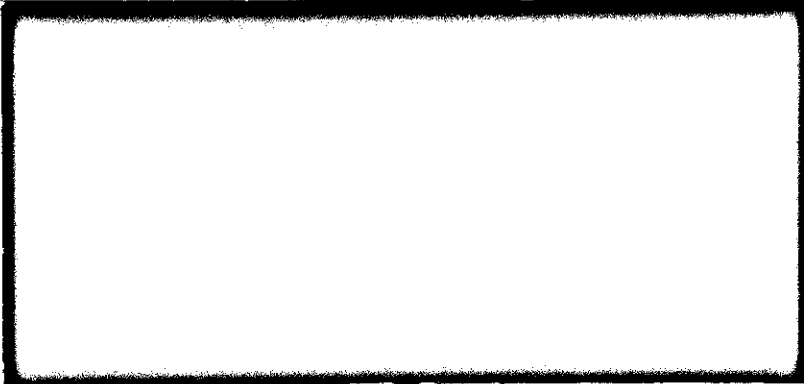


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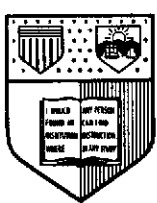
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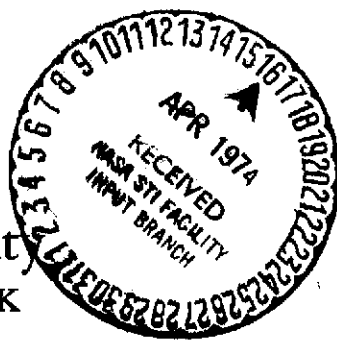
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PERTURBATION THEORY OF STRUCTURE
IN CLASSICAL LIQUID MIXTURES:
APPLICATION TO METALLIC SYSTEMS
NEAR PHASE SEPARATION
by
Robert Lloyd Henderson

Ph.D. Thesis
January 1974

Research Group:
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ABSTRACT

This work concerns the partial structure factors of classical simple liquid mixtures near phase separation. The theory is developed for particles interacting through pair potentials, and is thus appropriate both to insulating fluids, and also to metallic systems if these may be described by an effective ion-ion pair interaction. The motivation arose from consideration of metallic liquid mixtures, in which resistive anomalies have been observed near phase separation. The pair potential is written as $v_{ij} = v_{ij}^{\text{ref}} + v_{ij}^1$, where v_{ij}^{ref} is the pair interaction appropriate to a reference fluid and is chosen so that v_{ij}^1 may be treated as a perturbation. We study how to correct a mean field theory appropriate to such a potential for the effects of correlated motions in the reference fluid. The work is cast in terms of functions f_{ij} which are closely related to the direct correlation functions of Ornstein and Zernike. Exact equations for the f_{ij} are derived by a method, originally developed for the study of the quantum electron gas, which treats the densities of the

mixture as basic variables in a linear response problem. We obtain approximate solutions to these equations which, however, are exact to first order in v_{ij}^1 in the long wavelength limit, and which explicitly include the effects of reference system correlations. These solutions are then used to calculate the long wavelength form of the structure factors of metallic alloys, where we select for v_{ij}^{ref} the potentials appropriate to a mixture of hard spheres. We seek to observe the singularities, at $k = 0$, associated with phase separation (in the critical region) and the long wavelength behavior which accompanies these singularities. The results are qualitatively in accord with our physical expectations. Quantitative agreement with experiment seems to turn on the selection of the hard core reference potential in terms of the metallic effective pair potential, a task for which a successful systematic procedure has yet to be found. It is suggested that the present effective pair potentials are perhaps not properly used to calculate the metallic structure factors at long wavelength. Suggestions are made for application of these results to the thermodynamic and structural properties of insulating fluids. In the case of metallic systems, a qualitative explanation of the resistive anomaly is proposed, and suggestions made for a quantitative test of the hypothesis.

I. Introduction and Statement of the Problem

The work reported here arose from consideration of a single experimental result, the resistance anomaly observed in some binary liquid metal alloys as the phase separation temperature is approached. The importance of this result is that the theoretical difficulty it presents has its origin in a central problem of the theory of classical liquids, namely, the calculation of liquid structure from the interactions among the particles of the liquid. In this section, we shall describe these experiments and develop our analysis of these experiments to the point where a clear statement of the problem and program of this thesis can be made.

I-A. Phase Separation and the Experiment of Schürmann and Parks

To set the stage, we must begin with a recital of the basic facts of phase separation in binary systems. Consider a binary system composed of N_1 particles of type 1 and N_2 particles of type 2. The thermodynamic state of this system may be considered a function of three variables; pressure p , temperature T , and concentration $x = N_2 / (N_1 + N_2)$. The phase diagram relevant to this work is that formed, at constant p , in the x - T plane. Fig. 1 represents schematically a portion of an x - T diagram of the type important to our work. It represents, in fact, an abstraction from the x - T diagram

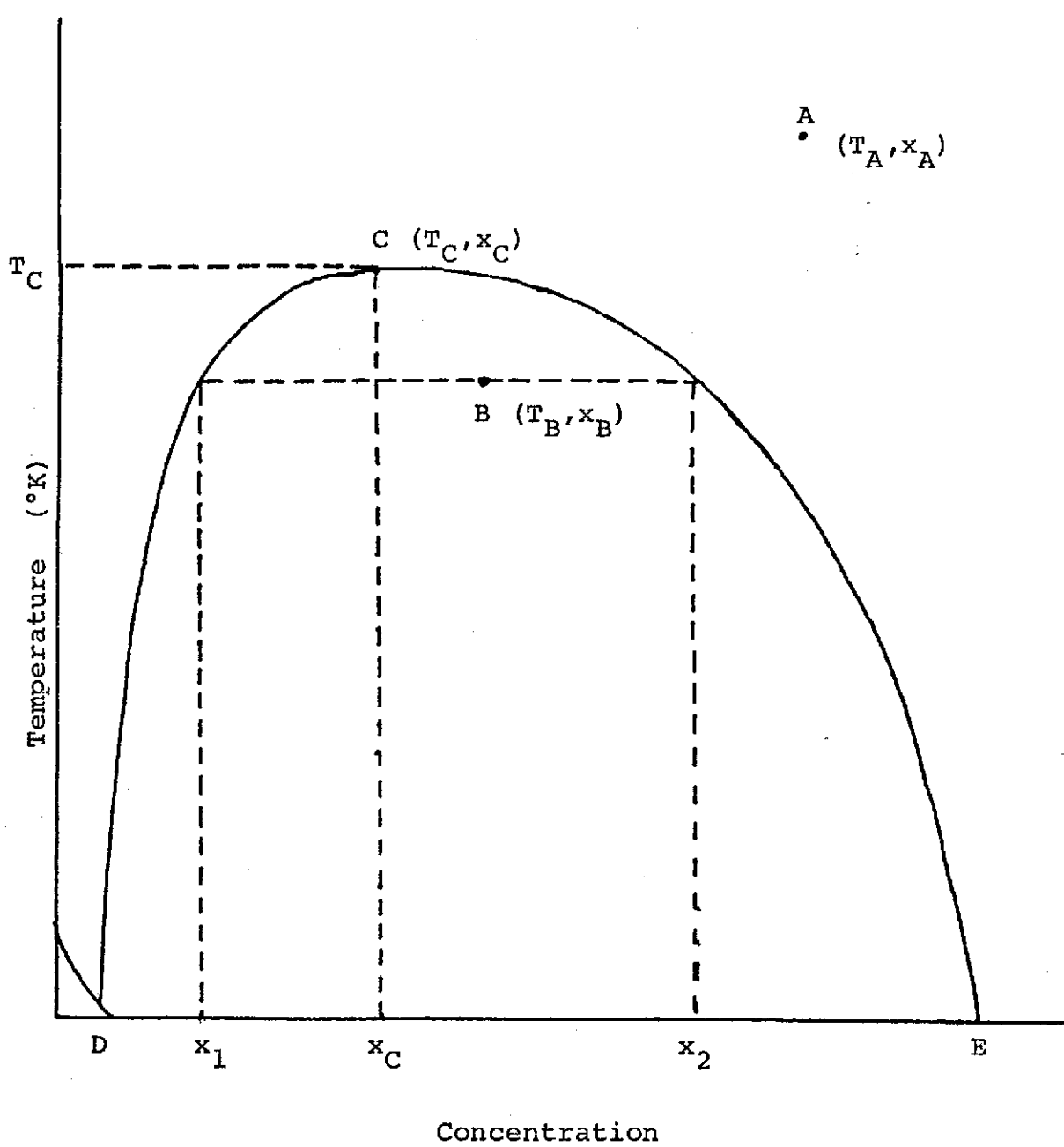


Figure 1

Portion of an x-T phase diagram of a binary system which exhibits phase separation.

compiled by Schürmann (1971) for the Li-Na system.

The phase diagram specifies, for each point (x,T) , the stable configuration of the corresponding mixture. In Fig. 1, points from the small triangular region at the lower left correspond to a solid phase. The phase boundary from D to E separates the remainder of the region shown into two liquid phases. For a point above the boundary, say the point A specified by (x_A, T_A) , the stable configuration is a single, uniformly mixed, alloy of concentration x_A . For a point below the boundary, say the point specified by (x_B, T_B) , the stable configuration is a separated phase. In this phase, two distinct alloys are present simultaneously. (Under the influence of gravitation, these alloys will occupy two separate regions of the container, divided by a meniscus.) These alloys are described by concentrations $x_1 < x_B$ and $x_2 > x_B$, where x_1 and x_2 are determined by T_B alone as the concentrations at which the phase boundary cuts the line $T = T_B$. This construction is illustrated in Fig. 1. The relative amounts of these two alloys are determined from x_1 and x_2 , the given x_B , and the requirement that all particles be accounted for.

At points above the phase boundary, where a single uniform alloy can be maintained at equilibrium, the components are said to be miscible. The boundary defines a critical temperature T_C above which the components are miscible in all proportions. The point C at which the line $T = T_C$ intersects the phase boundary is the critical point, and defines a

critical concentration x_C . T_C and x_C are indicated in Fig. 1. The transition of an alloy from the uniform to the separated phase is known as phase separation.

The experiments which motivated this work are concerned with what happens in the stable uniform alloy at temperatures just above phase separation. Schürmann and Parks (1971) have measured the electrical resistance as a function of temperature at various concentrations in two metallic binary systems, Li-Na and Ga-Hg. As we shall outline shortly, the electrical resistance provides an integrated measure of fluctuation effects. The purpose of these experiments was to determine if changes in the fluctuation spectrum would cause the resistance to show any precursive behavior, that is, to respond in an observable way as phase separation is approached. Such a response might be considered analogous to the critical opalescence of the critical liquid-gas system.

No precursive behavior was observed at any concentration in the Ga-Hg system. In the Li-Na system, some degree of precursive behavior appeared at most concentrations, and the effect became more pronounced as the concentration varied toward the critical value. The effect takes the following form. If the temperature is decreased, starting at a point well removed from phase separation, the resistance decreases at first in a nearly linear fashion. As the temperature of separation is approached, however, the resistance begins to decrease more rapidly, so that a plot of resistance vs. T develops a pronounced curvature, and the resistance attains

a value at separation which lies below the linear extrapolation of the high temperature results.

I-B. The Resistance Anomaly and Liquid Structure

To understand the significance of these experiments, we consider first the theory of conduction in liquid metal alloys. The simplest successful theory was proposed for the case of a pure fluid by Ziman (1961). The theory was generalized to the case of binary alloys by Ziman and Faber (1965). The development of the theory has been aided by the introduction of adequate models for the electron-ion pseudopotential and the liquid structure. Calculations for pure simple liquid metals (Ashcroft and Lekner, 1966) and for liquid binary alloys of simple metals (Ashcroft and Langreth, 1967, A, B, to be referred to as Al-I and Al-II respectively) have achieved reasonable agreement with experiment. Although this success remains something of a mystery, we base our analysis on the Ziman theory. The theory, as we shall see, encompasses, in a reasonable way, the possibility of an anomaly near phase separation.

In the formulation of Al-II, the result of the Ziman and Faber theory for the resistivity of a binary alloy is written

$$\rho_{\text{elec}} = \frac{4\pi^3\hbar}{e^2k_F} z^* \int_0^1 dy y^3 \{ 2\sqrt{x(1-x)} S_{12}(y) v_1(y) v_2(y) + xS_{11}(y) (v_1(y))^2 + (1-x)S_{22}(y) (v_2(y))^2 \}. \quad (1-1)$$

For this discussion, we need not give careful definitions to

most of the pieces of this expression. The liquid metal is viewed as a system of rigid ion cores, of types one and two, moving about in a sea of nearly free conduction electrons. Defined relative to this model, k_F is the usual Fermi wave vector, Z^* is a (concentration dependent) effective valence, x is the concentration variable we have already defined, y is a wave number variable measured in units of $2k_F$, and the functions $v_i(y)$ are dimensionless form factors for the screened electron-ion interactions. The key functions of our work are the functions $S_{ij}(y)$, the partial structure factors, for they are the only functions in (1-1) which contain detailed information on the ionic positions. They are defined by

$$S_{ij}(\underline{k}) = (N_i N_j)^{-\frac{1}{2}} \langle \hat{\rho}_i(\underline{k}) \hat{\rho}_j(-\underline{k}) \rangle - (N_i N_j)^{\frac{1}{2}} \delta_{\underline{k},0} . \quad (1-2)$$

Here, N_1 and N_2 are the particle numbers defined above, $\langle \rangle$ denotes a thermal average, and the operators $\hat{\rho}_i(\underline{k})$ are defined by

$$\hat{\rho}_i(\underline{k}) = \sum_m e^{i\underline{k} \cdot \underline{r}_m^i} , \quad (1-3)$$

where \underline{r}_m^i denotes the position of the m^{th} particle of type i .

The operators $\hat{\rho}_i(\underline{k})$ have the property that

$$\rho_i(\underline{k}) = \langle \hat{\rho}_i(\underline{k}) \rangle , \quad (1-4)$$

where $\rho_i(\underline{k})$ is the $\underline{k}^{\text{th}}$ Fourier coefficient of the equilibrium density of particles of type i . From (1-2), we see that the $S_{ij}(\underline{k})$ represent the static density fluctuation spectrum of

the liquid. It is reasonable to expect the density fluctuations to reflect in some way the nearness of the phase separation instability. This idea provided the original motivation for the resistivity measurements, and lies at the heart of our work.

It will be useful in this work to present here a few more relations involving the structure factors. A more detailed discussion of such matters is reserved for an appendix (A) on the classical n-body distribution functions.

Many of the general points we need to make can be made in reference to pure fluids, avoiding the clutter of notation introduced by consideration of binary systems. For a pure fluid, we can define a single static structure factor $S(\underline{k})$ by

$$S(\underline{k}) = \frac{1}{N} \langle \sum_{nm} e^{i\underline{k} \cdot (\underline{r}_n - \underline{r}_m)} \rangle - N \delta_{\underline{k},0} , \quad (1-5)$$

where N is the number of particles and \underline{r}_n denotes the position of the n^{th} particle. This function is related by Fourier transform to the radial distribution function $g(\underline{r})$:

$$g(\underline{r}) = 1 + \frac{V}{N} \int \frac{d\underline{k}}{(2\pi)^3} e^{-i\underline{k} \cdot \underline{r}} (S(\underline{k}) - 1) , \quad (1-6)$$

where V is the volume of the system.* The function $g(\underline{r})$ is proportional to the conditional probability that a particle will be found at \underline{r} , given a particle at the origin. Finally, the functions $S(\underline{k})$ and $g(\underline{r})$ are related to the two body distribution function $\rho_2(\underline{r}, \underline{r}')$. This function has the property

*The integral in this equation, incidently, defines the Fourier transform convention which we adopt throughout this work.

that $\rho_2(\underline{r}, \underline{r}') d\underline{r} d\underline{r}'$ is the probability of finding simultaneously one particle in the volume element $d\underline{r}$ about \underline{r} and another in the element $d\underline{r}'$ about \underline{r}' . In the translationally invariant system, $\rho_2(\underline{r}, \underline{r}') = \rho_2(\underline{r} - \underline{r}')$ and

$$g(\underline{r}) = (V/N)^2 \rho_2(\underline{r}) . \quad (1-7)$$

The generalization of (1-6) to binary systems is

$$g_{ij}(\underline{r}) = 1 + \frac{V}{N} \int \frac{d\underline{k}}{(2\pi)^3} e^{-i\underline{k} \cdot \underline{r}} (S_{ij}(\underline{k}) - \delta_{i,j}) , \quad (1-8)$$

where $g_{ij}(\underline{r})$ now represents, suitably normalized, the probability of finding a particle of type j at a distance \underline{r} from a given particle of type i . Clearly, $g_{ij}(\underline{r}) = g_{ji}(\underline{r})$. The generalization of (1-7) is straightforward.

