60±0.05	0.347	0.347	0.133
6	4.4642	9.1±0.4	2.46±0.05	1.350	1.355	0.439
8	4.4654	9.2±0.6	5.73±0.06	3.10	3.14	1.05
10	4.4677	9.4±0.6	10.17±0.07	5.36	5.51	2.00
12	4.4815	9.6±0.8	15.39±0.08	7.89	8.29	3.25
14	4.4769	10.0±1.0	21.09±0.10	10.10	10.95	4.73
16	4.4841	10.7±1.1	27.00±0.10	12.0	13.5	6.36
18	4.4930	12.4±1.2	33.12±0.12	13.9	16.1	8.10
20	4.5040	16.2±1.5	40.11±0.14	15.9	18.9	9.94
23.5	4.5287	-	51.54±0.14	-	-	-

a) Data of Batchelder, Losee and Simmons (1967)

b) Calculated by Batchelder, Losee and Simmons (1967) from the relation $C_p = C_v + \beta^2 TV/\chi_T$. Error due to the uncertainties in β and χ_T rises to ± 0.7J mole^{-1} $^\circ$K^{-1} at 20°K.

c) Smoothed data of Fenichel and Serin (1966) and Fagerstroem and Hallet (1965) as given by Batchelder, Losee and Simmons (1967). Fenichel and Serin estimate their error in C_p to be $\pm 2\%$.

d) Calculated from the relation $S = \int_o^T (C_p/T)dT$.

(ii) Values of V/V(0) as a function of p at 4°K,
    (Stewart 1956).

p	V/V(0)	p	V/V(0)
1000	0.927 ± 0.004	8000	0.770 ± 0.012
2043	0.882 ± 0.006	10000	0.747 ± 0.013
3000	0.858 ± 0.007	12000	0.728 ± 0.014
4000	0.832 ± 0.008	16000	0.696 ± 0.015
60000	0.797 ± 0.010	20000	0.669 ± 0.017

Solid argon

(i) Zero pressure values of $a_o, \chi_T, \beta, C_v C_p$ and S as
    functions of T.

T	a_o [a]	χ_T [b]	β [a]	C_v [c]	C_p [d]	S [e]
10	5.3117	3.77	1.38	3.294	3.305	1.096
15	5.3138	3.83	3.48	8.01	8.12	3.320
20	5.3179	3.93	5.55	12.16	12.51	6.278
25	5.3235	4.05	7.14	15.30	16.02	9.460
30	5.3305	4.21	8.54	17.49	18.67	12.62
35	5.3386	4.38	9.69	19.13	10.85	15.67
40	5.3477	4.59	10.68	20.25	22.54	18.56
45	5.3576	4.83	11.64	20.95	23.87	21.30
50	5.3684	5.10	12.54	21.54	25.13	23.87
55	5.3801	5.42	13.49	21.94	26.27	26.31
60	5.3926	5.81	14.50	22.19	17.31	28.63
65	5.4062	6.27	15.63	22.34	28.36	30.84
70	5.4209	6.82	16.99	22.60	29.71	32.98
75	5.4369	7.46	18.55	22.94	31.33	35.05
80	5.4546	8.24	20.31	23.34	33.17	37.09
83	5.4660	8.76	21.47	24.02	34.84	38.31

a) Data of Peterson, Batchelder and Simmons (1966).

b) Data quoted by Peterson, Batchelder and Simmons (1966). Error rises to $\pm 10\%$ at the higher temperatures.

c) Calculated from the relation $C_p = C_v + \beta^2 TV/\chi_T$ by Peterson, Batchelder and Simmons (1966). Error due to the uncertainty in χ_T rises to $\pm 1.1 J$ mole^{-1} $^\circ K^{-1}$ at $83^\circ K$.

d) Data of Flubacher, Leadbetter and Morrison (1961) as quoted by Peterson, Batchelder and Simmons (1967). Flubacher, Leadbetter and Morrison estimate their error in C_p to be $\pm 2\%$ at the lowest temperatures, decreasing to $\pm 0.2\%$ for T $20^\circ K$ but increasing to $\pm 0.5\%$ at the highest temperatures.

e) Calculated from the relation $S = \int_0^T (C_p/T)dT$.

(ii) Values of V/V(0) as a function of p at $77^\circ K$ (Stewart 1956).

p	V/V(0)	p	V/V(0)
1000	0.939 ± 0.003	8000	0.795 ± 0.010
2043	0.901 ± 0.005	12000	0.758 ± 0.012
4000	0.853 ± 0.007	16000	0.730 ± 0.013
6000	0.820 ± 0.009	20000	0.714 ± 0.014

Solid krypton

(i) Zero pressure values of a_o, χ_T, β, c_p and S as functions of T.

