EFFECTS OF ANHARMONICITY ON THE INTER-MOLECULAR POTENTIALS DERIVED FROM CRYSTAL PROPERTIES

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ABSTRACT. The effect of anharmonicity on the intermolecular potentials derived from crystal properties (using Einstein approximation) has been considered for an elaborate six-parameter potential. The results obtained in this paper show that crystal properties cannot be used for an accurate determination of the pair-wise additive intermolecular potential.

INTRODUCTION

The effect of anharmonicity on the intermolecular potentials derived from crystal properties on the Einstein approximation has not yet been determined satisfactorily. Calculations performed by Zucker (1958) for the Lennard-Jones (12:6) potential show that the effect of anharmonicity cannot be neglected. On the other hand, Guggenheim and McGlashan (1960), have used mainly crystal properties to determine the intermolecular potential of argon on an elaborate six-parameter model. Guggenheim and McGlashan (1960) could not assess the effect of anharmonicity and they assumed it to be negligibly small. They argued that due to the limitations of the Lennard-Jones (12:6) potential the conclusion reached by Zucker (1958) regarding the effect of anharmonicity is uncertain. Consequently, it is very desirable to obtain an estimate of the effect of anharmonicity on the crystal properties for the six-parameter potential itself.

Another factor which should play a significant part (Jansen, 1963; Barker, 1964) in the determination of intermolecular potentials from crystal properties is the contribution of many-body interaction, i.e. the intermolecular potential can no longer be considered as pair-wise additive. In principle, bulk properties of scalar character are not particularly suitable for obtaining information on non-additive forces as their functional dependence on these forces is too implicit (Jansen, 1963). However, some information on the non-additive interactions can be obtained by an accurate analysis of the gaseous and the solid state properties of the same substance.

Recently, Barker (1964) has obtained the intermolecular potential of argon on the core potential by utilising only low-pressure gaseous properties in which effects of many-body interactions and anharmonicity may be neglected. The potential energy curve thus obtained is much closer to six-parameter potential

than to the Lennard-Jones (12:6) potential. The force parameters for argon as obtained by us in this paper from crystal properties at $0°$K are quite different from those obtained from gaseous data (Barker, 1964). This probably shows that the core potential is sensitive and flexible enough to show the effects of anharmonicity and may-body interactions if they are of significant magnitude. We have used the core potential to calculate the entropy of solid argon at different temperatures.

CALCULATIONS AND RESULTS

The core potential with a spherical core of diameter γ may be written as,

$$\Phi(r) = 4\epsilon \left[\left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{12} - \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{6} \right] \qquad \ldots (1)$$

where r is the internuclear distance, ϵ the depth of the potential $r^* - r/\sigma$ and $\gamma^* = \gamma/\sigma$. σ is the value of r for which $\Phi(r) = 0$. At 0 K anharmonicity effect is present only in zero-point energy and we shall neglect it. We have used the heat sublimation L_0 and the lattice distance at $0°$K for calculating the force constants of argon for the core potential. The equations used are the following

$$L_0 = 2N\epsilon \left[C_{12} \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{12} - C_6 \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{6} \right] \qquad \ldots (2)$$

and

$$C_6 = 2C_{12} \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{6} + \left[\frac{h^2}{8\pi^2 m\sigma^2\epsilon(1-\gamma^*)^2} \right.$$

$$77C \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right) - 10C_8$$

$$- 22C_{14} \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{10} - 5C_8 \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right) \qquad \ldots (3)$$

$C_6, C_8 \ldots$ etc. are crystal constants which depend on the lattice (Hirschfelder *et al*, 1954).

In the calculation of σ and ϵ from eqs. (2) and (3) we have assumed γ^* to have the same value as determined by Barker (1964). The results obtained are shown in table I together with the values for the Lennard-Jones (12:6) potential. It may be seen that unlike the Lennard-Jones (12 :6) potential the two sets of constants for the core potential as determined from the gaseous and crystal data differ considerably from each other.