We can collect what has been said so far into a first statement of the problem of this work. That problem is to calculate the partial static structure factors of the alloy with sufficient precision that the onset of phase separation can be observed and the resistance anomaly explained.

I-C. Expectations

The development of our approach has been guided to a considerable extent by our expectations for the form of the outcome.

The first, and most important, of these expectations concerns the limit as $\underline{k} \rightarrow 0$, and takes the following form. At all points (x, T) , we can in principle calculate the

structure factors of the uniform phase. (For this purpose, points below the phase boundary are exceptional only in that the appropriate Gibbs energy is higher than that of some separated phase.) A thermodynamic analysis (outlined in appendix B) shows that such calculations will yield, at each concentration, a temperature at which the partial structure factors will diverge as $k \rightarrow 0$. When plotted vs. concentration, these temperatures will form a curve suggesting, but not strictly reproducing, the phase boundary. This curve lies in general below the phase boundary, rising to join it at only one point, the critical point. We shall seek to calculate this line of hypothetical singularities at $k = 0$, and identify its highest point as the critical point.

A second guide in this work has been a conjecture that it is the small k behavior associated with this $k = 0$ singularity which gives rise to the resistance anomaly. As this conjecture is at variance with that of Schürmann and Parks (1971), we should outline the manner in which the small k behavior might account for the observed effects.* First, in the resistance data for the Li-Na system, some degree of

*This conjecture is also at variance with that of Fisher and Langer (1968), who suggest that the observed resistance anomalies at magnetic critical points must not be due to long range correlations, because of the finite mean free path of the conduction electrons. Their point, however, is that the electron mean free path is limited by scattering other than spin scattering (e.g. phonons, impurities), while for the liquid metal alloy, we consider that the only scattering present is the scattering from density fluctuations treated in the Ziman formula. The electrons may thus be scattered by even long wavelength fluctuations.

anomalous behavior is observed at most concentrations, but the effect clearly becomes more pronounced as the concentration is varied toward the critical value. This observation seems to reflect the relation, described above, between the phase boundary and the line of singularities.

Secondly, we must ask why the effect is observed in Li-Na but not in Ga-Hg. Consider the form of (1-1). The upper limit on the integral is $2k_F$, which depends on the effective valence of the alloy. Now the partial structure factors are characterized by strong first peaks (AL-II), and the valence dependence of the integration limit is such that these peaks lie within the range of integration for Ga-Hg, but just outside it for Li-Na. Thus, when we observe that large k effects are heavily weighted by the factor y^3 , it is reasonable that a small k effect will be lost in Ga-Hg, but (barely) observable in Li-Na. We note in support of these ideas that the effect in Li-Na is very small. Even at the critical concentration the resistance at separation lies less than 1% below the linear extrapolation of the high temperature results.

Finally, we must ask why the resistance is depressed by this effect, when the structure factors of (1-1) are diverging. When Bhatia and Thornton (1970) discussed these singularities, they in fact suggested that the resistance should go up. In this matter, we can only note that the complexities of the alloy (e.g. the factors S_{11} and S_{22} diverge positively while S_{12} diverges negatively) are such that a clear prediction may

not be possible.

I-D. Structure of Metallic Liquids - Previous Results

To arrive at a final statement of the problem, we need to review the assumptions and principle results of the theory of liquid metal structure, as it existed at the inception of this work.

At the level appropriate here, the theory of liquid metals rests on several standard assumptions. The fundamental assumption is the validity of the adiabatic approximation, which asserts that, on the time scale of ionic motions, the relatively light and mobile conduction electrons adjust instantly to any change in ionic configuration. This means that, for purposes of determining ionic motion, the electronic configuration may be considered to be completely specified by only the volume V and the ionic positions, which we denote by the general variable R . Then the total energy may also be considered a function of only V and R , and denoted by $E_{\text{metal}}(V,R)$. A second assumption (actually implicit in this definition of $E_{\text{metal}}(V,R)$) is that the ions exhibit no internal structure. The final assumption is that the ions form a classical system so that their motion may be determined by classical dynamics.

With these assumptions, the problem of ionic structure factors and motion is cast as the problem of a classical liquid, with, however, a complicated energy function. In theories of classical liquids, the assumption is almost

universally made that the energy function depends only on the particle positions R , and is expressible as a sum of pair interactions. That is, it is assumed that the energy may be written as

$$U(R) = \frac{1}{2} \sum_{i \neq j} v(\underline{r}_i - \underline{r}_j) . \quad (1-9)$$

Ashcroft and Langreth (1967C, AL-II) have proposed an approximate form for $E_{\text{metal}}(V,R)$ in which all dependence on R can be accounted for in a sum over an effective, volume dependent, pair interaction between ions. (The total energy of the liquid, however, is not recovered by a sum of the form (1-9), since the sum excludes some volume dependent terms.) This effective pair potential will be denoted by v^{AL} . These results suggested that classical liquid theory might be applied to the ions of a simple liquid metal at constant volume by using v^{AL} as the pair interaction. This idea has opened the way to important progress in understanding liquid metal structure. Though we shall mount a selective challenge to this idea in section V, it formed a crucial starting assumption of the present work.

The important strides in understanding liquid metal structure have come with the application of the hard sphere model. When the potential v^{AL} is viewed in real space (AL-II), it is characterized by a short range, harshly repulsive core, and a weak, long range, generally attractive tail. The simplest non-trivial model of such a potential is that acting between hard spheres of diameter σ :

$$v^{HC}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases} \quad (1-10)$$

The structure factors appropriate to the hard sphere model fluid are reasonably well known from machine calculations (Alder and Wainwright, 1958; Alder and Hoover, 1968; Wood, 1968; Rowlinson, 1968) and in the analytic Percus-Yevik (PY) approximation (Percus and Yevik, 1958; Wertheim, 1963; Thiele, 1963; Lebowitz, 1964; Ashcroft and Lekner, 1966; AL-I).

Even before the form of v^{AL} was suggested, Ashcroft and Lekner had applied the hard sphere model to pure simple liquid metals with considerable success. They showed that the hard sphere structure factors of the PY approximation could be adjusted by selection of σ to give an excellent fit to the experimental structure factors of these systems in the region of the first peak and, to a lesser extent, down to the smallest wave vectors for which experimental data were available. Using these hard sphere structure factors in the Ziman formula, they calculated the electrical resistivity and achieved reasonable agreement with experiment. They also noted that the hard sphere diameter σ used to achieve the structural fit corresponded, near the solidification point of each element, to a packing fraction* of about 45%. This compares favorably with the value of 49% at which machine calculations place the crystallization of the hard sphere liquid (Hoover and Ree, 1968).

*The packing fraction is the ratio of the volume occupied by the hard spheres to the total volume of the system (eq. (5-9)).

When the potential v^{AL} was introduced, Ashcroft and Langreth showed that it bore a simple physical relation to the hard core diameters of the Ashcroft-Lekner work. They went on to generalize this relation to the case of a binary alloy, and use the structure factors of the hard sphere mixture (in the PY approximation) in a successful calculation of alloy resistivities (restricted, of course, to alloys which do not separate).

The hard sphere success, however, does not appear to include an accounting for phase separation. Phase separation has not been observed in hard sphere mixtures either by machine calculation (Alder, 1964 (M.D.) and Rotenberg, 1965 (M.C.)) or by analytic study from the PY approximation (Lebowitz and Rowlinson, 1964). Although this is apparently still an open question, the negative result is not unexpected. The hard sphere potential defines no energy scale, but only a scale of length. Then a phase transition in a hard sphere fluid can be driven only by geometry. When we consider phase separation in mixtures, we note that both the uniform and separated phases are characterized by disordered alloys, so that we do not expect geometry to play the dominant role in the transition. (We shall, in any case, treat the important hard sphere systems of this work in the PY approximation, within which these systems are known to be stable.) The plan of our work will then be to go beyond the hard sphere model in order to understand phase separation.

I-E. Statement of the Problem and Outline of the Thesis

What is needed is a theory of structure which preserves the successes of the hard sphere model, but goes beyond this model in order to account for phase separation. The natural suggestion is that we try to calculate the liquid structure by a perturbation theory which begins in zero order with the hard sphere liquid.

The actual program set for this work results from combining this suggestion with one further hypothesis. That hypothesis addresses the following question. The perturbation theory we envision will find its most natural formulation for potentials of the form

$$v = v^{HC} + v^1, \quad (1-11)$$

where v^1 is the perturbation. But the potential v^{AL} cannot be cast in this form, since all potentials of this form have a rigorous hard core, while v^{AL} has a core with a steep but finite slope. It is our hypothesis that the "softness" of the core has little effect on the physics of phase separation, and thus, at least for a first attempt at this problem, we need not consider the more elaborate perturbation theory required to treat this softness.* Rather, we assume that the essential physics of phase separation is implicit in a potential of the form (1-11), and develop our theory for such a potential. We call this potential the "hard core plus tail"

*Such theories have been developed. See for instance Andersen et al. (1971) and Barker and Henderson (1967B).

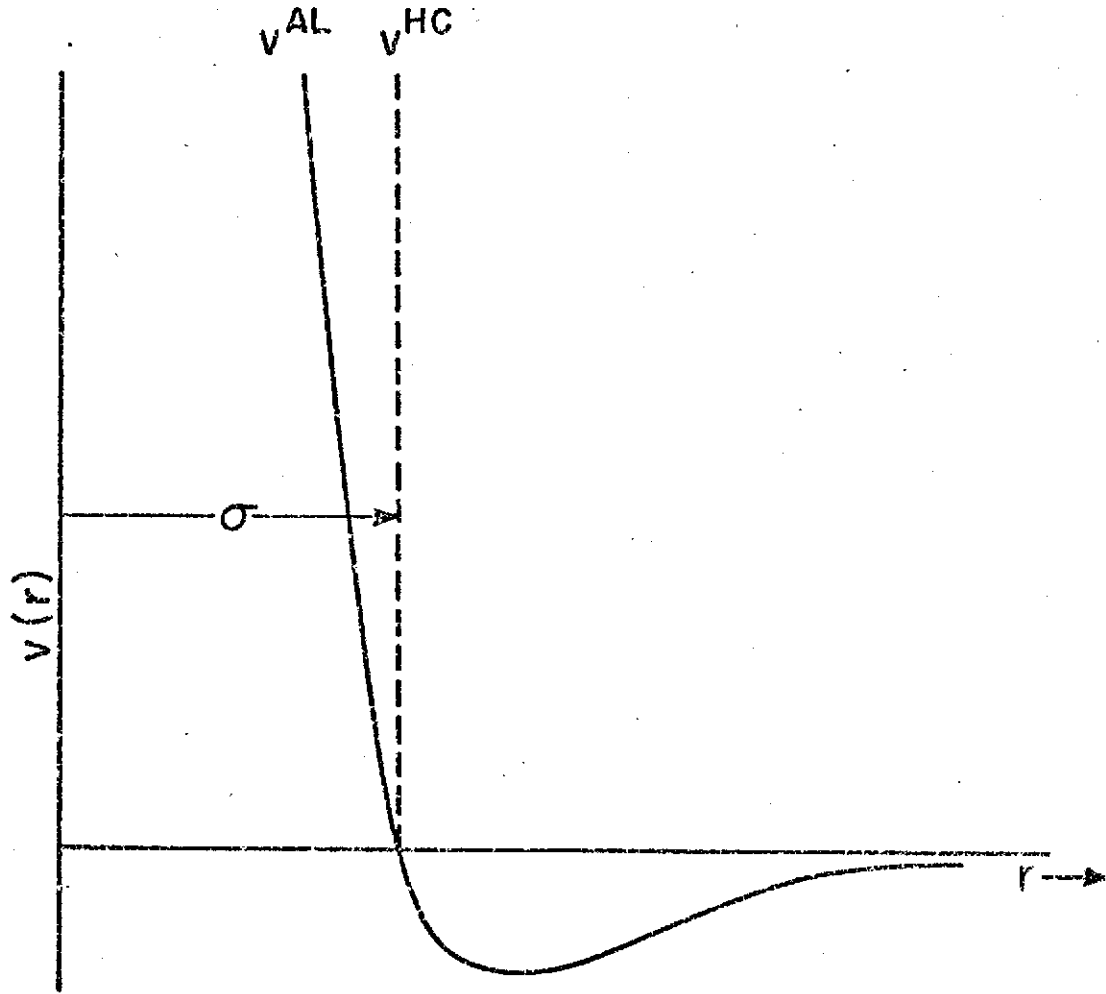


FIGURE 2

Schematic showing $v^{AL}(r)$ and v^{HC} . A hard core plus tail model of v^{AL} will be v^{HC} plus that part of v^{AL} which lies outside the core.

potential. In Fig. 2, we present a schematic showing a potential v^{AL} , and a hard core plus tail model of this potential.

Based on these considerations, the program set for this work was to develop a suitable perturbation approach to the hard core plus tail liquid, and then to perform calculations for real liquid metal systems by constructing hard core plus tail models of the potentials v^{AL} . In section II, we discuss the general nature of the perturbation problem in liquids, and then present and discuss the mean field theories which provided the motivation for our approach. In sections III and IV, we develop our approach to the problem, first through a set of general equations, and then through a study of approximate solutions to these equations. The best solutions appear at long wavelengths. In section V, we turn to the application of these results to liquid metallic systems. We perform calculations for both pure fluids and binary systems. This work ultimately encounters a fundamental difficulty in the use of the pair potential v^{AL} for calculations at long wavelength. We do not undertake to resolve this difficulty, but we do suggest that our calculations are perhaps best viewed as model calculations, which incorporate some, but not all, of the essential features of metallic systems. The calculated results are in accord with our physical expectations. Although a resistivity calculation is not presented, suggestions are made for the form of a calculation to test the hypotheses described above. Finally, in section VI, we review

and discuss what has been learned, and suggest further lines of work both for the perturbation theory itself and for its application to metallic systems.

II. General Discussion and Mean Field Theory

In this and the next two sections, we shall develop our approach to the perturbation theory of the hard core plus tail mixture. In recent years, a good deal of effort has been devoted to the perturbation theory of simple liquids. (For a recent review, see Barker and Henderson, 1972). Some of this work, dealing with the softness of the core, has already been mentioned. The major lines developed in this work have been directed, initially at least, at the calculation of thermodynamic and structural properties of Lennard-Jones fluids away from any critical points. In contrast, the thrust of our effort has been to develop an approach specifically designed for the problem of critical fluctuations in binary metallic liquid systems. The result has been that our work did not grow directly from any of the major lines of recent perturbation theory, but developed instead out of consideration of the simplest mean field theory of the hard core plus tail liquid. In this section, we shall first review briefly some of the main lines of liquid perturbation theory, for the insights they offer into the general nature of the problem, and then turn to a more detailed presentation and discussion of the mean field approach. In order not to clutter this section with the notation of mixtures, we shall make its general points in reference to pure fluids, except where explicitly noted.

II-A. General Discussion

We seek a perturbation theory which begins with a "reference" fluid described by a pair interaction v^{ref} , and considers the properties of a "real" fluid described by a pair interaction, v , of the form

$$v = v^{\text{ref}} + v^1. \quad (2-1)$$

The plan is to calculate the properties of such a fluid as an expansion in v^1 about the properties of the reference fluid. We shall ultimately select for the reference potential the hard core potential of eq. (1-10).

This program faces a major difficulty in principle, namely, that the ultimate reference system, the hard sphere liquid, is incompletely understood. The limits of our knowledge are best expressed in the language of the n -body distribution functions. (See Appendix A). Of these, only the one and two-body distribution functions are known with any accuracy for the hard sphere liquid. But straightforward expansions in v^1 of either the Helmholtz free energy (Zwanzig, 1954) or structure factors (Coopersmith and Brout, 1963; also Brout, 1965) of the "real" fluid lead rapidly to terms requiring higher distribution functions of the reference fluid. This difficulty is of crucial importance in determining the form ultimately taken by any of the perturbation theories, including our own.

This point is usually made in another way. Although the calculation of ρ_2^{ref} for the hard core liquid is a field in

itself, the fundamental assumption of all the perturbation theories, again including our own, is that ρ_2^{ref} is a known function.

The present activity in the perturbation theories of liquids begins with the work of Zwanzig (1954) who derived the expansion for the free energy of a fluid with the pair potential of the form (2-1). The expansion takes the form

$$F = F^{\text{ref}} + \frac{1}{2} \int d\underline{r} d\underline{r}' v^1(\underline{r}-\underline{r}') \rho_2^{\text{ref}}(\underline{r}, \underline{r}') + o(v^1)^2. \quad (2-2)$$

Here, F and F^{ref} are the free energies of the "real" and reference fluids respectively, and the other elements have already been defined. All higher terms in this series involve reference distribution functions of order higher than two. In early work (e.g. Smith and Alder, 1959), the series was truncated after the first order term so that only ρ_2^{ref} was required. Though we start from a different viewpoint, an expansion similar to (2-2) eventually plays an important role in our work.