T	a_o	χ_T	β [b]	c_p [e]	S [f]
4.25	5.6459[a]	2.91	-	-	-
5	-	-	-	0.3721	0.07
10	-	-	-	1.418	0.54
10.3	5.6470[a]	2.90±0.15[a]	-	-	-
15	-	-	-	2.798	1.38
17.5	-	2.84±0.42[a]	-	-	-
20	5.655[b]	-	4.8	3.817	2.32
25	-	2.77±0.40[a]	-	4.516	3.25
30	-	-	-	4.990	4.11
31.7	-	3.17±0.27[a]	-	-	-
39.2	-	3.37±0.25[a]	-	-	-
40	5.678[b]	-	7.7	5.612	5.65
45.9	5.6860[a]	3.47±0.24[a]	-	-	-
50	-	-	-	5.978	6.94
53.3	-	3.66±0.31[a]	-	-	-
58	5.710[c]	-	-	-	-
60	5.7111[b]	3.79±0.46[a]	9.7	6.296	8.06
67.1	-	4.25±0.33[a]	-	-	-
68	5.734[c]	-	-	-	-
70	-	-	-	6.569	9.05
74.0	5.7345[a]	4.46±0.25[a]	-	-	-
77.3	5.7409[a]	4.82±0.15[a]	-	-	-
80	5.751[b]	-	11.0	6.824	9.95
90	5.773[b]	-	11.2	7.146	10.77
90.8	-	5.52±0.48	-	-	-
100	-	-	-	7.585	11.55
110	-	-	-	8.139	12.29
115	5.798[d]	-	-	8.552	12.66

a)   Data of Urvas, Losee and Simmons (1967).

b)   Data of Figgins and Smith (1960).

c)   Data of Cheeseman and Soane (1957).

d)   Data of Clusius and Weigand (1960).

e)   Data of Beaumont, Chihara and Morrison (1961).

f)   Calculated from the relation $S = \int_0^T (C_p/T)dT$.

(ii) Values of V/V(0) as a function of p at 77°K (Stewart 1955)

p	V/V(0)	p	V/V(0)
200	0.990 ± 0.001	2000	0.928 ± 0.004
400	0.981 ± 0.001	3000	0.905 ± 0.005
600	0.972 ± 0.001	4000	0.887 ± 0.006
1000	0.958 ± 0.002		

Solid xenon

(i) Zero pressure values of a_o, χ_T, β, C_p and S as functions of T.

T	a_o	χ_T	β	C_p	$S^{f)}$
10	$6.133^{a)}$	–	$1.0^{d)}$	$1.87^{d)}$	–
20	$6.136^{a)}$	$2.85 \pm 0.20^{c)}$	$2.8^{a)}$	$4.22^{d)}$	2.88
	$6.137^{b)}$		$3.0^{b)}$		
	$6.137 \pm 0.004^{c)}$				
30	$6.145^{a)}$	–	$4.4^{a)}$	–	–
40	$6.154^{a)}$	–	$5.5^{a)}$	–	–
	$6.157^{b)}$		$5.8^{b)}$		
50	$6.166^{a)}$	$3.10 \pm 0.20^{c)}$	$6.3^{a)}$	$6.00^{e)}$	7.60
	$6.167 \pm 0.006^{c)}$				
60	$6.180^{a)}$	–	$6.9^{a)}$	–	–
	$6.183^{b)}$		$6.5^{b)}$		
70	$6.195^{a)}$	–	$7.5^{a)}$	–	–
75	$6.202^{a)}$	$3.75 \pm 0.30^{c)}$	$7.7^{a)}$	$6.39^{e)}$	10.11
	$6.203 \pm 0.007^{c)}$				

Solid xenon (Cont.)

T	a_o	χ_T	β	C_p	S[f]
80	6.210[b]	-	6.7[b]	-	-
100	6.238[b]	-	6.8[b]	6.74[e]	12.00
	6.243 ± 0.009[c]		7.0 ± 0.7[c]		
120	6.268[b]	-	6.8[b]	-	-
125	6.287 ± 0.006[c]	5.25 ± 0.50[c]	8.4 ± 0.8[c]	7.30[e]	13.57
150	6.331 ± 0.007[c]	6.55 ± 0.90[c]	10.3 ± 1.0[c]	8.02	14.97

a) Data of Sears and Klug (1962).

b) Data of Eatwell and Smith (1961).

c) Data of Packard and Swenson (1963).

d) Data of Fenichel and Serin (1966).

e) Smoothed data of Clusius and Riccoboni (1938) as quoted by Packard and Swenson (1963).

f) Calculated from the relation $S = \int_0^T (C_p/T)dT$ by Packard and Swenson (1963) using the C_p data of Clusius and Riccoboni (1938).