TABLE 1

Constants for the core potential and Lennard-Jones (12:6) potential

	Constants determined from					
	Crystal Properties			Gaseous Properties		
	γ^*	$\sigma^\circ A$	$\epsilon/k^\circ K$	γ^*	$\sigma^\circ A$	$\epsilon/k^\circ K$
Core potential	0.1	0.348	117.25	0 1	3.363	142.9 [1]
Lnnard-Jones (12 : 6)	0.0	3.403	122.46 [2]	0.0	3.409	119.49 [3]

(1) Barker, *et al* (1964).

(2) Zucker, (1956).

(3) Whalley *et al* (1955).

For the core potential. the frequency of vibration on the Einstein approximation is given by,

$$\nu = \frac{2\epsilon}{\pi^2 m\sigma^2 (1-\gamma^*)^2} \left[22C_{14} \left(\frac{1-\gamma^*}{r^*-\gamma^*} \right)^{14} - C_8 \left(\frac{1}{r^*-\gamma^*} \frac{\gamma^*}{} \right)^8 \right] \qquad \dots \quad ((4)$$

In order to check the reliability of the force parameters calculated by us we have calculated the Debye temperature at $0^\circ K$ from the relation

$$\theta_0 = (5/3)^{\frac{1}{3}} \frac{h\nu}{k} \qquad \dots \quad (5)$$

The frequency ν being obtained from eq. (4). The experimental value of θ_0 is $93.3^\circ K$ and those calculated by using the force constants determined from crystal data and gaseous data are $94.1^\circ K$ and $77.5^\circ K$ respectively. The excellent agreement between the experimental value of θ_0 and the value calculated from the crystal properties at $0^\circ K$ show that this set of constants should reproduce satisfactorily other crystal properties at higher temperatures minius anharmonicity effects. Since the force parameters for the core potential have been determined by fitting with solid state data at $0^\circ K$, they should adjust themselves to take into account the many-body interactions.

The molar entropy of the crystal can be expressed as,

$$S/R = \frac{3}{2} x \coth \frac{x}{2} - 3 \ln \left(2 \sinh \frac{x}{2} \right) \qquad \dots \quad (6$$

where

$$x = \frac{h\nu}{kT} \qquad \dots \quad (7)$$

The entropy values at different temperatures have been calculated on the core potential from both the sets of constants using eqs. (4)—(6). The results together

with the experimental values are shown in table II. The quantities $(S_G-S_C)/R$ and $(S_E-S_C)/R$ represent approximately the effect of many body interactions and anharmonicity respectively.

TABLE II

Entropy values calculated for the core potential, at $p \to 0$

T°K	From gaseous properties data $(S/R)_G$	From crystal properties data $(S/R)_C$	Experimental $(S/R)_E$[a]	$1 - y \, \mathrm{cosech}^2 \, x/2$
20	0.642	0.380	0.754	1.0655
30	1.458	1.038	1.524	
40	2.223	1.713	2.231	1.1403
50	3.099	2.399	2.854	
60	3.731	3.106	3.417	1.0953
70	4.247	3.653	3.938	
80	4.638	4.199	4.431	1.0745

[1] Guggenheim et al (1960).

We shall now utilise the results obtained above to see if the consideration of anharmonicity improve the agreement between experiment and theory on the six-parameter potential. The six parameter potential in the neighbourhood of its minimum may be written as (Guggenheim et al, 1960).

$$\phi(r) = -\epsilon + k\left(\frac{r-r_m}{r_m}\right)^2 - \alpha\left(\frac{r-r_m}{r_m}\right)^3 + \beta\left(\frac{r-r_m}{r_m}\right)^4 \qquad (7)$$

where ϵ is the depth of the potential well at $r = r_m$. when r is very large $\varphi(r)$ vaies primarily as r^{-6} and may be written as

$$\phi(r) = -\lambda\left(\frac{r_m}{r}\right)^6 \qquad \dots \quad (8)$$

On the Einstein approximation for the acoustic modes of vibration of the frequency ν is given by

$$\frac{2\pi^2 m\nu^2 r_m}{12} = \tfrac{1}{3}k(1+\Delta)^{-1}(1+3\Delta) - \alpha\Delta(1+\Delta)^{-1}(1+2\Delta) + 2\beta\Delta^2(1+\Delta)(1+\Delta)^{-1}$$