In later work, Barker and Henderson (1967A) studied the second order term in (2-2). This term contains reference three and four-body distribution functions, ρ_3^{ref} and ρ_4^{ref} , which, for these purposes, are essentially inaccessible to present analytic and "machine experiment" techniques. Viewed in one way, the work of Barker and Henderson shows that these complicated functions actually contain more information than is needed to calculate the second order term. They cast the required information into a form which is reasonably

accessible to analytic approximation (1967A) and machine calculation (Barker and Henderson, 1972). The Barker-Henderson theory has found its chief application to the thermodynamic (and some structural) properties of Lennard-Jones fluids. (These are reviewed by Barker and Henderson, 1972.) Though the approach and application are very different from ours, there are ultimately some points of contact between the Barker-Henderson work and our own. These will be pointed out in the concluding discussions of section VI.

Turning from thermodynamics to consideration of the structure factors, we find that the direct expansion of $S(\underline{k})$ in powers of v^1 yields, even in first order, terms requiring hard sphere distribution functions of order greater than two. This expansion was presented by Brout and Coopersmith (1963), who attempted to surmount this difficulty by approximating the higher order distribution functions with a superposition of the functions ρ_2^{ref} . Since their work, it has been shown that this problem has a solution in principle, which can be obtained by beginning the perturbation theory not about the hard core fluid, but about the ideal gas, for which, of course, all distribution functions are known. The result is a series in the full potential v . (The development of this series is presented in several places. For presentation, discussion and references, see Rushbrooke (1968).) If the potential v is then split into v^{ref} and v^1 , partial summations can be performed which eliminate v^{ref} in favor of ρ_2^{ref} , yielding a series in which each term can be evaluated knowing

only ρ_2^{ref} and v^1 . This development forms the basis of recent work by Andersen and Chandler (1972), to which the reader is referred for discussion and references. Though we shall not have occasion to use this series explicitly, we have in fact studied it in some detail, and its existence and form have influenced this work at some points. These points will be mentioned as they appear. The Andersen-Chandler work itself has some relation to our own, and we shall have occasion to mention it later on.

As discussed at the outset, our work, despite its links to these various approaches, has developed primarily from consideration of the mean field theory of the hard core plus tail system, to which we now turn.

II-B. The Mean Field Theory

At the base of our work is the observation that the structure factor $S(\underline{k})$ bears a simple relation to the static density response function of the liquid. Consider a static external field $\phi(\underline{r})$ applied to a pure liquid of mean density ρ_0 . The liquid will respond to this field by assuming a configuration in which the local density, given by $\rho(\underline{r})$, will not in general be uniform. If the density response $\delta\rho(\underline{r}) = \rho(\underline{r}) - \rho_0$ is given in reciprocal space by

$$\delta\rho(\underline{k}) = \chi(\underline{k})\phi(\underline{k}) + o(\phi)^2, \quad (2-3)$$

then, for a classical system,

$$\chi(\underline{k}) = -\beta\rho_0 S(\underline{k}) . \quad (2-4)$$

(Here, $\beta = 1/k_B T$.) This result may be straightforwardly derived from the definition of $S(\underline{k})$ and the statistical definition of the density thermal average. The function $\chi(\underline{k})$ is the linear density response function of the liquid. Though the relation (2-4) is a simple proportionality, it is convenient to cast the development of this and the following two sections in terms of χ rather than S , for that development leans heavily on the linear response interpretation of S .

To display the mean field theories, and for later use in the formalism, it is useful to develop the following notation. We first give a name to the inverse of χ by defining

$$f(\underline{k}) = -\frac{1}{\chi(\underline{k})} . \quad (2-5)$$

The comparison of "real" and reference fluids then takes the following form. The "real" system, with potential v , is characterized by a response function $\chi(\underline{k})$, while the reference system, with potential v^{ref} , is characterized by the response function $\chi^{\text{ref}}(\underline{k})$. These functions in turn, through the form (2-5), define functions $f(\underline{k})$ and $f^{\text{ref}}(\underline{k})$. Then, with the natural definition

$$f^1(\underline{k}) = f(\underline{k}) - f^{\text{ref}}(\underline{k}) , \quad (2-6)$$

we can write

$$\chi(\underline{k}) = \frac{\chi^{\text{ref}}(\underline{k})}{1 - \chi^{\text{ref}}(\underline{k}) f^1(\underline{k})} . \quad (2-7)$$

If we substitute (2-7) into (2-3), the result can be written

$$\delta\rho(\underline{k}) = \chi^{\text{ref}}(\underline{k})\phi^{\text{eff}}(\underline{k}) + o(\phi)^2, \quad (2-8)$$

where, in real space, the "effective potential" ϕ^{eff} takes the form

$$\phi^{\text{eff}}(\underline{r}) = \phi(\underline{r}) + \int d\underline{r}' f^1(\underline{r}-\underline{r}')\delta\rho(\underline{r}'). \quad (2-9)$$

In words, these last equations cast the response of the real fluid as the response of the reference fluid to an effective potential which contains both the applied potential and the effects of the perturbing pair potential v^1 .

The simplest mean field approximation is to let the reference system be an ideal gas ($v^{\text{ref}} = 0$) and take for ϕ^{eff} the "Hartree" potential; i.e.*

$$\chi^{\text{ref}}(\underline{k}) = -\beta\rho_0. \quad (2-10)$$

and

$$\phi^{\text{eff}}(\underline{r}) = \phi(\underline{r}) + \int d\underline{r}' v(\underline{r}-\underline{r}')\delta\rho(\underline{r}'). \quad (2-11)$$

Then, clearly $f^1 = v$, and we have

$$\chi(\underline{k}) = \frac{-\beta\rho_0}{1 + \beta\rho_0 v(\underline{k})}. \quad (2-12)$$

These steps represent a classical realization of the familiar random phase approximation to the response of the quantum

*The result (2-10) can be calculated directly, but it also follows quickly, via eqs. (1-6) and (2-4), from the well known result that $g(\underline{r}) = 1$ for an ideal gas.

electron gas. Stroud (1973) has already used the generalization of this approach for a two component system to consider phase separation in binary liquid metal alloys.

It is our purpose to consider the case in which $v^{\text{ref}} = v^{\text{HC}}$. A natural approximation (in the spirit of (2-11)) would be to let ϕ^{eff} be a Hartree potential based only on v^1 :

$$\phi^{\text{eff}}(\underline{r}) = \phi(\underline{r}) + \int d\underline{r}' v^1(\underline{r}-\underline{r}') \delta\rho(\underline{r}') . \quad (2-13)$$

In this form, $f^1 = v^1$ and we have

$$\chi(\underline{k}) = \frac{\chi^{\text{HC}}(\underline{k})}{1 - \chi^{\text{HC}}(\underline{k})v^1(\underline{k})} . \quad (2-14)$$

Such a theory, however, suffers from a peculiar ambiguity. The problem is that, for $v^{\text{ref}} = v^{\text{HC}}$, the region $r < \sigma$ can never be sampled. Then the physics of the liquid must be independent of the form given to $v^1(\underline{r})$ for $r < \sigma$. This requirement is clearly not met by the form (2-14).

To perform, with any confidence, a modification of (2-14) which removes this difficulty, we must return to the beginning and develop a systematic theory. But that is not the purpose of this section. Our purpose here is to present the flavor of the mean field idea, and to describe some calculations which, by pointing out the faults and virtues of that idea, motivate the development of our formalism. For these purposes, the ambiguity of (2-14) is really only a technical point. We therefore proceed at this point simply by stating that if one considers the systematic perturbation series and the partial summation represented by (2-14), it is seen that a simple

modification, which represents a similar partial summation, is to write

$$\chi_{MF} = \frac{\chi^{HC}(\underline{k})}{1 - \chi^{HC}(\underline{k}) f_{MF}^1(\underline{k})}, \quad (2-15)$$

where

$$f_{MF}^1(r) = \begin{cases} 0 & r < \sigma \\ v^1(r) & r > \sigma \end{cases}. \quad (2-16)$$

In this form, the theory is independent of $v^1(r)$ for $r < \sigma$. As indicated in the notation, we shall refer to this as the mean field theory of the hard core plus tail liquid.

II-C. Discussion of the Mean Field Theory

Mean field theories represent a common first approach to the physics of a phase transition. In this problem as well, the mean field theory achieves a measure of success. In a calculation best detailed in section V, we applied the mean field approach to the Li-Na binary system. The program was to model the Li-Na system with a hard core plus tail mixture, and apply the generalization of (2-15) and (2-16) for this case. We sought to identify the locus in the x-T plane of points at which the mean field partial structure factors diverge as k approaches 0. Within a crude but reasonable model, the line of singularities can readily be calculated. The result is a curve which, in shape, symmetry, and position in the plane, strongly suggests the experimental Li-Na phase boundary. (See Fig. 3.)

Despite this success, the mean field theory suffers from

a serious inadequacy when applied to such dense systems. The nature of the difficulty can be illustrated by considering an extreme case and then observing parallels between this case and the case of the dense fluid. Suppose we let the density increase until the hard core reference "fluid" forms a rigorously close packed lattice. Then the subsequent addition of any tail potential v^1 will clearly have no effect on the structure, because the particles are unable to move in response to that potential. For any v^1 , we have in this limit $\chi = \chi^{HC}$. Now, the structure factor and hence χ^{HC} of a close packed lattice of hard spheres is a series of δ -function spikes. The formula (2-15) is thus clearly inadequate. The origin of the difficulty is that the mean field formulation treats the response of each particle to the fields of the other particles as if those fields were part of the applied external field. In fact, the accessible responses to the two types of field are very different. In this limit of close packing, the particles will execute a strong collective response to an external field with the periodicity of the lattice (this is the meaning of the spikes in χ), but can execute no relative motion, and hence no response to fields fixed to the particles themselves.

The essential features of this situation survive, in muted form, when we allow the density to relax to liquid densities. The particles can now execute some relative motion, but the motion is nevertheless severely limited by the hard core packing. In this sense, the success of the hard

sphere model at these densities (and away from critical points) is a reflection of the rigorous close packing result $\chi = \chi^{HC}$. In reflection of another close packing result, the hard core structure factors at these densities are characterized by strong (but now finite) peaks, indicating strong collective responses to applied fields of certain wavelengths. Thus, when the effect of a tail potential is examined in the mean field theory, this theory erroneously predicts a large effect at the wavelengths of the hard sphere peaks. We observed this failure in a calculation of a hard core plus tail model of pure liquid liquid Na. For a model appropriate to temperatures just above solidification, the mean field theory failed catastrophically at the first peak. This failure completely destroyed the excellent agreement in this region between the structure of the simple hard core model and the experimental structure factor of Na. This calculation is reported in section V.*

*An approach which appears to surmount this difficulty is the "optimized random phase approximation" of Chandler et al (1972) (see also Andersen and Chandler (1972)). This work replaces the mean field formulation (2-16) with the two equations

$$f^1(r) = v^1(r) \quad \text{for } r > \sigma ,$$

and

$$g(r) = 0 \quad \text{for } r < \sigma$$

leaving $f^1(r)$ for $r < \sigma$ to be determined. Here, $g(r)$ is the radial distribution function, defined in (1-6), for the "real" fluid, so that the second equation represents an exact result for a hard core plus tail fluid. These equations turn out to be sufficient to determine $f^1(r)$ for all r , and hence χ and $S(k)$. The resulting structure factors (for a hard core plus tail model appropriate to a Lennard-Jones fluid) show quite reasonable behavior in the neighborhood of the first hard

Based on these considerations, an important thrust of our work was to discover how to treat these collective or "correlation" effects. Keeping in mind the limit of close packing, we sought a theory which would be adequate in this limit, and thus deal at least with reference system correlations.

Though the mean field theory suffers from this difficulty, its success with the line of singularities at $k = 0$ has been an important influence on our work. First of all, it tends to support our hypothesis that the hard core plus tail potential contains the essential physics of phase separation. In fact, during the development effort, our faith in this hypothesis rested in large measure on a crude form of this calculation.

A second influence is more important, and also more subtle. The point concerns the relation (2-7) between χ , χ^{ref} , and f^1 . This relation is, of course, just definition, and yet it represents a rearrangement of the perturbation series in the sense that χ contains terms of all orders in f^1 . Thus, the mean field theory may be viewed equivalently either as an (incomplete) low order approximation to f^1 or as a selection of terms of all orders in the series for χ . Viewed in the light of this observation, the success of the mean field theory in locating the phase boundary suggests that, in

(continued from previous page) sphere peak. The first formula, however, is quite arbitrary at this stage, and, as it represents a severe restriction on the form of f^1 , considerable justification is required before the results can be understood. The systematic viewpoint and exact results developed in this thesis might possibly shed some light on its meaning.

some sense, whatever physics attaches to the function f^1 may be more simply related to the phase transition than the physics attached to χ . Such considerations have implicitly motivated the shape of our effort, which is to study the physics of f^1 , and ultimately to seek a theory of phase separation by completing the low order approximation to f^1 .

Our search into the physics of f^1 began with consideration of its role in the effective potential formulation defined by (2-8) and (2-9). By these definitions, the real fluid response to the applied field is cast as the reference system response to an effective field in which f^1 plays a central role. We might ask, what is the correct effective potential? As it turns out, this question has been asked before, in the study of the dielectric response of the quantum electron gas. There, the reference system is a non-interacting Fermi gas, and the effective potential is usually formulated as

$$\phi^{\text{eff}} = \phi + \phi_H + \phi_{\text{ex}} + \phi_{\text{corr}}. \quad (2-17)$$

where ϕ_H is the Hartree potential of (2-11), and ϕ_{ex} and ϕ_{corr} are corrections for exchange and correlation. (See, for example, Ballentine (1967).) A study of this work led us to study the work of Hohenberg and Kohn (1964) and Kohn and Sham (1965), who, considering the non-uniform electron gas, presented a formally exact prescription for the potentials ϕ_{ex} and ϕ_{corr} . Elements of their work, transcribed to the case

of a hard core plus tail mixture, form the basis of our work.
We now turn to the development of our approach.

III. The Formal Development

III-A. The Basic Equations

In this subsection, we use the statistical mechanics of a classical fluid in the presence of external fields to derive the basic equations of our work. Because we shall need the generalization to binary alloys, we shall work from the outset with a multi-component mixture.

We consider an m-component mixture containing N_i particles of type i, for $i = 1, 2, \dots, m$. We shall evaluate thermal averages in a canonical ensemble at constant temperature T, volume V, and particle numbers N_i . We consider the mixture in the presence of a set of external fields. The configurational free energy of the mixture may be written

$$F_{\phi}^U = -\frac{1}{\beta} \ln \frac{1}{N_1! N_2! \dots N_m!} \int dR e^{-\beta U(R)} e^{-\beta \phi(R)}, \quad (3-1)$$

where the integral over dR is over all co-ordinates of the particles, $U(R)$ denotes the potential energy of interaction among the particles, and $\phi(R)$ represents the energy of interaction between the particles and the external fields. We shall ultimately take $U(R)$ to be a sum over pair potentials, though, for now, it can remain unspecified. For $\phi(R)$, we intend from the outset a sum over single particle potentials. That is,

$$\phi(R) = \sum_i \sum_{\ell=1}^{N_i} \phi_i(\underline{r}_{\ell}^i), \quad (3-2)$$

where ϕ_i is a field which couples only to the particles of

type i , and \underline{r}_ℓ^i denotes the position of the ℓ^{th} particle of type i . We shall ultimately consider the effects of varying both U and ϕ , and have thus included their specification, as super- and subscripts, in our notation for the free energy.

We are interested in the linear response of the densities of this system to the external fields. The necessary terminology is defined in generalization of that describing single component fluids. We denote the local thermal average density of particles of type i by $\rho_i(\underline{r})$. In the absence of any external fields, this density will be uniform, taking everywhere the value $\rho_i^0 = N_i/V$. When the external fields ϕ are applied, the density need not be uniform. We denote the density in the presence of the fields by $\rho_i^\phi(\underline{r})$, and define the density response by

$$\delta\rho_i^\phi(\underline{r}) = \rho_i^\phi(\underline{r}) - \rho_i^0 . \quad (3-3)$$

The most general linear relation between the $\delta\rho_i^\phi$ and the ϕ_i is of the form

$$\delta\rho_i^\phi(\underline{k}) = \sum_j \chi_{ij}(\underline{k}) \phi_j(\underline{k}) + o(\phi)^2 . \quad (3-4)$$

This relation defines the linear response functions χ_{ij} of the mixture. A calculation analogous to that giving (2-4) yields

$$\chi_{ij}(\underline{k}) = -\beta\sqrt{\rho_i^0\rho_j^0} S_{ij}(\underline{k}) , \quad (3-5)$$

where the S_{ij} are the partial structure factors of (1-2).