(ii) Values of V/V(0) as a function of p at 150°K (Packard and Swenson 1963).

p	V/V(0)	p	V/V(0)
1	0.952	12	0.775
2	0.919	14	0.760
4	0.873	16	0.747
6	0.840	18	0.736
8	0.814	20	0.726
10	0.794		

The error in V/V(0) is ± 0.005 at all pressures.

Appendix 6

Results of EXP-6 Cell Model Calculations with Triplet Dispersion Interactions Included in the Static Lattice for Solid Neon, Argon, Krypton and Xenon

The symbols used in this appendix represent the same properties as they do in Appendix 4. The properties are expressed in the same units as are the corresponding ones in Appendix 4.

Solid neon

(i) Zero pressure values of a_o, χ_T, β, c_v, c_p and S as functions of T.

T	a_o	χ_T	β	c_v	c_p	S
0	4.4637	9.00	0.	0	0	0
8	4.4640	9.07	2.58	1.25	1.26	0.22
12	4.4682	9.55	12.05	5.56	5.80	1.51
16	4.4790	10.61	24.38	10.21	11.42	3.93
20	4.4975	12.41	37.62	13.70	16.83	7.08
23.5	4.5207	14.85	50.66	15.76	21.41	10.15

(ii) Values of $V/V(0)$ as a function of p at $4°K$

p	2043	4000	6000	8000	10000	12000	16000	20000
$V/V(0)$	0.894	0.843	0.807	0.781	0.759	0.742	0.713	0.691

Solid argon

(i) Zero pressure values of a_o, χ_T, β, C_v, C_p and S
as functions of T.

T	a_o	χ_T	β	C_v	C_p	S
0	5.3111	3.75	0	0	0	0
10	5.3113	3.80	0.93	1.93	1.93	0;36
20	5.3174	3.99	5.93	11.76	12.16	4.84
30	5.3313	4.33	9.43	17.42	18.83	11.17
40	5.3503	4.78	11.75	19.93	22.60	17.15
50	5.3729	5.34	13.66	21.05	25.12	22.48
60	5.3991	6.07	15.54	21.52	27.18	27.24
70	5.4290	7.00	17.66	21.64	29.15	31.58
83	5.4748	8.75	21.19	21.50	32.03	36.78

(ii) Values of V/V(0) as a function of p at 77°K.

p	2043	6000	8000	12000	16000	19000
V/V(0)	0.906	0.826	0.800	0.762	0.734	0.717

Solid krypton

(i) Zero pressure values of a_o, χ_T, β, C_v, C_p and S
   as functions of T.

T	a_o	χ_T	β	C_v	C_p	S
0	5.459	2.91	0	0	0	0
10	5.6464	2.93	1.42	1.033	1.037	0.25
20	5.6530	3.06	5.20	3.629	3.744	1.89
40	5.6793	3.50	8.21	5.118	5.626	5.21
60	5.7136	4.10	9.83	5.367	6.317	7.64
80	5.7543	4.93	11.49	5.371	6.840	9.53
100	5.8025	6.14	13.63	5.292	7.419	11.11
115.78	5.8476	7.58	15.99	5.198	8.010	12.24

(ii) Values of V/V(0) as a function of p at 77°K.

p	200	400	600	1000	2000	3000	4000
V/V(0)	0.991	0.983	0.975	0.962	0.934	0.912	0.894

Solid xenon

(i) Zero pressure values of a_o, χ_T, β, C_v, C_p and S
   as functions of T.