$$(1+\tfrac{5}{8}\Delta) - 5\frac{C_8-12}{12}\lambda(1+\Delta)^{-8} \qquad - \quad (9)$$

where

$$= \left(\frac{r-r_m}{r_m}\right)$$

The molar total energy U can be expressed as

$$U/RT = \frac{12}{2kT}\left[-\epsilon+k\Delta^2-\alpha\Delta^3+\beta\Delta^4-\frac{C_6-12}{12}\lambda(1+\Delta)^{-6}+\tfrac{3}{2}x\coth\frac{x}{2}\right] \quad \dots \quad (10)$$

being taken as zero for infinitely dispersed atoms at rest. The expression for S/R on the six-parameter potential remains the same as that given by eq. (5). We have also the relation,

$$pV/RT = -\frac{2}{kT}\left[2k\Delta(1+\Delta)-3\alpha\Delta^2(1+\Delta)+4\beta\Delta^3(1+\Delta)+6\frac{C_6-12}{12}\lambda(1+\Delta)^{-6}\right]$$

$$\frac{3}{\pi^2 m v^2 r_m^2}\tfrac{1}{2}x\coth\frac{x}{2}\left[\frac{2}{3}\,k(1+\Delta)^{-1}-\alpha(1+\Delta)^{-1}(1+4\Delta+2\Delta^2)\right.$$

$$\left.+4\beta\Delta(1+\Delta)^{-1}\left(1+3\Delta+\frac{5}{3}\Delta^2\right)+40\frac{C_6-12}{12}\lambda(1+\Delta)^{-8}\right] \quad (11)$$

where p is the pressure and V the molar volume.

Initially we have neglected anharmonicity and taken $\beta=0$ and for λ/k the quantum mechanically calculated value $150°K$ was chosen. By using the experimental values of the lattice distance and entropy values (given in column 3 of table II) at $80°K$ and $40°K$ and following the method described by Guggenheim and McGlashan (1960) we have calculated the constants α, k and r_m.

When the atom is displaced from its lattice site by a distance with components ξ, η, ζ along the principal axes of the crystal the increase in energy is given by

$$(\xi^2+\eta^2+\zeta^2)\frac{12}{r_m^2}\left[\frac{1}{3}\,k(1+\Delta)^{-1}(1+3\Delta)-\alpha\Delta(1+\Delta)^{-1}(1+2\Delta)+2\beta\Delta^2(1+\Delta)^{-1}\right.$$

$$\left(1+\frac{5}{3}\Delta\right)-5\frac{C_6-12}{12}\lambda(1+\Delta)^{-8}\right]+(\xi^4+\eta^4+\zeta^4)\frac{12}{r_m^4}\times\frac{5}{3}\left[-\frac{1}{5}\alpha(1+\Delta)^{-1}\right.$$

$$\left.+\frac{1}{5}\beta(1+\Delta)^{-1}(1+5\Delta)-14\frac{C_{10}-12}{12}\lambda(1+\Delta)^{-10}\right]+0(\rho^6) \quad \dots \quad (12)$$

higher order in ρ being neglected. When anharmonic terms in eq. (12) are considered, the energy level along any of the perpendicular axes is given by

$$(n+\tfrac{1}{2})x+(n^2+n+\tfrac{1}{2})y \quad \dots \quad (13)$$

y is defined as,

$$y = -\frac{3h^2}{8\pi^4 m^2 r_m^4 v^2 kT}\left[\alpha(1+\Delta)^{-4}-\beta(1+\Delta)^{-1}(1+5\Delta)+70\frac{C_{10}-12}{12}\lambda(1+\Delta)^{-10}\right]$$

$$\dots \quad (14)$$

We have also (taking $\beta = 0$ in the harmonic approximation)

$$U/RT = \frac{12}{2kT}\left[-\epsilon+k\Delta^2-\alpha\Delta^3+\beta\Delta^4-\frac{C_6-12}{12}\lambda(1+\Delta)^{-6}\right.$$

$$\left.+\frac{3}{2}\,x\coth\frac{x}{2}\left[1-y\left(\text{cosech}^2\frac{x}{2}-\frac{\coth x/2}{x}\right)\right]\right] \qquad (15)$$