The following development parallels the work of Hohenberg and Kohn (1964) and Kohn and Sham (1965), as generalized to

finite temperatures by Mermin (1965). As the argument is somewhat involved, it may be useful to give an overview before beginning in earnest. The physical point which provides the basis for the work concerns the relations between the densities $\rho_i(\underline{r})$, the external fields $\phi_i(\underline{r})$, and the free energy F_ϕ^U . We shall throughout the first part of the argument consider $U(R)$ to be specified. Then it is clear that the potentials ϕ_i are sufficient to determine the $\rho_i(\underline{r})$ and F_ϕ^U . This fact has been indicated above by placing the superscript ϕ on ρ_i . Suppose instead we specify the densities $\rho_i(\underline{r})$, and denote by ϕ^ρ a set of external fields which gives rise to these $\rho_i(\underline{r})$. The important question is, to what extent are ϕ^ρ and hence $F_{\phi^\rho}^U$ determined by the ρ_i ? The answer can be obtained from a variational principle and is, not surprisingly, that ϕ^ρ is determined to within constant terms, and hence, by (3-1), $F_{\phi^\rho}^U$ is also determined within constant terms. We can show further, however, that even the constants cancel from the combination

$$G(\rho, U) = F_{\phi^\rho}^U - \sum_i \int d\underline{r} \phi^\rho(\underline{r}) \rho_i(\underline{r}) , \quad (3-6)$$

so that, as indicated in the notation, G is uniquely determined by the densities $\rho_i(\underline{r})$ (assuming, as stated above, that $U(R)$ has been previously specified.) Then for given U , the function $G(\rho, U)$ may be expanded (formally at least) in a functional Taylor series about some specified density functions $\rho_i(\underline{r})$. If the expansion is carried out about the particular set ρ_i° defined above, the coefficients of the

second order terms turn out to be just generalizations of the functions f introduced for pure fluids in section II. By writing $G(\rho, U)$ for real and reference fluids, we thus generate equations for the functions which are generalizations of f^1 . These form the "basic equations" promised in the title of this subsection.

We shall, in this argument, consider at some points that the densities $\rho_i(\underline{r})$ are the starting point, so that we consider ρ_i and ϕ^0 , and at other points that the potentials ϕ_i are the starting point so that we consider ϕ , and ρ_i^ϕ . We shall endeavor to be clear, both in context and notation, which view we adopt at each point. At the outset, until we prove the uniqueness theorem, we must consider that we start with the potentials ϕ_i .

The argument begins with a variational principle. Consider the functional of $P(R)$, $U(R)$, and $\phi(R)$ defined by

$$\begin{aligned} \Omega(P, U, \phi) = \int dR P(R) \{ U(R) + \phi(R) + \frac{1}{\beta} \ln P(R) \\ + \frac{1}{\beta} \sum_i \ln(N_i!) \} , \end{aligned} \quad (3-7)$$

where U and ϕ are defined above, and $P(R)$ is some distribution function satisfying

$$\int dR P(R) = 1 . \quad (3-8)$$

If we select for P the particular function P^ϕ defined by

$$P^\phi(R) = e^{-\beta U(R)} e^{-\beta \phi(R)} / \left(\int dR e^{-\beta U(R)} e^{-\beta \phi(R)} \right) , \quad (3-9)$$

the functional Ω reduces to the free energy of (3-1):

$$\Omega(P^\phi, U, \phi) = F_\phi^U. \quad (3-10)$$

A straightforward adaptation to a canonical ensemble of a grand canonical argument by Mermin (1965) yields the minimum principle

$$\Omega(P, U, \phi) > \Omega(P^\phi, U, \phi), \quad (3-11)$$

for any $P \neq P^\phi$ which satisfies (3-8).

In using this minimum principle, we will limit our consideration to the set of P 's which may be generated by evaluating (3-9) for all possible fields ϕ . Since the special function P^ϕ of the minimum principle is a member of this restricted set, the minimum principle will still apply within this restricted set.

We can now prove the necessary uniqueness theorem. Consider two external fields ϕ and ϕ' of the form (3-2), with single particle potentials $\phi_i(\underline{r})$ and $\phi'_i(\underline{r})$ respectively. The uniqueness theorem asserts that if $\rho_i^\phi(\underline{r}) = \rho_i^{\phi'}(\underline{r})$ for all i , then for each i , $\phi_i(\underline{r}) - \phi'_i(\underline{r})$ is a constant independent of \underline{r} . To prove this, we suppose the opposite and deduce an absurdity. We suppose that $\rho_i^\phi(\underline{r}) = \rho_i^{\phi'}(\underline{r})$ for all i , and that there exists at least one i for which $\phi_i(\underline{r}) - \phi'_i(\underline{r})$ is not just a constant. The potentials ϕ and ϕ' will define, through (3-9) and (3-1), distribution functions P^ϕ and $P^{\phi'}$ and free energies F_ϕ^U and $F_{\phi'}^U$. Under the hypothesis that $\phi_i(\underline{r}) - \phi'_i(\underline{r})$ is not just a constant for at least one i , we have $P^\phi \neq P^{\phi'}$,

so that the minimum principle applies. In particular

$$F_{\phi'}^U = \Omega(P^{\phi'}, U, \phi') \tag{3-12}$$

$$< \Omega(P^{\phi}, U, \phi') = \Omega(P^{\phi}, U, \phi) + \int dR P(R) \{ \phi'(R) - \phi(R) \}$$

or

$$F_{\phi'}^U < F_{\phi}^U + \sum_i \int d\underline{r} \rho_i^{\phi}(\underline{r}) \{ \phi'_i(\underline{r}) - \phi_i(\underline{r}) \} , \tag{3-13}$$

where, for the last step, we make use of (3-2) and the statistical definition of $\rho_i(\underline{r})$ given in appendix A. Now the argument to (3-13) can be repeated with primed and unprimed interchanged, yielding

$$F_{\phi}^U < F_{\phi'}^U + \sum_i \int d\underline{r} \rho_i^{\phi'}(\underline{r}) \{ \phi_i(\underline{r}) - \phi'_i(\underline{r}) \} . \tag{3-14}$$

If we now suppose that $\rho_i^{\phi}(\underline{r}) = \rho_i^{\phi'}(\underline{r})$ for all i , addition of (3-13) and (3-14) yields immediately $0 < 0$. This proves the uniqueness theorem.

With this theorem, we can now consider the meaning of taking the $\rho_i(\underline{r})$ as our starting point. We take these to be any densities which may be induced in the system by some external fields ϕ . If we denote by ϕ^{ρ} any potentials which give rise to these densities, the uniqueness theorem asserts that ϕ^{ρ} is determined within constants. If we then proceed to form a distribution function P^{ρ} by inserting one of the potentials ϕ^{ρ} into (3-9), we see that the undetermined constants in ϕ^{ρ} cancel, so that the distribution function P^{ρ} is determined uniquely by the $\rho_i(\underline{r})$. Then, by inserting P^{ρ} into

(3-7), we may define a unique functional of ρ , ϕ , and U , denoted by $F(\rho, \phi, U)$, as

$$F(\rho, \phi, U) \equiv \Omega(P^\rho, \phi, U) \quad (3-15)$$

$$= \int dR P^\rho(R) \{U(R) + \phi(R) + \frac{1}{\beta} \ln P^\rho(R) + \frac{1}{\beta} \sum_i \ln(N_i!)\}.$$

In terms of this functional, (3-10) implies

$$F(\rho, \phi^\rho, U) = F_{\phi^\rho}^U, \quad (3-16)$$

and (3-11) implies

$$F(\rho', \phi^\rho, U) > F(\rho, \phi^\rho, U) \quad \text{for } \rho \neq \rho'. \quad (3-17)$$

Finally, since P^ρ is a unique functional of the $\rho_i(\underline{r})$, (3-15) may be written

$$F(\rho, \phi, U) = \sum_i \int d\underline{r} \phi_i(\underline{r}) \rho_i(\underline{r}) + G(\rho, U) \quad (3-18)$$

where

$$G(\rho, U) = \int dR P^\rho(R) \{U(R) + \frac{1}{\beta} \ln P^\rho(R) + \frac{1}{\beta} \sum_i \ln(N_i!)\} \quad (3-19)$$

is a unique functional of U and the densities $\rho_i(\underline{r})$. This is the function G introduced in equation (3-6), as can be seen by setting $\phi = \phi^\rho$ in (3-18), and using (3-16).

As we described after (3-6), since $G(\rho, U)$ is a unique functional of ρ , we are at liberty to write a formal expansion of $G(\rho, U)$ about its value in the uniform system, specified by

the densities ρ_i° . We proceed as follows. Consider that for $\phi = 0$, (3-18) reads

$$F(\rho, 0, U) = G(\rho, U) . \quad (3-20)$$

Further, since the ρ_i° are the densities appropriate to $\phi = 0$, (3-17) yields

$$F(\rho, 0, U) > F(\rho^\circ, 0, U) \quad \text{for } \rho \neq \rho^\circ , \quad (3-21)$$

where ρ° denotes the set of densities ρ_i° . From (3-20) and (3-21), we see that $G(\rho, U)$ satisfies

$$G(\rho, U) > G(\rho^\circ, U) \quad \text{for } \rho \neq \rho^\circ . \quad (3-22)$$

G thus has a stationary point at ρ_i° , and an expansion about this point must be of the form*

$$\begin{aligned} G(\rho, U) = & G(\rho^\circ, U) \\ & + \frac{1}{2} \sum_{ij} \int d\underline{r} \, d\underline{r}' \, \delta\rho_i(\underline{r}) \delta\rho_j(\underline{r}') f_{ij}(\underline{r}-\underline{r}') \\ & + o(\delta\rho)^3 . \end{aligned} \quad (3-23)$$

*We note that the relationship between $G(\rho, U)$ and f_{ij} is not unique. In the canonical ensemble from which we have derived these results, the particle numbers N_i are fixed, so that for any allowable $\rho_i(\underline{r})$ (which can be obtained by the application of an external field), we must have

$$\int d\underline{r} \, \delta\rho_i(\underline{r}) = 0 .$$

Then on the right side of (3-23), the addition of any constant term to the f_{ij} will not change the value of the integral. This difficulty is not important, however, because the physics of our problem is not contained in the results of setting \underline{k} rigorously equal to zero (since these results are ensemble dependent), but only in the results in the limit as \underline{k} approaches zero. As the development proceeds, we shall thus

It is the functions f_{ij} which play the central role in our work. For the case $m = 1$, the single function f reduces to the function f defined in section II. To see this, and make use of these functions, we consider now how they relate to the response functions χ_{ij} . We use (3-23) and the definition of the response functions to generate an expansion of F_{ϕ}^U in powers of the ϕ_i , and compare with the result of a direct expansion of (3-1).

From (3-18) and (3-16), we have

$$F_{\phi\rho}^U = G(\rho, U) + \sum_i \int d\underline{r} \phi_i^\rho(\underline{r}) \rho_i(\underline{r}) . \quad (3-24)$$

If we insert the expansion (3-23) of $G(\rho, U)$ and make use of

$$G(\rho^0, U) = F_{\phi=0}^U , \quad (3-25)$$

which follows from (3-20) and (3-16), we find

$$\begin{aligned} F_{\phi\rho}^U = F_{\phi=0}^U + \sum_i \phi_i^\rho(0) \rho_i^0 + \sum_i \frac{1}{V} \sum_{\underline{k}} \phi_i^\rho(-\underline{k}) \delta\rho_i(\underline{k}) \\ + \sum_{\ell m} \frac{1}{2V} \sum_{\underline{k}} \delta\rho_\ell(\underline{k}) \delta\rho_m(-\underline{k}) f_{\ell m}(\underline{k}) + o(\delta\rho)^3 . \end{aligned} \quad (3-26)$$

Here, we have rewritten the integrals from (3-24) and (3-23) as sums in reciprocal space. ($\phi_i^\rho(0)$ denotes the zeroeth Fourier coefficient of $\phi_i^\rho(\underline{r})$.) We can now pass from an expansion in $\delta\rho_i(\underline{r})$ to an expansion in the ϕ_i by expanding $\delta\rho_i$ in (3-26) in powers of ϕ_i using (3-4). This yields

(continued from previous page) ignore further difficulties of this nature. This policy will result in several equations to which, for precision, one should add the words "plus terms independent of \underline{r} ."

$$\begin{aligned}
 F_{\phi}^U &= F_{\phi=0}^U + \sum_{\underline{i}} \phi_{\underline{i}}(0) \rho_{\underline{i}}^{\circ} \\
 &+ \sum_{\underline{i} \underline{j}} \frac{1}{V} \sum_{\underline{k}} \phi_{\underline{i}}(\underline{k}) \phi_{\underline{j}}(-\underline{k}) \{ \chi_{\underline{i} \underline{j}}(\underline{k}) + \frac{1}{2} \sum_{\underline{\ell} \underline{m}} f_{\underline{\ell} \underline{m}}(\underline{k}) \chi_{\underline{\ell} \underline{i}}(\underline{k}) \chi_{\underline{m} \underline{j}}(-\underline{k}) \} \\
 &+ o(\phi)^3 .
 \end{aligned} \tag{3-27}$$

Since the functions $\rho_{\underline{i}}(\underline{r})$ have now disappeared from the formulas, we have dropped the superscripts ρ . The expansion is now an expansion of F_{ϕ}^U in powers of the $\phi_{\underline{i}}$.

But the expansion in powers of the $\phi_{\underline{i}}$ may be generated without going through the $\delta\rho_{\underline{i}}$ expansion and hence without introducing the functions $f_{\underline{i} \underline{j}}$. We simply replace the potential ϕ in (3-1) by $\lambda\phi$ and expand in powers of λ .

$$\begin{aligned}
 \frac{\partial F_{\lambda\phi}^U}{\partial \lambda} &= \frac{\int dR \phi(R) e^{-\beta U(R)} e^{-\beta \lambda \phi(R)}}{\int dR e^{-\beta U(R)} e^{-\beta \lambda \phi(R)}} \\
 &= \sum_{\underline{i}} \int d\underline{r} \phi_{\underline{i}}(\underline{r}) \rho_{\underline{i}}^{\lambda\phi}(\underline{r}) ,
 \end{aligned} \tag{3-28}$$

where the single particle densities have been introduced just as in passing from (3-12) to (3-13). For the second derivative, we formally differentiate the right side of (3-28) and make use of the linear response form (3-4):

$$\begin{aligned}
 \frac{\partial^2 F_{\lambda\phi}^U}{\partial \lambda^2} &= \sum_{\underline{i}} \frac{1}{V} \sum_{\underline{k}} \phi_{\underline{i}}(-\underline{k}) \frac{\partial}{\partial \lambda} \rho_{\underline{i}}^{\lambda\phi}(\underline{k}) \\
 &= \sum_{\underline{i} \underline{j}} \frac{1}{V} \sum_{\underline{k}} \phi_{\underline{i}}(-\underline{k}) \phi_{\underline{j}}(\underline{k}) \chi_{\underline{i} \underline{j}}(\underline{k}) + o(\lambda) .
 \end{aligned} \tag{3-29}$$

Then writing a Taylor series for $F_{\lambda\phi}^U$ about $\lambda = 0$, and setting $\lambda = 1$, we have

$$F_{\phi}^U = F_{\phi=0}^U + \sum_i \phi_i(0) \rho_i^0 + \frac{1}{2} \sum_{ij} \frac{1}{V} \sum_{\underline{k}} \phi_i(-\underline{k}) \phi_j(\underline{k}) \chi_{ij}(\underline{k}) + o(\lambda)^3. \quad (3-30)$$

We are now in a position to identify the f_{ij} . Compare the result (3-30) to (3-27), using the facts that these expressions must be identical for all potentials ϕ , and that both χ_{ij} and f_{ij} are symmetric in \underline{k} .* We must have

$$\sum_{\underline{lm}} f_{\underline{lm}}(\underline{k}) \chi_{\underline{li}}(\underline{k}) \chi_{\underline{mj}}(\underline{k}) = -\chi_{ij}(\underline{k}) \quad \text{for all } i, j. \quad (3-31)$$

The structure of (3-31) is made clear if we define the matrices F , with elements f_{ij} , and X , with elements χ_{ij} . Noting from the definition (1-2) of $S_{ij}(\underline{k})$ that $\chi_{ij} = \chi_{ji}$, we see that (3-31) reads simply

$$X F X = -X \quad (3-32)$$

so that[†]

$$F = -X^{-1}. \quad (3-33)$$

*For χ_{ij} , this symmetry is well known. For the f_{ij} , it follows because the $f_{ij}(\underline{r}-\underline{r}')$ defined by (3-23) depend only on properties of the uniform fluid, hence only on $|\underline{r}-\underline{r}'|$.

†We note here another difficulty at $k = 0$. For (3-33) to hold, the matrix X must have an inverse. But the condition $\delta\rho_i(k=0) = 0$, which holds for this canonical ensemble, together with (3-4), implies that $\chi_{ij}(k=0) = 0$, so that X^{-1} is undefined for $k = 0$. It is, however, defined for all other \underline{k} , and hence in the physically interesting limit as $k \rightarrow 0$.