T	a_o	χ_T	β	C_v	C_p	S
0	6.1310	2.90	0	0	0	0
10	6.1318	2.92	1.66	1.691	1.699	0.50
20	6.1381	3.02	4.26	4.210	4.310	2.63
40	6.1595	3.30	5.84	5.360	5.708	6.17
80	6.2137	4.06	7.21	5.563	6.446	10.39
115	6.2707	5.05	8.51	5.477	6.943	12.81
150	6.3397	6.61	10.41	5.338	7.593	14.74
160	6.3624	7.23	11.13	5.292	7.834	15.23

(ii) Values of V/V(0) as a function of p at 150°K.

p	2	5	8	14	20
V/V(0)	0.916	0.852	0.811	0.758	0.722

Appendix 7

The Characterisation of an n Parameter Potential Function from Second Virial Data by Least Squares Refinement

Let us suppose that the potential function to be characterised contains n adjustable parameters P_i (i=1,...,n) and that there are k different experimental values of the second virial coefficient available, where k > n. If the experimental values of the second virial coefficient are B_j^{expt} (j=1,...,k), then the parameters which give the optimum least squares fit with experiment are those which minimise the quantity:

$$\sum_{j=1}^{k} \left(B_j^{expt} - B_j^{calc} \right)^2 \qquad (A.7.1)$$

where B_j^{calc} are the calculated second virial coefficients. Let us assume a first approximation to P_i (i=1,...,n) to be P_{io} (i=1,...,n) and that a better fit with experiment is given by $P_{io} + \delta P_i$ (i=1,...,n). On expanding B_j^{calc} as a Taylor series in δP_i (i=1,...,n) and truncating after linear terms, we obtain:

$$B_j^{calc} \simeq B_{jo}^{calc} + \sum_{i=1}^{n} \delta P_i \left(\partial B_j^{calc} / \partial P_i \right)_o \quad (j=1,\cdots,k) \qquad (A.7.2)$$

where a zero subscript on a quantity denotes that
quantity evaluated for $P_i=P_{io}$ (i=1,...,n). On sub-
stituting (A.7.2) into (A.7.1) and minimising with
respect to the quantities δP_i (i=1,...,n) we obtain
the so called normal equations, which may be written
in matrix notation thus:

$$A = B \delta P \qquad\qquad (A.7.3)$$

where A is a column vector with elements:

$$a_i = \sum_{m=1}^{k} \left(B_m^{expt} - B_{mo}^{calc} \right)\left(\partial B_m^{calc} / \partial P_i \right)_0 \quad (i=1,\ldots,n)$$

B is a symmetric nxn matrix with elements:

$$b_{ij} = \sum_{m=1}^{k} \left(\partial B_m^{calc} / \partial P_i \right)_0 \left(\partial B_m^{calc} / \partial P_j \right) \quad \begin{pmatrix} i=1,\ldots,n; \\ j=1,\ldots,n \end{pmatrix}$$

and δP is a column vector with elements δP_i (i=1,...,n).

Replacing the partial derivatives by difference
quotients evaluated by making a small (e.g. 1%) change
in the differentiating variable, the set of equations
(A.7.3) are straightforwardly solved for δP_i (i=1,...,n).
On adding these quantities to P_{io} (i=1,...,n), we obtain
a better set of parameters, which, in turn, may be used
to obtain an even better set. The procedure may be
cycled until the shifts in the parameters are minimal.

Appendix 8

Experimental and EXP-6 Calculated Values of the Second
Virial Coefficients of Neon, Argon, Krypton and Xenon

In this appendix T stands for temperature and B(T)
for the second virial ceofficient at temperature T. T is
expressed in $^{\circ}K$ and B(T) in cm^3 $mole^{-1}$.

Neon

T	$B(T)^{d)}$	$B(T)^{b)}$	$B(T)^{c)}$	$B(T)^{d)}$
123.16	$1.233^{e)}$	1.265	1.847	1.303
131.94	$2.915^{f)}$	2.549	3.194	2.687
170.15	$6.302^{f)}$	6.408	7.237	6.841
173.16	$6.750^{e)}$	6.629	7.468	7.079
223.16	$9.374^{e)}$	9.310	10.026	9.958
273.16	$10.767^{g)}$	10.860	11.869	11.617
298.16	$11.389^{g)}$	11.400	12.425	12.193
323.16	$11.822^{g)}$	11.835	12.872	12.656
348.16	$12.188^{g)}$	12.190	13.234	13.033
373.16	$12.481^{g)}$	12.483	13.531	13.343
398.16	$12.824^{g)}$	12.725	13.776	13.599
423.16	$13.079^{g)}$	12.927	13.979	13.813
473.16	$13.426^{h)}$	13.241	14.289	14.141
573.16	$13.695^{h)}$	13.624	14.657	14.536
673.16	$13.776^{h)}$	13.817	14.829	14.728
773.16	$13.736^{h)}$	13.903	14.893	14.808
873.16	$13.886^{h)}$	13.928	14.895	14.822
973.16	$13.982^{h)}$	13.914	14.859	14.797

a) Experimental values

b) EXP-6 values calculated from the second virial
parameters in Table 6 (p.161)

c) EXP-6 values calculated from the "pairwise additive"
parameters in Table 2 (p.74)

d) EXP-6 values calculated from the "triplet" parameters in Table 5 (p.148)

e) Holborn and Otto (1925)

f) Kamerlingh Onnes and Crommelin (1915); Kamerlingh Onnes, Crommelin and Martinez (1919)

g) Michels, Wassenaar and Louwerse (1960)

h) Nicholson and Schneider (1955).