$$S/RT = \frac{3}{2}\,x\coth\frac{x}{2}\left[1-y\,\text{cosech}^2\frac{x}{2}\right]-3\ln(2\sinh x/2) \qquad (16)$$

$$pV/kT = -\frac{2}{kT}\left[2k\Delta(1+\Delta)-3\alpha\Delta^2(1+\Delta)+4\beta\Delta^3(1+\Delta)+6\frac{C_6-12}{12}\lambda(1+\Delta)^{-6}\right]$$

$$-\frac{3}{\pi^2 m\nu r_m^2}\frac{1}{2}\,x\coth\frac{x}{2}\left[1-y\,\text{cosec}\,h^2\frac{x}{2}+\frac{dy/dr}{dx/dr}\coth\,x/2\right]\,\times$$

$$\left[\frac{2}{3}\,K(1+\Delta)^{-1}-\alpha(1+4\Delta+2\Delta^2)+4\beta\Delta(1+\Delta)^{-1}\left(1+3\Delta+\frac{5}{3}\Delta^2\right)\right.$$

$$\left.-40\frac{C_8-12}{12}\lambda(1+\Delta)^{-8}\right] \qquad \ldots\,(17)$$

TABLE III
Force constants of argon for six-parameter model

Set No.	$\lambda/k°K$	r_m Å	ϵ/k °K	$10^{-2}{}_{k/k}°K$	$10^{-3}{}_{a/k}°K$	$10^{-4}{}_{\beta/k}°K$	Ref.
1	150	3.805	139.11	60.0	24.5	0	This work
2	150	3.818	139.5	44.3	18.3	0	Ref. 4.
3	150	3.812	137.5	44.9	19.6	1.96	

TABLE IV
Experimental and the calculated values of the molar enthalpy for $p \to 0$

T°K	H/R (Calculated) from Set 1	H/R (Experimental)[a]
20	−924.4	−922.0
40	−872.1	−878.0
60	−811.7	−819.0
80	−748.1	-748.1

(1) Guggenheim *et al*, (1960).

In order to ascertain the effect of anharmonicity the values of y were obtained from eq. (16) by using the experimental value of entropy and the values of α, k r_m as obtained earlier. The values of the term $(1-y \operatorname{cosech}^2 x/_2)$ at different temperatures are shown in column 5 of table II. Once the factor y is known, ϵ/k can be calculated from eq. (15) by using the experimental value of U. The values of the constants obtained for the six-parameter potential are shown in table III. In order to calculate pV/RT it is necessary to obtain dy/dr and dx/dr. From the values of y the corresponding β values may be calculated from eq. (14) and eq. (16) gives

$$rdy/dr \ = \ \frac{3h^2}{8\pi^4 m^2 r_m^4 v^2 kT} \left[\ \alpha(1+\Delta)^{-1}+4\beta(1+\Delta)^{-1}+700 \ \frac{C_{10}-12}{12} \ \lambda(1+\Delta)^{-10} \right] \quad (18)$$

From Eqs. (6) and (9)

$$r\,dx/dr \ = \ \frac{3x}{\pi^2 m r_m^2 v^2} \left[\frac{2}{3} \ (1+\Delta)^{-1}\cdot \ \alpha(1+\Delta)^{-1}(1+4\Delta+2\Delta^2) \right.$$

$$\left. + \ 4\beta\Delta(1+\Delta)^{-1}\left(1-3\Delta+\frac{0}{3}\Delta^2\right)+40 \ \frac{C_8-12}{12} \ \lambda(1+\Delta)^{-8} \right] \quad \dots \quad (19)$$

COMPARISON WITH EXPERIMENT

Since experimental entropy values have been utilised for the determination of the potential parameters, these cannot be used for the comparison between the theory and the experiment. From table IV it may be seen that by considering anharmonicity effects the agreement between the experimental and the calculated values of molar enthalpy is well within 1% at all temperatures. The experimental and the calculated values of the lattice parameter and the lattice volume at $p-0$ are shown in table V. It may be seen that the agreement between experiment and theory is slightly better when anharmonicity is taken into account. In the calculated values from set no. 3 the anharmonicity is considered but it is assumed too small. However, the most sensitive test for anharmonicity effects is the pressure variation of the quantity pV/RT. A convenient way of expressing this is the quantity $V(o)-V(p)$, $V(p)$, $V(p)$ being the molar volumes at zero pressure and p at m; respectively. The quantity $V(p)$ was calculated from eq. (11) by using all the sets of constants given in table II (the anharmonic terms being ommitted for sets 2 and 3). The experimental and the calculated values of the quantity $V(o)-V(p)$ are shown in table VI,