For a single component fluid, (3-33) reduces to (2-5), and we see that we have recovered the function f whose physics we set out to investigate. From (3-33), the generalization to a two-component fluid is immediate:

$$\begin{aligned} \chi_{11} &= \frac{-f_{22}}{f_{11}f_{22}-(f_{12})^2} ; \quad \chi_{22} = \frac{-f_{11}}{f_{11}f_{22}-(f_{12})^2} \\ \chi_{12} &= \frac{f_{12}}{f_{11}f_{22}-(f_{12})^2} \end{aligned} \tag{3-34}$$

Here, we have noted that since $\chi_{ij} = \chi_{ji}$, (3-33) implies that F is also a symmetric matrix.

We note that the functions f_{ij} bear simple relations to the familiar direct correlation functions c_{ij} of Ornstein and Zernike (1914). Comparing (2-5) and (3-34) to the expressions in Ashcroft-Lekner and AL-II, we find

$$f(\underline{k}) = \frac{1}{\beta\rho_0} \{1 - \rho_0 c(\underline{k})\}$$

and (3-35)

$$f_{11} = \frac{1}{\beta\rho_1^0} (1 - \rho_1^0 c_{11}) ; \quad f_{22} = \frac{1}{\beta\rho_2^0} (1 - \rho_2^0 c_{22}) ; \quad f_{12} = \frac{1}{\beta} c_{12} .$$

This completes the formal development for a general system. The key results of this work have been somewhat scattered by the development. They are equations (3-6) and (3-23), which define $G(\rho, U)$ and its expansion and thus define the problem to be solved for the f_{ij} , and equation (3-33), relating f_{ij} to the χ_{ij} . The argument to this point essentially represents a realization for a classical fluid of the

case of "almost constant density" studied for the quantum electron gas by Hohenberg and Kohn (1964).

In our problem, we wish to compare the real liquid to some reference liquid, specifically to the hard sphere liquid. Dividing the pair potential v into $v^{\text{ref}} + v^1$ separates U into $U^{\text{ref}} + U^1$. Then consider $G(\rho, U^{\text{ref}})$, which by (3-6), is given by

$$G(\rho, U^{\text{ref}}) = F_{\phi^{\rho, \text{ref}}}^{U^{\text{ref}}} - \sum_i \int d\underline{r} \phi_i^{\rho, \text{ref}}(\underline{r}) \rho_i(\underline{r}) . \quad (3-36)$$

Here, we have explicitly noted that since ϕ^{ρ} must be a potential which gives rise to the densities $\rho_i(\underline{r})$, it will in general be a different function in the reference and real fluids. This function $G(\rho, U^{\text{ref}})$ will have an expansion of the form (3-23) with f_{ij} replaced by f_{ij}^{ref} , where the f_{ij}^{ref} are in turn related through (3-33) to the χ_{ij}^{ref} . Defining

$$\begin{aligned} G_1(\rho) &\equiv G(\rho, U) - G(\rho, U^{\text{ref}}) \\ &= F_{\phi^{\rho}}^U - F_{\phi^{\rho, \text{ref}}}^{U^{\text{ref}}} - \sum_i \int d\underline{r} \rho_i(\underline{r}) \{ \phi_i^{\rho}(\underline{r}) - \phi_i^{\rho, \text{ref}}(\underline{r}) \} , \end{aligned} \quad (3-37)$$

and

$$f_{ij}^1 \equiv f_{ij} - f_{ij}^{\text{ref}} \quad (3-38)$$

it is clear that $G_1(\rho)$ has the expansion

$$\begin{aligned} G_1(\rho) &= G_1(\rho^{\circ}) + \frac{1}{2} \sum_{ij} \int d\underline{r} d\underline{r}' \delta \rho_i(\underline{r}) \delta \rho_j(\underline{r}') f_{ij}^1(\underline{r}-\underline{r}') \\ &+ o(\delta \rho)^3 \end{aligned} \quad (3-39)$$

Equations (3-37) and (3-39) define the problem to be solved for the f_{ij}^1 . We note that the relation between f^1 and χ has already been given for a single component fluid (eq. (2-7)).

For the two-component fluid, we find from (3-34)

$$\chi_{11} = \frac{\chi_{11}^{\text{ref}}}{D} \{1 + (f_{22}^1/f_{22}^{\text{ref}})\} ; \chi_{22} = \frac{\chi_{22}^{\text{ref}}}{D} \{1 + (f_{11}^1/f_{11}^{\text{ref}})\} ;$$

$$\chi_{12} = \frac{\chi_{12}^{\text{ref}}}{D} \{1 + (f_{12}^1/f_{12}^{\text{ref}})\} .$$

where

$$D = 1 - \chi_{11}^{\text{ref}} f_{11}^1 - \chi_{22}^{\text{ref}} f_{22}^1 - 2 \chi_{12}^{\text{ref}} f_{12}^1$$

$$+ \{ \chi_{11}^{\text{ref}} \chi_{22}^{\text{ref}} - (\chi_{12}^{\text{ref}})^2 \} \{ f_{11}^1 f_{22}^1 - (f_{12}^1)^2 \} .$$

Note that in χ_{11} , any zeroes of f_{22}^{ref} will be cancelled by the χ_{11}^{ref} (from (3-34)), and that similar results hold for the other functions. Then the search for singularities of the χ 's is the search for the zeroes of D.

This completes the development of the basic equations of our perturbation theory. The basic equations are (3-37) and (3-39), which define the problem to be solved for the f_{ij}^1 , and the relation (3-33) with its realizations (2-5), (3-34), (2-7) and (3-40), (3-41), relating the f's and the χ 's.

III-B. Analysis of the Basic Equations

In this section, we study the role played by the functions f_{ij}^1 in (3-37) and (3-39), in order eventually to suggest

suitable approximations. Because we shall seek forms for $G_1(\rho)$, we shall throughout this section consider that the $\rho_i(\underline{r})$ are given.

We must specify the form of $U(R)$. It is to be a sum over pair potentials:

$$U(R) = \frac{1}{2} \sum_{ij} \sum_{\ell \neq m} v_{ij}(\underline{r}_\ell^i - \underline{r}_m^j), \quad (3-42)$$

where v_{ij} is the pair potential acting between a particle of type i and a particle of type j , and \underline{r}_ℓ^i was defined below (3-2). We note the symmetry $v_{ij} = v_{ji}$. We note that the restriction $\ell \neq m$ is harmless but unnecessary in those terms in which $i \neq j$.

We shall specialize for a time to the case of a single component fluid.

The structure of our equations takes its simplest form in the limit as $T \rightarrow 0$. It is thus instructive to examine this limit as an idealization, even though no classical fluid exists at $T = 0$. In this limit, the entropy term in the free energy vanishes, leaving only the energy terms $\langle U \rangle$ and $\langle \Phi \rangle$, where, as in section I, $\langle \rangle$ denotes a thermal average. As described in appendix A, to evaluate $\langle U \rangle$, we must introduce the two body distribution function $\rho_2(\underline{r}, \underline{r}')$ defined above (1-7), while we can evaluate $\langle \Phi \rangle$ in terms of the single particle densities $\rho_i(\underline{r})$. With these considerations, we may write

$$F_{\phi}^U = \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \rho_2^0(\underline{r}, \underline{r}') + \int d\underline{r} \phi^0(\underline{r}) \rho(\underline{r}) \quad (3-43)$$

+ terms which vanish as $T \rightarrow 0$,

where $F_{\phi^{\rho}}^U$ denotes, just as in the last section, that free energy determined within a constant by $\rho(\underline{r})$. The particular distribution function $\rho_2^{\circ}(\underline{r}, \underline{r}')$ is thus to be calculated from $P^{\circ}(R)$ and is uniquely determined by $\rho(\underline{r})$. For the reference fluid, we have similarly

$$F_{\phi^{\rho}, \text{ref}}^{U, \text{ref}} = \frac{1}{2} \int d\underline{r} d\underline{r}' v^{\text{ref}}(\underline{r}-\underline{r}') \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') + \int d\underline{r} \rho(\underline{r}) \phi^{\rho, \text{ref}}(\underline{r}) \quad (3-44)$$

+ terms which vanish as $T \rightarrow 0$.

We have explicitly noted that the two body distributions determined by $\rho(\underline{r})$ are in general different for reference and real fluids.

From (3-43) and (3-44), we can form $G_1(\rho)$ of (3-37). We find

$$G_1(\rho) = \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \rho_2^{\circ}(\underline{r}, \underline{r}') - \frac{1}{2} \int d\underline{r} d\underline{r}' v^{\text{ref}}(\underline{r}-\underline{r}') \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \quad (3-45)$$

+ terms which vanish as $T \rightarrow 0$.

To accomplish the expansion (3-39), we let $\rho_2^{\circ}(\underline{r}, \underline{r}')$ and $\rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}')$ denote respectively the distribution functions determined for the real and reference fluids by the uniform density $\rho = \rho_0$. Then, by (3-45),

$$G_1(\rho) = G_1(\rho_0) + \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \{ \rho_2^{\circ}(\underline{r}, \underline{r}') - \rho_2^{\circ}(\underline{r}, \underline{r}') \} - \frac{1}{2} \int d\underline{r} d\underline{r}' v^{\text{ref}}(\underline{r}-\underline{r}') \{ \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \}$$

+ terms which vanish as $T \rightarrow 0$. (3-46)

Comparison with (3-39) then yields

$$\begin{aligned} & \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, v(\underline{r}-\underline{r}') \{ \rho_2^\rho(\underline{r}, \underline{r}') - \rho_2^\circ(\underline{r}, \underline{r}') \} \\ & - \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, v^{\text{ref}}(\underline{r}-\underline{r}') \{ \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} \\ & = \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, \delta\rho(\underline{r}) \delta\rho(\underline{r}') f^1(\underline{r}-\underline{r}') + o(\delta\rho)^3 \end{aligned} \quad (3-47)$$

+ terms which vanish as $T \rightarrow 0$.

The meaning of this equation is as follows. If we expand the left side in powers of $\delta\rho$, then in the limit as $T \rightarrow 0$, the coefficient of the second order term becomes identical to f^1 . Then we see that to calculate $f^1(\underline{r})$ at $T = 0$, we must discover how to expand $\rho_2^\rho(\underline{r}, \underline{r}')$ and $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ in powers of $\delta\rho$. An equivalent observation has been of importance in the study of the degenerate electron gas, which, at metallic densities, may be considered for many purposes to be at zero temperature.

We turn now to finite temperatures, where we must include the entropy term in F . We shall derive two results. The first results from the effort to solve the finite T problem by the kind of energy consideration which works at $T = 0$. For all T , we define a function f_E^1 by setting the left side of (3-47) equal to

$$\frac{1}{2} \int d\underline{r} \, d\underline{r}' \, \delta\rho(\underline{r}) \delta\rho(\underline{r}') f_E^1(\underline{r}-\underline{r}') + o(\delta\rho)^3. \quad (3-48)$$

That is, we define f_E^1 to be the coefficient at any T of the

second order term in the $\delta\rho$ expansion of the left side of (3-47)*. Since, as noted above, this coefficient reduces to f^1 as $T \rightarrow 0$, we have the relation

$$\lim_{T \rightarrow 0} f^1(\underline{r}) = \lim_{T \rightarrow 0} f_E^1(\underline{r}) . \quad (3-49)$$

To discover the relation that exists between f^1 and f_E^1 at finite temperatures, we make use of the thermodynamic identity

$$F - T \left(\frac{\partial F}{\partial T} \right)_{V, N, \phi} = E , \quad (3-50)$$

where F is the configurational free energy of the system under consideration, and E is its potential energy. We explicitly note that the usual thermodynamic derivative is taken with the external field $\phi(\underline{r})$ held fixed. To apply this relation to this work, we must instead form thermodynamic derivatives at constant density $\rho(\underline{r})$. A straightforward calculation (suppressing V and N , which are constant in either case) yields

$$\left(\frac{\partial F}{\partial T} \right)_{\rho} = \left(\frac{\partial F}{\partial T} \right)_{\phi} + \sum_{\underline{k}} \left(\frac{\partial F}{\partial \phi_{\underline{k}}} \right)_{T, \phi'} \left(\frac{\partial \phi_{\underline{k}}}{\partial T} \right)_{\rho} , \quad (3-51)$$

where $\phi_{\underline{k}}$ is the k^{th} Fourier coefficient of $\phi(\underline{r})$, and the notation ϕ' indicates that all the $\phi_{\underline{k}}$ are held fixed except

*To see that this expansion must contain no first order term, consider that the general first order term will be of the form

$$\int d\underline{r} a(\underline{r}) \delta\rho(\underline{r}) .$$

But $a(\underline{r})$ can depend only on the properties of the uniform fluid, so that it must, in reality, be independent of \underline{r} . Then we are left with a term of the form

$$a \int d\underline{r} \delta\rho(\underline{r}) .$$

But this is identically zero by the canonical ensemble restriction of constant particle number. (See note to (3-23)).

the one appearing explicitly in the derivative. But direct calculation from (3-1) shows that

$$\left(\frac{\partial F}{\partial \phi_{\underline{k}}}\right)_{T, \phi'} = \frac{1}{V} \rho(-\underline{k}) . \quad (3-52)$$

Substituting this result into (3-51), and rewriting the sum in reciprocal space as an integral in real space yields

$$\left(\frac{\partial F}{\partial T}\right)_{\rho} = \left(\frac{\partial F}{\partial T}\right)_{\phi} + \left(\frac{\partial}{\partial T}\right)_{\rho} \int d\underline{r} \phi^{\rho}(\underline{r}) \rho(\underline{r}) . \quad (3-53)$$

(The superscript ρ has been added to ϕ to make explicit the dependence implied in (3-51).) Then, using (3-50), we may write

$$F - T \left(\frac{\partial F}{\partial T}\right)_{\rho} = E - \left(\frac{\partial}{\partial T}\right)_{\rho} \int d\underline{r} \phi^{\rho}(\underline{r}) \rho(\underline{r}) . \quad (3-54)$$

We find, for $F_{\phi^{\rho}}^U$,

$$\begin{aligned} (1 - T \left(\frac{\partial}{\partial T}\right)_{\rho}) F_{\phi^{\rho}}^U &= \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \rho_2^{\rho}(\underline{r}, \underline{r}') \\ &+ (1 - T \left(\frac{\partial}{\partial T}\right)_{\rho}) \int d\underline{r} \phi^{\rho}(\underline{r}) \phi(\underline{r}) , \end{aligned} \quad (3-55)$$

where we have formed the potential energy E just as discussed above (3-43). If we now operate with $(1 - T \left(\frac{\partial}{\partial T}\right)_{\rho})$ on $G_1(\rho)$ from (3-37), and use (3-55), the terms in ϕ^{ρ} and $\phi^{\rho, \text{ref}}$ are seen to cancel, and we are left with

$$\begin{aligned} (1 - T \left(\frac{\partial}{\partial T}\right)_{\rho}) G_1(\rho) &= \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \rho_2^{\rho}(\underline{r}, \underline{r}') \\ &- \frac{1}{2} \int d\underline{r} d\underline{r}' v^{\text{ref}}(\underline{r}-\underline{r}') \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') . \end{aligned} \quad (3-56)$$

This implies

$$\begin{aligned}
 & (1-T \left(\frac{\partial}{\partial T} \right)_{\rho}) \{G_1(\rho) - G_1(\rho_0)\} \\
 & = \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, v(\underline{r}-\underline{r}') \{ \rho_2^0(\underline{r}, \underline{r}') - \rho_2^0(\underline{r}, \underline{r}') \} \\
 & \quad - \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, v^{\text{ref}}(\underline{r}-\underline{r}') \{ \rho_2^{0, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{0, \text{ref}}(\underline{r}, \underline{r}') \}.
 \end{aligned} \tag{3-57}$$

If we now expand both sides of this equation in powers of $\delta\rho$, making use of (3-39) for the left side and (3-48) for the right, and equate the second order terms, we find

$$\begin{aligned}
 & (1-T \left(\frac{\partial}{\partial T} \right)_{\rho}) \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, \delta\rho(\underline{r}) \delta\rho(\underline{r}') f^1(\underline{r}-\underline{r}') \\
 & = \frac{1}{2} \int d\underline{r} \, d\underline{r}' \, \delta\rho(\underline{r}) \delta\rho(\underline{r}') f_E^1(\underline{r}-\underline{r}') .
 \end{aligned} \tag{3-58}$$

Since this must be true for all $\delta\rho$, and since f^1 and f_E^1 must be symmetric in \underline{r} , we must have

$$(1-T \frac{\partial}{\partial T}) f^1(\underline{r}) = f_E^1(\underline{r}) . \tag{3-59}$$

(We need no longer form the derivative at constant ρ , since f^1 depends only on the properties of the uniform fluid.) This equation is one of the desired finite T results. It is a temperature differential equation to be solved subject to the boundary condition that $f^1 = f_E^1$ at $T = 0$. It shows the added complexity introduced into the problem by the necessary inclusion of the entropy term in the free energy.