Argon

T	B(T)[a]	B(T)[b]	B(T)[c]	B(T)[d]
81.948	-272.9[e]	-277.7	-239.0	-264.9
87.120	-245.9[e]	-245.8	-214.3	-237.3
92.777	-216.9[e]	-217.4	-191.8	-212.2
97.653	-194.85[e]	-197.0	-175.32	-193.83
102.081	-179.10[e]	-181.1	-162.22	-179.31
105.885	-167.82[e]	-168.96	-152.15	-168.18
108.073	-161.54[e]	-162.58	-146.80	-162.27
115.227	-144.85[e]	-144.14	-131.16	-145.06
119.997	-134.25[e]	-133.60	-122.10	-135.11
129.556	-114.93[e]	-115.72	-106.52	-118.05
133.16	-107.98[f]	-109.89	-101.38	-112.45
138.16	-100.88[f]	-102.50	- 94.82	-105.30
143.16	- 94.43[f]	- 95.81	-88.84	-98.79
144.599	-93.18[e]	-94.00	-87.21	-97.02
146.047	-92.08[e]	-92.23	-85.62	-95.29
148.16	-88.45[f]	-89.72	-83.37	-92.83
150.66	-85.65[f]	-86.88	-80.80	-90.04
153.16	-82.97[f]	-84.16	-78.34	-87.37
157.411	-80.34[e]	-79.80	-74.37	-83.07
163.16	-73.25[f]	-74.37	-69.41	-77.69
173.16	-65.21[f]	-66.03	-61.74	-69.39
188.16	-54.83[f]	-55.61	-52.06	-58.94
190.519	-52.85[e]	-54.16	-50.71	-57.48

Argon (Cont.)

T	B(T)[a]	B(T)[b]	B(T)[c]	B(T)[d]
203.16	-46.52[f]	-47.10	-44.08	-50.34
223.16	-37.43[f]	-37.92	-35.40	-41.00
248.16	-28.57[f]	-28.94	-26.84	-31.80
273.16	-21.27[g]	-21.89	-20.08	-24.56
298.16	-15.76[g]	-16.24	-14.62	-18.71
323.16	-11.24[g]	-11.59	-10.13	43.90
348.16	- 7.249[g]	-7.721	-6.382	-9.886
373.16	-3.999[g]	-4.446	-3.205	-6.485
398.16	-1.181[g]	-1.643	-0.484	-3.574
423.16	1.384[g]	0.782	1.867	-1.056
473.16	4.99[h]	4.76	5.72	3.07
573.16	10.77[h] 9.8[i]	10.37	11.12	8.87
673.16	15.74[h] 13.1[i]	14.10	14.68	12.70
773.16	17.76[h] 16.0 [i]	16.74	17.16	15.37
873.16	19.48[h]	18.68	18.96	17.32
923.16	18.9[i]	19.47	19.68	18.10
1073	19.9[i]	21.31	21.13	19.89
1223.16	21.1[i]	22.60	22.43	21.13

a) Experimental values

b) EXP-6 values calculated from the second virial parameters in Table 6 (p.161)

c) EXP-6 values calculated from the "pairwise additive" solid state parameters in Table 2 (p.74)

d) EXP-6 values calculated from the "triplet" solid state parameters in Table 5 (p.148)

e) Weir, Wynne Jones, Rowlinson and Saville (1967 - but communicated to the author prior to publication)

f)   Michels, Levelt and de Graaf (1958)

g)   Michels, Wijker and Wijker (1949)

h)   Whalley and Schneider (1955)

i)   Lecocq (1960).