TABLE V

Experimental and the calculated values of the lattice distance and
the molar volume $V(o)$ at $p \to 0$

| TeK | Calculated from | | | | Experimental[n] | |
| | Set No. 1 | | Set No. 3 | | | |
	$r_m{}^*Å$	V cm³/mol	$r_m{}^*Å$	V cm³/mol	$r_m{}^*Å$	V cm³/mol
20	3.767	22.770	3.768	22.820	3.760	22.650
40	3.778	22.974	3.784	23.080	3.780	23.005
60	3.827	33.875	3.810	23.557	3.818	23.706
80	3.869	24.674	3.850	24.307	3.860	24.500

[n] Pollack, (1964).

$r_m{}^* = r/\sqrt{2}$, r being the lattice distance.

TABLE VI

Experimental and the calculated values of the quantity $V(o) - V(p)$
at various pressure and $T = 65°K$

| Pressure p (atm.) | Calculated from | | | Experimental |
	Set 1	Set 2	Set 3	
193.6	0.23	0.32	0.31	0.26
387.1	0.45	0.63	0.57	0.50
483.1	0.54	0.78	0.72	0.59
580.7	0.63	0.97	0.82	0.71
967.8	0 97	1.33	1.25	1.09

DISCUSSION OF RESULTS

It may be seen from table VI that the agreement between experimental
and calculated values is much better if anharmonicity is considered (set 1).
For set 3 the agreement is slightly better than set 2, which is probably due to the
reason that anharmonicity is very slightly taken into account in set 3. Since
$V(o) - V(p)$ is most sensitive to the effect of anharmonicity, results show that
anharmonicity does play a significant role in determining the crystal properties.
The term $(1 - y \operatorname{cosec} h^2 x/2)$ which is a measure of the effect of anharmonicity

show a maximum value around 40°K which is in agreement with the temperature variation of the Gruneisen parameter γ' for argon (Pollack, 1964). The calculated values of the quantity $V(o) - V(p)$ is slightly lower than the experimental values when anharmonicity is considered whereas if this is neglected the calculated values are higher than the experimental values. One reason for the over correction for anharmonicity is the approximate equations used for considering anharmonicity and the other reason may be that we have used the experimental values of the lattice distance in our calculation which means that anharmonicity has already been taken into account partially.

It is relevant here to consider the uncertainty in the anharmonicity effect found by us due to the use of the Einstein approximation which does not consider the coupling between the harmonic oscillators. However, it has been shown by Zucker (1958) that the Hankel's modification of the Einstein model (which does not include harmonic coupling) gives much better agreement between experiment and theory than the Debye approximation (which considers inter-dependence of the oscillators, but does not include anharmonic effect). Near 0°K the two methods are in very good agreement and difference between them increases as the temperature increases (Zucker, 1958). This probably proves that if the constants for the intermolecular potential fitted to data at 0°K then only the consideration of anharmonicity effects can explain the experimental data satisfactorily. In the present paper we have followed a similar procedure and the most of the effects obtained by us must be due to anharmonicity.

Regarding the effect of many body interactions several observations are relevant. In agreement with the calculations performed by Jansen (1963a, 1963b), Barker (1964) has observed that for argon non-additive interaction contributes about 30% to the heat of sublimation L_0 at 0°K. The effect of non-additive interaction on entropy is shown by the term $(S_C - S_G)/R$ in table II. It must be pointed out that $(S_C - S_G)/R$ gives only qualitative magnitude of the many body effect on entropy. Since it is not possible to obtain the effect of non-additive interactions accurately from theory it is not justified to use solid state properties even in conjunction with gaseous properties for the determination of intermolecular potentials.

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