We can, however, derive a second expression which shows that we can regain the conceptual simplicity of the $T = 0$ problem if we are content to calculate f^1 only to first order

in the perturbation v^1 . We make use of the well known technique for expanding the free energy in powers of v^1 (Zwanzig, 1954). For an m-component mixture, we have from (3-1)

$$e^{-\beta F_{\phi\rho}^U} = \frac{1}{N_1! \dots N_m!} \int dR e^{-\beta U(R)} e^{-\frac{\beta}{V} \sum_i \sum_{\underline{k}} \hat{\rho}_i(\underline{k}) \phi_i^\rho(-\underline{k})}, \quad (3-60)$$

where we have written $\phi(R)$ in terms of the Fourier components of the $\phi_i(\underline{r})$ and of the density operator defined in (1-3).

Then, if we also write (3-60) for the reference fluid, we find

$$e^{-\beta \{F_{\phi\rho}^U - F_{\phi\rho,ref}^{U^{ref}}\}} = \left\langle e^{-\beta U^1(R)} e^{-\frac{\beta}{V} \sum_i \sum_{\underline{k}} \hat{\rho}_i(\underline{k}) \phi_i^{\rho,1}(-\underline{k})} \right\rangle_{\rho,ref}, \quad (3-61)$$

where

$$\phi_i^{\rho,1}(\underline{r}) = \phi_i^\rho(\underline{r}) - \phi_i^{\rho,ref}(\underline{r}), \quad U^1(R) = U(R) - U^{ref}(R), \quad (3-62)$$

and

$$\langle A \rangle_{\rho,ref} = \frac{\int dR A(R) e^{-\beta U^{ref}(R)} e^{-\beta \phi^{\rho,ref}(R)}}{\int dR e^{-\beta U^{ref}(R)} e^{-\beta \phi^{\rho,ref}(R)}} \quad (3-63)$$

In this notation, (3-37) reads

$$F_{\phi\rho}^U - F_{\phi\rho,ref}^{U^{ref}} = G_1(\rho) + \frac{1}{V} \sum_i \sum_{\underline{k}} \rho_i(\underline{k}) \phi_i^{\rho,1}(-\underline{k}). \quad (3-64)$$

(Note that $\rho_i(\underline{k})$ in (3-64) is not an operator.) Now from (1-3), we have

$$\hat{\rho}_i(\underline{k}=0) = N_i = \rho_i(\underline{k}=0). \quad (3-65)$$

Inserting (3-64) and (3-65) into (3-61), we find

$$\begin{aligned}
 & e^{-\beta\{G_1(\rho) + \frac{1}{V} \sum_i \sum_{\underline{k}} \rho_i(\underline{k}) \phi_i^{\rho,1}(-\underline{k})\}} \\
 &= e^{-\beta \sum_i \rho_i \phi_i^{\rho,1}(0)} \left\langle e^{-\beta U^1(R)} e^{-\frac{\beta}{V} \sum_i \sum_{\underline{k} \neq 0} \hat{\rho}_i(\underline{k}) \phi_i^{\rho,1}(-\underline{k})} \right\rangle_{\rho, \text{ref}} .
 \end{aligned} \tag{3-66}$$

Cancelling the terms in $\underline{k} = 0$ yields

$$\begin{aligned}
 & e^{-\beta\{G_1(\rho) + \frac{1}{V} \sum_i \sum_{\underline{k} \neq 0} \rho_i(\underline{k}) \phi_i^{\rho,1}(\underline{k})\}} \\
 &= \left\langle e^{-\beta U^1(R)} e^{-\frac{\beta}{V} \sum_i \sum_{\underline{k} \neq 0} \hat{\rho}_i(\underline{k}) \phi_i^{\rho,1}(-\underline{k})} \right\rangle_{\rho, \text{ref}} .
 \end{aligned} \tag{3-67}$$

For $U^1(R)$, we have

$$U^1(R) = \frac{1}{2} \sum_{ij} \sum_{\ell \neq m} v_{ij}^1(\underline{r}_\ell^i - \underline{r}_m^j) , \tag{3-68}$$

where the v_{ij}^1 are the perturbing pair potentials. We introduce an expansion parameter λ by replacing v_{ij}^1 by λv_{ij}^1 in $U^1(R)$. We may then formally introduce the λ expansions

$$\begin{aligned}
 G_1(\rho) &= \lambda A(\rho) + \lambda^2 B(\rho) + \dots \\
 \phi_i^{\rho,1}(\underline{k}) &= \lambda a_i(\underline{k}) + \lambda^2 b_i(\underline{k}) + \dots \quad (\underline{k} \neq 0), \\
 U^1(R) &\rightarrow \lambda U^1(R) .
 \end{aligned} \tag{3-69}$$

If we insert these expansions into (3-67), and expand all around in powers of λ , we find (when we note that $\langle \hat{\rho}_i(\underline{k}) \rangle_{\rho, \text{ref}} = \rho_i(\underline{k})$ by definition)

$$A(\rho) = \langle U^1(R) \rangle_{\rho, \text{ref}} . \tag{3-70}$$

This expression can be written in terms of the two body distribution functions of the reference fluid. In analogy to the notation already introduced for pure fluids, we denote by $\rho_{ij}^{\rho}(\underline{r}, \underline{r}')$ the two body function, for one particle of type i and the other of type j , which is uniquely determined by the densities $\rho_i(\underline{r})$. (We omit the subscript "2" since it is cumbersome and, with two indices i, j , redundant.) Then (3-70) reads

$$A(\rho) = \frac{1}{2} \sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^1(\underline{r}-\underline{r}') \rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}') , \quad (3-71)$$

so that, using (3-69),

$$\begin{aligned} G_1(\rho) - G_1(\rho_0) &= \frac{1}{2} \lambda \sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^1(\underline{r}-\underline{r}') \{ \rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_{ij}^{\rho_0, \text{ref}}(\underline{r}, \underline{r}') \} \\ &+ o(\lambda)^2 . \end{aligned} \quad (3-72)$$

(The superscripts "ref" and " ρ_0 " are introduced here in strict analogy to the pure fluid case.) Finally, if we also expand $f_{ij}^1(\underline{r})$ in powers of λ ,

$$f_{ij}^1(\underline{r}) = \lambda a_{ij}^1(\underline{r}) + o(\lambda)^2 , \quad (3-73)$$

we can write the expansion of (3-39) as

$$\begin{aligned} G_1(\rho) - G_1(\rho_0) &= \frac{1}{2} \sum_{ij} \int d\underline{r} d\underline{r}' \delta\rho_i(\underline{r}) \delta\rho_j(\underline{r}') \{ \lambda a_{ij}^1(\underline{r}-\underline{r}') + \dots \} \\ &+ o(\delta\rho)^3 . \end{aligned} \quad (3-74)$$

Comparing the terms of order λ between (3-72) and (3-74) shows that a_{ij}^1 satisfies

$$\begin{aligned} \sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^1(\underline{r}-\underline{r}') \{ \rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} \\ = \sum_{ij} \int d\underline{r} d\underline{r}' \delta\rho_i(\underline{r}) \delta\rho_j(\underline{r}') a_{ij}^1(\underline{r}-\underline{r}') + o(\delta\rho)^3. \end{aligned} \quad (3-75)$$

That is, when the left side of (3-75) is expanded in powers of $\delta\rho$, the coefficients of the second order terms are the a_{ij}^1 defined by (3-73), i.e. the first order terms in the expansions of the f_{ij}^1 in powers of the v_{ij}^1 . We note that, as promised, the form of this equation is quite like that of (3-47).

From a calculational standpoint, (3-75) represents perhaps the central result. As indicated at the end of section II, the success of the mean field calculation suggests that we seek a theory of phase separation by completing the low order approximation to f^1 . Equation (3-75) shows that the problem of calculating f_{ij}^1 to first order in v_{ij}^1 is equivalent to calculating $\rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}')$, the two body distribution function in the non-uniform reference fluid, to second order in the $\delta\rho_i(\underline{r})$.

From the standpoint of physical approximation, this result offers a certain conceptual simplicity. As we noted in section II, a more conventional expansion of $S_{ij}(\underline{k})$ (hence of $f_{ij}^1(\underline{k})$) encounters in the first term the three and four body distribution functions of the reference fluid. What we

have done is to provide an alternate form of the problem. Thus, one may either seek to evaluate a_{ij}^1 by evaluating ρ_2^0 , ρ_3^0 , and ρ_4^0 in the uniform reference fluid, as required by the conventional theory, or by evaluating ρ_2^0 in the non-uniform reference fluid, as required by (3-75). While ρ_3^0 and ρ_4^0 are wholly unknown, we might hope that our extensive knowledge and physical understanding of ρ_2^0 could be used to suggest successful approximations to ρ_2^0 . This is the approach which we ultimately adopt.

The important results of this section are the "zero temperature" equation (3-47), the finite temperature differential equation (3-59) (together with the boundary condition (3-49) and the definition (3-48) of f_E^1), and the first order equation (3-75). We turn now to the study of approximate solutions to these equations. We shall begin by reviewing, in the light of these formulas, the matters raised in section II. Then, after considering the possibility of a self-consistent approach, we turn to the development of the first order formulas on which we base our calculations.

IV. Approximate Solutions for the f_{ij}^1 and a_{ij}^1 .

IV-A. The Earlier Results

The simplest approximate solutions for f_{ij}^1 are those which give rise to the mean field theories of section II. We shall specialize, as in section II, to the case of single component systems.

Consider first the case in which the reference system is an ideal gas. For this case, we proposed in section II the "simplest mean field theory" specified by (2-12) or

$$f^1(\underline{r}) = v(\underline{r}) . \quad (4-1)$$

This approximation can be seen from our formalism to be the correct first order approximation to f^1 (a result which is well known from the perturbation series.) Consider the first order equation (3-75). For a pure fluid, it reads

$$\begin{aligned} \int d\underline{r} d\underline{r}' v^1(\underline{r}-\underline{r}') \{ \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} \\ = \int d\underline{r} d\underline{r}' \delta\rho(\underline{r}) \delta\rho(\underline{r}') a^1(\underline{r}-\underline{r}') + o(\delta\rho)^3 . \end{aligned} \quad (4-2)$$

When we take the reference system to be an ideal gas, we have $v^{\text{ref}} = 0$, $v^1 = v$, and

$$\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') = \rho(\underline{r})\rho(\underline{r}') . \quad (4-3)$$

Thus, the left side of (4-2) becomes

$$\int d\underline{r} d\underline{r}' \delta\rho(\underline{r}) \delta\rho(\underline{r}') v(\underline{r}-\underline{r}') , \quad (4-4)$$

where we have made use of the canonical ensemble restriction
(see note to (3-23))

$$\int d\underline{r} \delta\rho(\underline{r}) = 0 . \quad (4-5)$$

Comparing (4-4) to the right side of (4-2), we conclude

$$a^1(\underline{r}) = v(\underline{r}) , \quad (4-6)$$

where we have assumed that $v(\underline{r}) = v(-\underline{r})$ (an assumption we shall make throughout this work) and required (4-4) and the right side of (4-2) to be identical for all $\delta\rho(\underline{r})$. Then

$$f^1(\underline{r}) = v(\underline{r}) + o(v)^2 , \quad (4-7)$$

so that (4-1) is just the first order approximation to $f^1(\underline{r})$.

We note that (3-75) allows a ready generalization of the simple mean field theory to multi-component systems. For $v_{ij}^{ref} = 0$, (3-75) yields

$$a_{ij}^1(\underline{r}) = v_{ij}(\underline{r}) . \quad (4-8)$$

(To produce (4-8) from (3-75), we must consider varying $\delta\rho_i(\underline{r})$ independently for each i .) Then to generalize (4-1), we just make the first order approximation

$$f_{ij}^1(\underline{r}) = v_{ij}(\underline{r}) . \quad (4-9)$$

The resulting partial structure factors for the two component case are precisely those used by Stroud (1973) in his study of phase separation.

The approximation (4-1) can also be understood in a more

subtle, but instructive, way from our equations before the first order approximation is made. Consider first the equation (3-47), which represents the limiting case as $T \rightarrow 0$. For the case of a pure fluid and an ideal gas reference system, this equation reduces to

$$\begin{aligned} & \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r}-\underline{r}') \{ \rho_2^\rho(\underline{r}, \underline{r}') - \rho_2^\circ(\underline{r}, \underline{r}') \} \\ & = \frac{1}{2} \int d\underline{r} d\underline{r}' \delta\rho(\underline{r}) \delta\rho(\underline{r}') f^1(\underline{r}-\underline{r}') + o(\delta\rho)^3, \end{aligned} \quad (4-10)$$

(where we have ignored the terms which vanish as $T \rightarrow 0$.) Now the ρ_2^ρ and ρ_2° are in general unknown functions, since they are the functions appropriate to the "real" fluid. But because the liquid exhibits no long range order, we do know the form of these functions when the points designated by \underline{r} and \underline{r}' are sufficiently far apart. Then the functions just assume the form (4-3):

$$\rho_2^\rho(\underline{r}, \underline{r}') = \rho(\underline{r})\rho(\underline{r}') . \quad (4-11)$$

We shall speak loosely of the particles being "correlated" in the short range in which $\rho_2^\rho(\underline{r}, \underline{r}')$ differs appreciably from (4-11). Now suppose in (4-10) that the potential $v(\underline{r})$ is well behaved at small \underline{r} , and of sufficiently long range that the dominant contribution to the integral on the left of (4-10) comes from regions beyond the range of correlations, that is, from regions where (4-11) is a good approximation. Then we might reasonably ignore the short range effects, and replace ρ_2^ρ everywhere by $\rho(\underline{r})\rho(\underline{r}')$. On making this replacement in

(4-10), we recover immediately the mean field form (4-1). To extend this result to finite temperature, we note that the left side of (4-10) is just the (implied) left side of (3-48) for this case, so that the approximation (4-11) yields immediately $f_E^1(\underline{r}) = v(\underline{r})$. This result is independent of temperature, so that solving (3-59) subject to the boundary condition (3-49) yields again (4-1). Thus, the mean field theory of (4-1) (or (2-12)) emerges at all temperatures from the neglect of short range correlations in $\rho_2^0(\underline{r}, \underline{r}')$.

Next, consider the case of an arbitrary reference system, for which we proposed the mean field form (2-14), or, more precisely,

$$f^1(\underline{r}) = v^1(\underline{r}) . \quad (4-12)$$

This approximation results in our formalism when we make the first order approximation $f^1 = a^1$, and evaluate a^1 in (3-75) with the approximation

$$\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') = \rho(\underline{r})\rho(\underline{r}') . \quad (4-13)$$

In words, for an arbitrary reference system, (4-12) represents f^1 calculated to first order in v^1 with neglect of reference system correlations.

We are now better able to understand the modification (2-16) which was introduced to remove the ambiguity of (4-12) (or (2-14)) in the special case $v^{\text{ref}} = v^{\text{HC}}$. Since two particles in a hard core fluid can never be found separated by a distance less than σ (where σ is the hard core diameter of

(1-10)), we must have $\rho_2^{\rho, HC}(\underline{r}, \underline{r}') = 0$, identically, when $|\underline{r} - \underline{r}'| < \sigma$. It is clear that the simplest approximation in the spirit of (4-13) which satisfies this condition is

$$\rho_2^{\rho, HC}(\underline{r}, \underline{r}') = \begin{cases} 0 & |\underline{r} - \underline{r}'| < \sigma \\ \rho(\underline{r})\rho(\underline{r}') & |\underline{r} - \underline{r}'| > \sigma \end{cases} \quad (4-14)$$

When a^1 is evaluated from (3-75) with this approximation, the form (2-16) results immediately from the first order approximation $f^1 = a^1$.

We are now better able to understand the significance of the correlation effects at liquid densities. At these densities, the hard sphere correlations have a range comparable to that of v^1 , so that the dominant contribution to the integral on the left of (3-75) (or (4-2)) comes from the region where (4-14) is a poor approximation.

Consider next the limit of close packing, which was introduced in section II to illustrate the correlation effects. Within the formalism we have developed, the case of close packing assumes a special importance, for it represents the one case, apart from the case of an ideal gas, for which we can write an explicit form for $\rho_2^{\rho}(\underline{r}, \underline{r}')$. In a close packed system, we may induce a non-uniform density $\rho(\underline{r})$ by applying a field $\phi(\underline{r})$ which has the periodicity of the lattice. But this density cannot change the conditional probability that a particle will be found at \underline{r}' given a particle at \underline{r} . Since this probability is given by $\rho_2^{\rho}(\underline{r}, \underline{r}')/\rho(\underline{r})$, we have

$$\frac{\rho_2^0(\underline{r}, \underline{r}')}{\rho(\underline{r})} = \frac{\rho_2^0(\underline{r}, \underline{r}')}{\rho_0} \quad (4-15)$$

or

$$\rho_2^0(\underline{r}, \underline{r}') = \frac{\rho(\underline{r})}{\rho_0} \rho_2^0(\underline{r}, \underline{r}') , \text{ close packing limit.} \quad (4-16)$$

We see immediately that $\rho_2^0(\underline{r}, \underline{r}')$ has no second order term in $\delta\rho$. Though some care is required, it is no surprise that these considerations can be made to yield $f^1(\underline{k}) = 0$ when \underline{k} is any reciprocal lattice vector, and hence, the desired result $\chi = \chi^{\text{HC}}$. Thus we have achieved one goal we set for this work, namely, to handle the close packing limit correctly.