Krypton

T	$B(T)$[a]	$B(T)$[b]	$B(T)$[c]	$B(T)$[d]
110.639	-370.5 [e]	-368.2	-300.3	-341.1
112.417	-354.4 [e]	-356.3	-291.7	-331.3
115.153	-334.1 [e]	-339.4	-279.3	-316.9
118.138	-315.9 [e]	-322.3	-266.8	-302.4
120.243	-307.4 [e]	-311.2	-258.5	-292.8
127.788	-273.6 [e]	-276.0	-231.9	-262.3
133.105	-251.44 [e]	-255.01	-215.69	-243.84
142.810	-220.07 [e]	-222.83	-190.41	-215.11
155.086	-188.73 [e]	-190.63	-164.63	-185.85
168.550	-162.88 [e]	-163.02	-141.76	-160.33
180.752	-142.84 [e]	-142.96	-124.92	-141.52
200.590	-116.56 [e]	-117.38	-103.04	-117.19
224.193	- 95.46 [e]	- 94.66	- 83.20	- 95.26
273.16	- 62.95 [f]	- 63.13	- 55.03	- 64.30
	- 62.70 [g]			
298.16	- 52.35 [f]	- 51.94	- 44.85	-53.16
323.16	-42.77 [f]	- 42.84	- 36.51	-44.05
	-42.78 [g]			
348.16	- 35.21 [f]	-35.32	-29.57	- 36.48
373.16	-28.86 [f]	-28.99	-23.70	-30.10
	-29.28 [g]			
398.16	-23.47 [f]	-23.60	-18.68	-24.64
423.16	-18.81 [f]	-18.96	-14.35	-19.93
	-18.13 [g]			

Krypton (Cont.)

T	B(T)[a]	B(T)[b]	B(T)[c]	B(T)[d]
448.16	-14.73[f]	-14.92	-10.57	-15.82
473.16	-11.11[f]	-11.37	-7.25	-12.22
	-10.75[g]			
498.16	- 8.402[f]	-8.239	-4.313	-9.030
523.16	-5.693[f]	-5.451	-1.698	-6.190
548.16	-3.167[f]	-2.957	0.644	-3.648
573.16	-1.115[f]	-0.712	2.751	-1.360
	0.420[g]			
673.16	7.240[g]	6.377	9.395	5.858
773.16	12.70[g]	11.40	14.08	10.96
873.16	17.19[g]	15.12	17.53	14.71

a) Experimental values

b) EXP-6 values calculated from the second virial parameters in Table 6 (p.161)

c) EXP-6 values calculated from the "pairwise additive" solid state parameters in Table 2 (p.74)

d) EXP-6 values calculated from the "triplet" solid state parameters in Table 5 (p.148)

e) Weir, Wynne Jones, Rowlinson and Saville (1967)

f) Beattie, Barriault and Brierly (1952)

g) Whalley and Schneider (1955).

Xenon

T	B(T)[a]	B(T)[b]	B(T)[c]	B(T)[d]
273.16	-154.74[e]	-155.82	-149.18	-171.48
298.16	-130.27[e]	-131.44	-127.08	-146.72
323.16	-110.98[e]	-111.93	-109.15	-126.73
348.16	- 95.10[e]	-95.97	-94.34	-110.26
373.16	-81.89[e]	-82.67	-81.90	-96.47
398.16	-70.62[e]	-71.44	-71.31	-84.76

Xenon (Cont.)

T	$B(T)^{a)}$	$B(T)^{b)}$	$B(T)^{c)}$	$B(T)^{d)}$
423.16	-61.02[e]	-61.83	-62.20	-74.70
448.20	-52.64[f]	-53.50	-54.27	-65.96
473.16	-47.36[g]	-46.25	-47.34	-58.33
473.21	-45.37[f]	-46.24	-47.33	-58.31
498.23	-39.05[f]	-39.84	-41.19	-51.57
523.25	-33.21[f]	-34.17	-35.74	-45.57
548.26	-28.02[f]	-29.11	-30.87	-40.22
573.16	-25.07[g]	-24.59	-26.50	-35.43
573.28	-23.55[f]	-24.57	-26.48	-35.41
673.16	-10.78[g]	-10.31	-12.66	-20.26
773.16	- 1.34[g]	- 0.22	- 2.89	- 9.54
873.16	7.95[g]	7.24	4.35	- 1.61
973.16	14.21[g]	12.97	9.88	4.47

a) Experimental values

b) EXP-6 values calculated from the second virial parameters in Table 6 (p.161)

c) EXP-6 values calculated from the "pairwise additive" solid state parameters in Table 2 (p.74)

d) EXP-6 values calculated from the "triplet" solid state parameters in Table 5 (p.148)

e) Michels, Wassenaar and Louwerse (1954)

f) Beattie, Barriault and Brierly (1951)

g) Whalley, Lupien and Schneider (1955)