Return now to the problem at liquid densities, and consider a more sophisticated approach than is represented by the mean field theories discussed so far. Consider the structure of equation (4-10), which holds for the case of an ideal gas reference system in the limit as $T \rightarrow 0$. It states that when the expression on the left is expanded in powers of $\delta\rho$, the function f^1 will appear as the coefficient of the second order term. In order to evaluate the expression on the left, however, it is necessary that we already know f^1 . This follows because $\rho_2^0(\underline{r}, \underline{r}')$ (which is the two body function in the uniform "real" fluid) is related through $g(\underline{r}-\underline{r}')$ to $S(\underline{k})$ and $\chi(\underline{k})$, and is thus sufficient to determine f^1 . If a stronger statement were true, if the knowledge of f^1 were sufficient to determine the entire left side of (4-10), we could define a self-consistent procedure for determining f^1 through (4-10). Such a statement is, of course, not true without further

approximation, since f^1 says nothing directly about $\rho_2^\rho(\underline{r}, \underline{r}')$.

Similar observations on the problem of the quantum electron gas have led Singwi and co-workers (1968, 1970) to suggest approximate forms for $\rho_2^\rho(\underline{r}, \underline{r}')$, for which, in the present context, a knowledge of f^1 is sufficient. The earliest of these was the form

$$\rho_2^\rho(\underline{r}, \underline{r}') = \rho(\underline{r})\rho(\underline{r}')g^\circ(\underline{r}-\underline{r}') , \quad (4-17)$$

where $g^\circ(\underline{r})$ is defined (as in section I) by $g^\circ(\underline{r}) = \rho_2^\circ(\underline{r}) / (\rho_0)^2$. With such approximations, Singwi et al. were able to define self-consistent methods for calculating the electron gas response functions. Within the classical formulation represented by (4-10), the particular approximation (4-17) yields

$$f^1(\underline{r}) = v(\underline{r})g^\circ(\underline{r}) , \quad (4-18)$$

which is to be solved self-consistently for f^1 and g° . We note in passing that, by (4-16), the particular approximation (4-17) fails in the limit of close packing, so that it is highly suspect in application to a dense fluid of hard cores.

The point we wish to consider here is not the particular form of these approximations, but rather the possibility of a self-consistent approach to our problem. When we turn to finite temperatures, we find that even the simple approximation (4-17) yields an exceedingly complicated problem. When substituted into (3-48), it will yield

$$f_E^1(\underline{r}) = v(\underline{r})g^\circ(\underline{r}) . \quad (4-19)$$

This is a temperature dependent result, so that, to find f^1 , we must integrate the equation (3-59), maintaining self-consistency throughout. Because of this complication, we have not attempted a self-consistent calculation in our problem, despite the success which has accompanied such calculations for the zero temperature electron gas.

We have instead elected to pursue our original plan of a hard core plus tail perturbation approach, and focus our attention on the first order equation (3-75), in which the expression on the left is a function only of v^1 and the properties of the reference fluid.

IV-B. The Solution for a_{ij}^1 .

We begin with the remark that (3-75) can in fact be solved exactly for a_{ij}^1 in terms of reference system distribution functions. This can be accomplished by expanding $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ in powers of the fields ϕ^{ρ} which give rise to $\delta\rho(\underline{r})$. Though this expansion will contain terms of first order in ϕ , we see from the form of (3-75) that the first terms surviving the integration on the left will be of second order in ϕ . It is then a simple matter to use the response functions χ to produce the second order terms in $\delta\rho$. Now the expansion of $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ in powers of ϕ^{ρ} introduces the higher order distribution functions $\rho_3^{\rho, \text{ref}}$ and $\rho_4^{\rho, \text{ref}}$, so that, as might be expected, the result of this approach is simply the more conventional form of f^1 alluded to in the discussion following (3-75). For the reasons outlined in that discussion,

we prefer to work with (3-75) directly, and seek approximations for $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$.

This task may be simplified by considering the problem in reciprocal space. Choose the densities $\delta\rho_i(\underline{r})$ to be given by

$$\delta\rho_i(\underline{r}) = \delta\rho_i \cos(\underline{k}_i \cdot \underline{r}) \quad , \quad i = 1, 2, \dots, m. \quad (4-20)$$

When the right side of (3-75) is evaluated for such densities, the full equation takes the form

$$\begin{aligned} & \sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^1(\underline{r}-\underline{r}') \{ \rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} \\ & = \frac{V}{2} \sum_{ij} \delta\rho_i \delta\rho_j a_{ij}^1(\underline{k}) (\delta_{\underline{k}_i, \underline{k}_j} + \delta_{\underline{k}_i, -\underline{k}_j}) + o(\delta\rho)^3. \end{aligned} \quad (4-21)$$

where we have introduced Fourier transforms, and the function $\delta_{\underline{k}, \underline{k}'}$ has its usual meaning. This result means that, in order to calculate the $a_{ij}^1(\underline{k})$ correctly at some \underline{k} , we have only to evaluate $\rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ for density variations specified, through (4-20), by the same \underline{k} . (The complexities of (4-21) are such that some care must be exercised in order to reach this conclusion for a multi-component system.) Then the problem of the $a_{ij}^1(\underline{k})$ can be solved independently at each wavelength.

1.) The long wavelength limit.

Consider first the case of a single component system on which we impress a long wavelength density variation. Clearly, as the wavelength of the density variation becomes infinite, $\delta\rho$ will go to a constant, and $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ can be

expanded in a conventional Taylor series in $\delta\rho$:

$$\begin{aligned} \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \\ = \delta\rho \frac{\partial}{\partial \rho_0} \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') + \frac{1}{2}(\delta\rho)^2 \frac{\partial^2}{\partial \rho_0^2} \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') + o(\delta\rho)^3. \end{aligned} \quad (4-22)$$

Now for wavelengths which are finite but still very long compared to the range of correlation, we can simply evaluate $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ at the local density. We generalize (4-22) for this case by

$$\begin{aligned} \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \\ = \frac{1}{2} \{ \delta\rho(\underline{r}) + \delta\rho(\underline{r}') \} \frac{\partial}{\partial \rho_0} \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \\ + \frac{1}{2} \delta\rho(\underline{r}) \delta\rho(\underline{r}') \frac{\partial^2}{\partial \rho_0^2} \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') + o(\delta\rho)^3. \end{aligned} \quad (4-23)$$

Within the range of correlations, by hypothesis, $\delta\rho$ does not vary significantly, so that (4-23) is identical to (4-22).

The particular form has been selected from considerations at long range. Beyond the range of correlation, where

$\rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') = \rho_0^2$, (4-23) reduces to the correct form $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') = \rho(\underline{r})\rho(\underline{r}')$. Substituting from (4-23) into (3-75), we read off immediately

$$a^1(\underline{r}) = \frac{1}{2} v^1(\underline{r}) \frac{\partial^2}{\partial \rho_0^2} \rho_2^{\circ, \text{ref}}(\underline{r}) \quad (4-24)$$

Here, we have noted explicitly that, because $\rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}')$ is

the function appropriate to a uniform fluid, it is a function only of $\underline{r}-\underline{r}'$. In Fourier transform, (4-24) becomes

$$a^1(\underline{k}) = \frac{1}{2} \int \frac{d\underline{k}'}{(2\pi)^3} v^1(\underline{k}') \frac{\partial^2}{\partial \rho_o^2} \rho_2^{\circ, \text{ref}}(\underline{k}-\underline{k}') . \quad (4-25)$$

This is the form of $a^1(\underline{k})$ which we expect to be valid for small values of \underline{k} . We shall consider the limits on its region of validity more precisely in the next section.

To extend this long wavelength approximation to the case of multi-component systems, we adopt the same basic procedure, but the argument is complicated by a lack of symmetry among the ρ_{ij}^0 in a non-uniform fluid. In particular, we find that, in general, $\rho_{ij}^0(\underline{r}, \underline{r}') \neq \rho_{ji}^0(\underline{r}, \underline{r}')$, that is, that ρ_{ij}^0 is not symmetric in the indices i, j . For instance, if \underline{r} and \underline{r}' are far enough apart, we have

$$\rho_{ij}^0(\underline{r}, \underline{r}') = \rho_i(\underline{r}) \rho_j(\underline{r}') \text{ and } \rho_{ji}^0(\underline{r}, \underline{r}') = \rho_j(\underline{r}) \rho_i(\underline{r}'), \quad (4-26)$$

and these certainly need not be equal. On the other hand, in the uniform fluid, the distribution functions are symmetric:

$$\rho_{ij}^0(\underline{r}, \underline{r}') = \rho_{ji}^0(\underline{r}, \underline{r}') . \quad (4-27)$$

Now, the long wavelength approximation is to be derived by treating the non-uniform fluid as locally uniform. We see that we must take care that the approximation does not introduce the wrong symmetry into the functions for the non-uniform fluid. We can do this by defining symmetric distribution functions for the non-uniform fluid as well. We define

$$\bar{\rho}_{ij}^0(\underline{r}, \underline{r}') = \frac{1}{2} \{ \rho_{ij}^0(\underline{r}, \underline{r}') + \rho_{ji}^0(\underline{r}, \underline{r}') \} . \quad (4-28)$$

These functions are explicitly symmetric in i, j , and thus, as we shall see, can be treated consistently with a "local density" approximation.

In terms of the $\bar{\rho}_{ij}^0$, the left side of (3-75) reads

$$\sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^1(\underline{r}-\underline{r}') \{ \bar{\rho}_{ij}^{0, \text{ref}}(\underline{r}, \underline{r}') - \bar{\rho}_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} , \quad (4-29)$$

where we have used $v_{ij}(\underline{r}) = v_{ji}(\underline{r})$ (noted below (3-42)). To make the long wavelength approximation, we first expand the $\bar{\rho}_{ij}^0$ for constant $\delta\rho$:

$$\begin{aligned} & \bar{\rho}_{ij}^{0, \text{ref}}(\underline{r}, \underline{r}') - \bar{\rho}_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') \\ &= \sum_{\ell} \delta\rho_{\ell} \frac{\partial}{\partial \rho_{\ell}^{\circ}} \rho_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') \quad (4-30) \\ &+ \frac{1}{2} \sum_{\ell m} \delta\rho_{\ell} \delta\rho_m \frac{\partial^2}{\partial \rho_{\ell}^{\circ} \partial \rho_m^{\circ}} \rho_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}') + o(\delta\rho)^3 \end{aligned}$$

where we have used (4-27) and (4-28) to replace $\bar{\rho}_{ij}^0$ by ρ_{ij}° . Just as in the single component case, we proceed to evaluate the form of $\bar{\rho}_{ij}^0$ beyond the correlation range, and then insert local densities into (4-29) in a manner consistent with this form. (We note that, by (4-27) and (4-28), both sides of the resulting equation will be symmetric in ij , so that the approximation is consistent in this sense.) Substituting the resulting approximation into (4-29) and thence into (3-75), we find

$$a_{ij}^1(\underline{k}) = \frac{1}{2} \sum_{\ell m} \int \frac{d\underline{k}'}{(2\pi)^3} v_{\ell m}^1(\underline{k}') \frac{\partial^2}{\partial \rho_i^{\circ} \partial \rho_j^{\circ}} \rho_{\ell m}^{\circ, \text{ref}}(\underline{k}-\underline{k}') , \quad (4-31)$$

in complete analogy to (4-25).

We pause to note that in the limit as $k \rightarrow 0$, (4-31) becomes

$$a_{ij}^1(0) = \frac{1}{2} \sum_{\ell m} \int \frac{d\underline{k}}{(2\pi)^3} v_{\ell m}^1(\underline{k}) \frac{\partial^2}{\partial \rho_i^{\circ} \partial \rho_j^{\circ}} \rho_{\ell m}^{\circ, \text{ref}}(\underline{k}) . \quad (4-32)$$

This limiting expression can in fact be obtained by a short argument from a grand ensemble. This argument is given in appendix C, and provides a check on our work.

2.) The problem of short wavelengths.

In section II, we discussed the difficulty encountered by the mean field theory (2-16), when applied to dense fluids, at wavelengths around the first peak of the reference (hard sphere) structure factor. There we introduced the idealization of a close packed lattice in order to interpret the difficulty. As we have seen, the formalism we have developed reproduces the expected form in the close packing limit. Despite this improvement, however, we still encounter considerable difficulty, at liquid densities, in formulating a successful approximation for values of \underline{k} near the reference peak. Reduced to simplest terms, the difficulty is that, while an explicit form (4-16) exists for $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$ in the close packing limit, we must proceed at liquid densities by approximation, and the formulas, for values of \underline{k} around the peak, are exceedingly sensitive to errors in f^1 . This

sensitivity results, of course, from the peak itself, since f_{ij}^1 appears in the combination $f_{ij}^1 \chi_{ij}^{ref}$ (and also in the more complex quadratic term of (3-41), for which similar considerations will hold.) In the single component case, for example, $\chi^{HC}(k)$ for k at the peak is nearly 100 times as large as for $k = 0$.

The difficulty might be measured against the problem in the electron gas. One approach which has been successful in the electron gas problem has been to define a short range correlation function, which, in the spirit of our work at long wavelengths, is evaluated at the local density. Singwi et al. (1970) take this approach in a paper subsequent to that discussed around (4-17). They define and evaluate at the local density a correlation function α which is a δ -function in the RPA, and which they expect to be short ranged as well in the fully correlated solution. Such an approach seems always to fail for the hard sphere liquid, because the hard sphere potential, unlike the Coulomb potential, defines a characteristic length σ which is, unfortunately, of order $2\pi/k_{peak}$ at liquid densities. It has not proven possible to define a correlation function whose range is smaller than σ , and which thus might believably be calculated at the local density when $k \sim k_{peak}$. We did make an attempt to evaluate at the local density the direct correlation function of Ornstein and Zernike (see (3-35)), which has a range of order σ . (The range is exactly σ in PY.) Not surprisingly, this calculation gave very poor results around the peak, and will not be reported in detail.

If an answer is found, we expect that it may arise from consideration of the finite size of the particles. To test a simple idea, we noted that, at liquid densities, the wavelength at k_{peak} is very nearly equal to a particle diameter and to the average particle spacing. It thus seems reasonable to suppose that at short distances, where the correlations are strong, a density variation appropriate to $k \sim k_{\text{peak}}$ might have effects similar to long wavelength density variations. (We are here moving in the direction of the reciprocal lattice vector concept appropriate to a crystalline solid.) Noting further that the long wavelength form (4-23) is correct beyond the correlation range at all wavelengths, these observations suggest that this form (4-23) might have a region of validity around the peak as well. As we shall report in the next section, the calculations yield interesting, but wholly inconclusive, evidence that this might be the case. Perhaps a more diligent pursuit of the short range analogy with a crystalline solid may yield a successful approximation.

We note finally that these difficulties do not have the effect of terminating (or invalidating) this effort. It is, after all, in the long wavelength region of the spectrum that we expect to observe the phase separation instability, and we have a clear approximation for this region. Further, as we shall see, the correlation effects we have learned to include are of considerable importance at long wavelengths as well. Thus, while there is still much to be learned, the progress which has been made in this effort can be put to good use.

As set forth in the opening section, the program of our work is to develop a suitable perturbation approach to the hard core plus tail mixture, and to apply this theory to liquid metal systems by constructing hard core plus tail models of the real potentials. With these last remarks on the short wavelength problem, that portion of our effort devoted purely to the perturbation development comes to an end. We turn now to the application of this work to liquid metal systems, to learn about these systems, and, of course, to learn more about the perturbation theory itself.

V. Application to Liquid Metal Systems

V-A. Systems and Models

To lay the ground work for this section, we must present the form of the effective pair potential v^{AL} , and define the parameters we shall use to discuss both the metallic systems themselves and the hard core plus tail models we shall propose for these systems.

The effective ion-ion pair potentials used in this work are those which Ashcroft and Langreth (AL-II) have used to discuss liquid metal structure. The potential is derived and discussed in AL-II. It consists of the direct Coulomb interaction between a pair of ions, and an indirect interaction between one ion and the polarization induced by the other in the gas of conduction electrons. In reciprocal space, it takes the form

$$v_{ij}^{AL}(\underline{k}) = \frac{4\pi Z_i Z_j e^2}{k^2} \left\{ 1 + \frac{v_i^{PS}(\underline{k}) v_j^{PS}(\underline{k})}{(4\pi/k^2)^2} \left(\frac{1}{\epsilon(\underline{k})} - 1 \right) \right\}. \quad (5-1)$$

Here, we have presented the interaction between an ion of species i and an ion of species j . Z_i and Z_j represent the respective valences, e is the electronic charge, $\epsilon(\underline{k})$ is the conduction electron dielectric function, and $v_i^{PS}(\underline{k})$ is related to the bare (unscreened) pseudopotential, $v_i^b(\underline{k})$, acting between a conduction electron and an ion of type i by

$$v_i^b(\underline{k}) = -Z_i e^2 v_i^{PS}(\underline{k}). \quad (5-2)$$

To specify the pseudopotential and dielectric function, we follow AL-II exactly. For v_i^{ps} we choose the empty core potential (Ashcroft, 1966) given by

$$v_i^{ps}(r) = \begin{cases} 0 & r < r_c^i \\ \frac{1}{r} & r > r_c^i \end{cases} \quad \text{or} \quad v_i^{ps}(k) = \frac{4\pi}{k^2} \cos(kr_c^i), \quad (5-3)$$

where r_c^i is a parameter to be specified for each species. We have used in this work the values of r_c^i listed by Ashcroft and Langreth (1967C). A more complete listing of suggested r_c^i values is given by Cohen and Heine (1970). (See also Stroud, 1973). For the dielectric function, we use

$$\epsilon(k) = 1 + \frac{\lambda^2}{y^2} F(y), \quad y = \frac{k}{2k_F},$$

$$F(y) = f(y) \{1 - \lambda^2 f(y) / (2y^2 + g)\}^{-1}$$

$$f(y) = \frac{1}{2} + \frac{1}{4y} (1 - y^2) \ln \left| \frac{1+y}{1-y} \right| \quad (5-4)$$

$$g = (1 + 0.158\lambda^2)^{-1}$$

$$\lambda^2 = (\pi a_0 k_F)^{-1}, \quad a_0 = \frac{\hbar^2}{me^2}, \quad k_F = (3\pi^2 \rho_e)^{1/3},$$

where ρ_e is the conduction electron density. These formulas completely specify the pair potential when the parameters r_c^i , Z_i , and ρ_e are known. The real space form of these potentials for some systems are calculated and presented in AL-II.

In calculating the potential for a given system, we shall consider that the parameters r_c^i and Z_i are characteristic of the species. Beyond the specification of the components, then, the parameter from which all else follows is the

conduction electron density ρ_e . In this work, we replace ρ_e by the usual dimensionless parameter r_s , defined by

$$r_s^3 = \frac{3}{4\pi a_0^3} \cdot \frac{1}{\rho_e} \quad (5-5)$$

This parameter is the radius, in atomic units, of a sphere with volume equal to the average volume per conduction electron. For a pure metal, r_s may be determined from a knowledge of the density and valence of the element.

The specification of r_s for the alloy is more complicated, since it will be a function of concentration. The alloy is specified by the average densities, ρ_1 and ρ_2 , of ions of species one and two. As indicated in section I, we find it convenient to replace these variables by

$$\rho = \rho_1 + \rho_2 \quad \text{and} \quad x = \frac{\rho_2}{\rho_1 + \rho_2} \quad (5-6)$$

To determine the total ionic density ρ , we shall make an interpolation between the densities ρ_i^p appropriate to the individual components in their pure state. The interpolation, used also in AL-II, is

$$\frac{1}{\rho(x)} = \frac{1-x}{\rho_1^p} + \frac{x}{\rho_2^p} \quad (5-7)$$

If r_s^1 and r_s^2 are the values of r_s appropriate respectively to pure species one and two, the equivalent interpolation in r_s is

$$r_s^3 = \frac{(1-x)Z_1(r_s^1)^3 + xZ_2(r_s^2)^3}{(1-x)Z_1 + xZ_2} \quad (5-8)$$

This completes the description of the metallic systems and their potentials.

We turn now to the description of the hard core plus tail models of these systems. Consider first the hard core reference fluids. To specify a single component hard sphere liquid, we require, in addition to the particle density ρ , the hard sphere diameter σ of the potential (1-10). We find it convenient in this description to replace σ with the packing fraction η defined (as on page 13) by

$$\eta = \frac{\pi}{6} \rho \sigma^3 = \frac{\text{volume occupied by hard spheres}}{\text{total volume}} . \quad (5-9)$$

The convenience of this arrangement lies in the fact that classical single-component hard sphere liquids of different densities but identical packing fractions are simply scaled versions of each other. Specifically, the structure factor of any such system, expressed as a function of the dimensionless wavenumber variable $y = k\sigma$, is completely determined by η alone.

To specify the two-component hard sphere liquid, we require, in addition to the densities ρ_1 and ρ_2 , two hard sphere diameters σ_1 and σ_2 , in terms of which the reference interactions take the form

$$v_{ij}^{HC}(r) = \begin{cases} \infty & r < \sigma_{ij} \equiv (\sigma_i + \sigma_j)/2 \\ 0 & r > \sigma_{ij} \end{cases} . \quad (5-10)$$

For the same scaling reasons applied to the single-component case, we replace the diameters σ_1 and σ_2 by η and α , defined

by

$$\eta = \frac{\pi}{6} (\rho_1 \sigma_1^3 + \rho_2 \sigma_2^3) = \frac{\text{volume occupied by hard spheres}}{\text{total volume}} \quad (5-11)$$

$$\alpha = \sigma_1 / \sigma_2 \quad (0 \leq \alpha \leq 1, \text{ by convention}) \quad .$$

In this case, the partial structure factors, expressed as functions of the dimensionless variable $y = k\sigma_2$, are uniquely determined by x , η , and α .

In our calculations for the hard sphere reference systems, we have used the structure factors determined from the PY approximation. (References were listed in section I.) Because the forms of these functions are given by Ashcroft and co-workers (1966, AL-I), and because, for our purposes, we need only be aware that they exist, we shall (mercifully) neglect to copy them into this document.

Finally, we consider the description of hard core plus tail models for the metallic systems. Once the reference hard sphere parameters have been selected, we pass to the hard core plus tail model by adding to the potential v^{HC} that part of v^{AL} which lies outside the core. That is, in the pure fluid case, our model potential will be

$$v(r) = \begin{cases} \infty & r < \sigma \\ v^{AL}(r) & r > \sigma \end{cases} \quad , \quad (5-12)$$

while for the binary case, the model potentials will be

$$v_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\ v_{ij}^{AL}(r) & r > \sigma_{ij} \end{cases} . \quad (5-13)$$

It is clear that the adequacy of these model potentials will depend greatly on the choice of the σ 's. This choice is, in fact, a central problem in this work, and will be discussed in detail later on.

To use our perturbation theory for the potentials (5-12) and (5-13), we need to specify the perturbation potentials v_{ij}^1 . It is clear that we have already made the partial specification $v_{ij}^1(r) = v_{ij}^{AL}(r)$ for $r > \sigma_{ij}$. The region $r < \sigma_{ij}$ is inaccessible, so that the form of v_{ij}^1 in this region is in principle immaterial. Indeed, as we shall indicate, this feature is explicitly represented in the formulas we have derived. Computational convenience, then, (meaning the use of (5-1) through (5-4)) usually dictates $v_{ij}^1(r) = v_{ij}^{AL}(r)$ in this region as well. Then, to study the model potentials (5-12) and (5-13) with the theory we have developed, we study the perturbation problem defined by

$$v^{ref} = v^{HC} \quad \text{and} \quad v_{ij}^1 = v_{ij}^{AL} . \quad (5-14)$$

V-B. The Mean Field Calculations

In this subsection, we present the mean field calculations referred to in section II. Consider first the line of singularities in the x - T plane. This is to be calculated by generalizing the mean field formula (2-16) to the case of a

binary system. That generalization may be established in precise analogy with the discussion around equation (4-14), and is, not surprisingly,

$$f_{ij}^1(r) = \{1 - H_{ij}(r)\} v_{ij}^1(r) \quad , \quad (5-15)$$

where

$$H_{ij}(r) = \begin{cases} 1 & r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases} \quad . \quad (5-16)$$

With the choice (5-14), the form of $f_{ij}^1(\underline{k})$ (i.e. the form in reciprocal space) is readily calculated by numerical convolution of $v_{ij}^{AL}(\underline{k})$ with the Fourier transform of H_{ij} .

To find the singularities in the $S_{ij}(\underline{k})$, we seek the zeroes of the denominator D of (3-41). Expressing the denominator in terms of the structure factors (using (3-5)), we can write

$$D = 1 + \beta\rho\{(1-x)S_{11}^{HC}f_{11}^1 + xS_{22}^{HC}f_{22}^1 + 2\sqrt{x(1-x)} S_{12}^{HC}f_{12}^1\} \\ + \beta^2\rho^2x(1-x)\{(S_{12}^{HC})^2 - S_{11}^{HC}S_{22}^{HC}\}\{(f_{12}^1)^2 - f_{11}^1f_{22}^1\} \quad . \quad (5-17)$$

We studied this denominator for the Li-Na system. The valences Z_1 and Z_2 are both unity, and we use $r_c^{Li} = .561 \text{ \AA}$ and $r_c^{Na} = .884 \text{ \AA}$. To simplify the calculation, we have taken both the density and the parameters α , η to be independent of temperature. Then both f_{ij}^1 and S_{ij}^{HC} are independent of temperature, so that (5-17) is a simple quadratic in β . We calculate r_s by interpolating with (5-8) between the representative

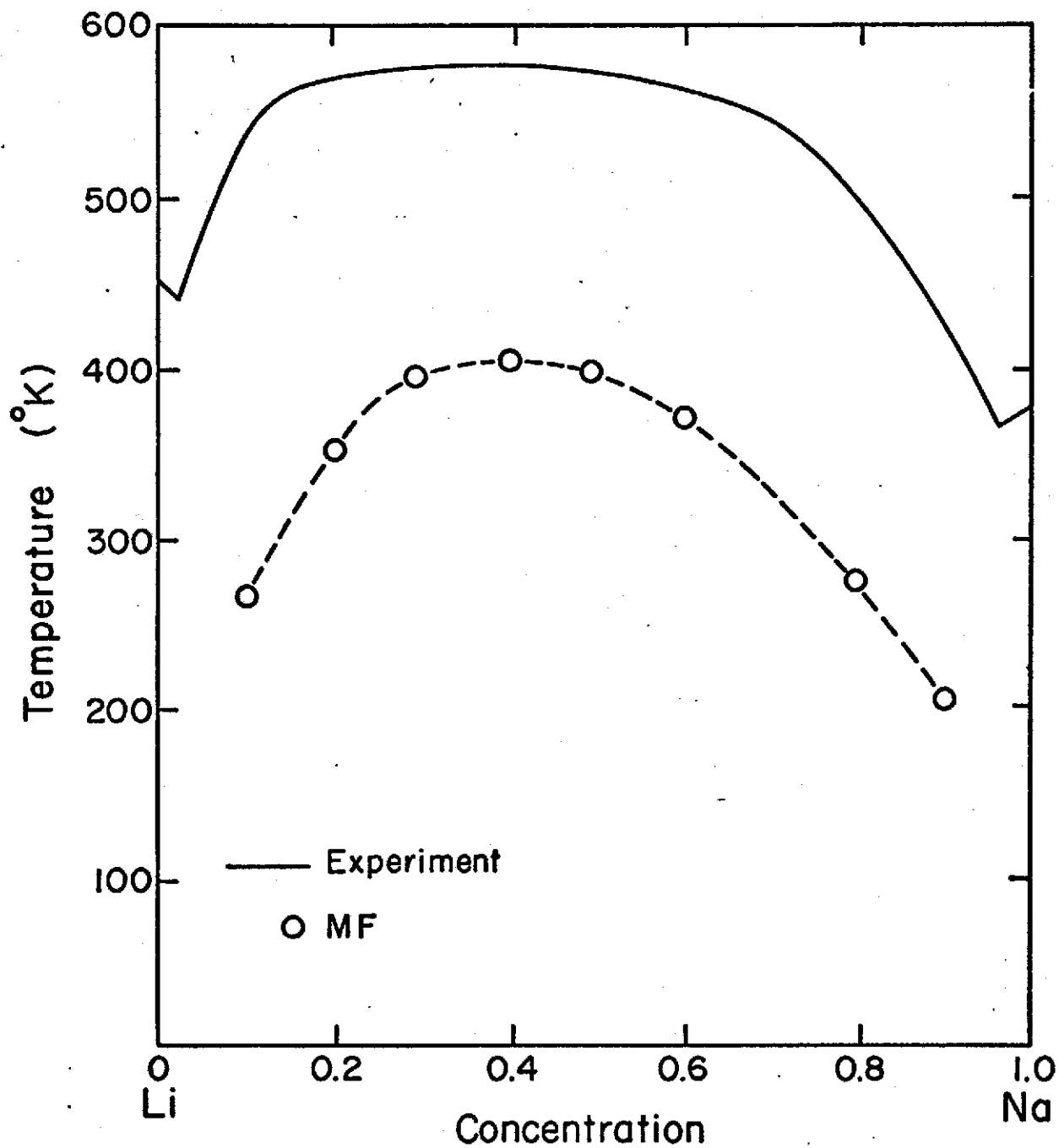


FIGURE 3

Comparison of experimental phase boundary and MF line of singularities in Li-Na. The parameters of the MF calculation are specified in the text.

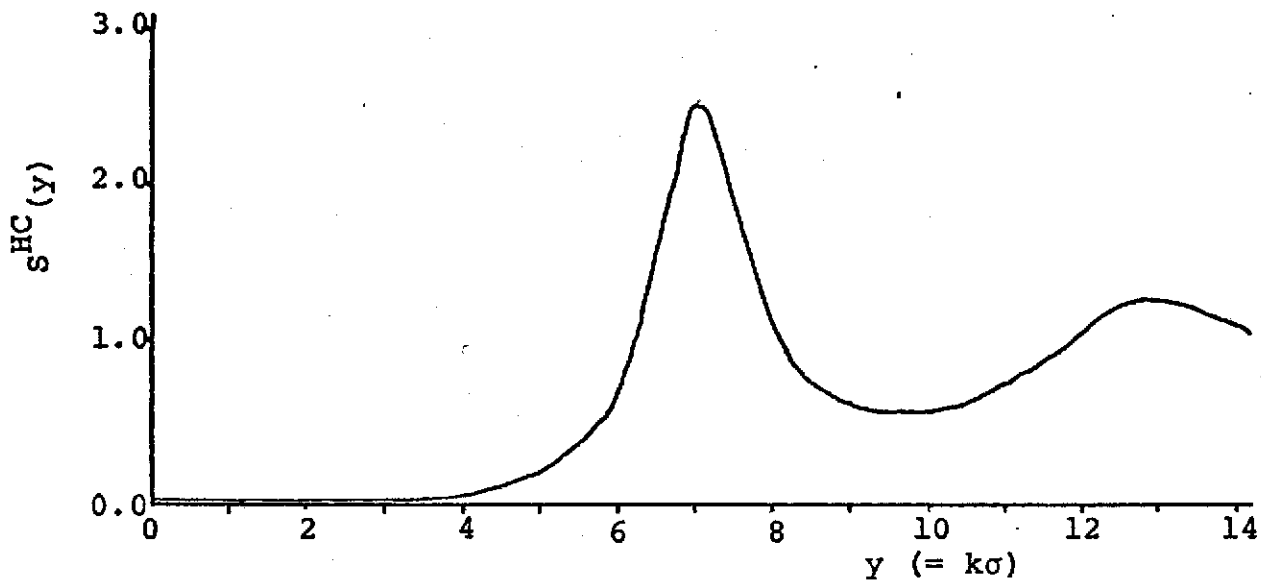
values $r_s^{\text{Li}} = 3.333$ and $r_s^{\text{Na}} = 4.064$. Finally, we choose α and η to be independent of concentration as well. The values used in this calculation are $\alpha = r_s^{\text{Li}}/r_s^{\text{Na}} = .8201$, and $\eta = .456$. (This value of η is that at which Ashcroft and Lekner achieved the pure fluid fit near solidification.)

With these assumptions and the mean field form (5-15), the line of singularities is calculated as follows. The calculation of $f_{ij}^1(\underline{k})$ is, as noted above, a straightforward numerical integration. At each concentration, we calculate these functions at $k = 0$, combine with $S_{ij}^{\text{HC}}(0)$ (from PY) to evaluate D , and solve the resulting quadratic for the two values of T at which $D = 0$. Since $\lim_{T \rightarrow \infty} D = 1$, the stability condition ($D > 0$) will be satisfied for values of T greater than the larger root. It is thus the larger root that we take as the desired singularity temperature. The resulting line of singularities in the x - T plane is presented in Fig. 3, and compared to the experimental Li-Na phase boundary of Schürmann (1971). It is clear that the curve has the proper shape and symmetry, and although the values of T are low, they are certainly of the right order of magnitude.

The second mean field calculation concerns the structure factor of pure liquid Na for arbitrary k . In terms of the structure factor, (2-7) reads

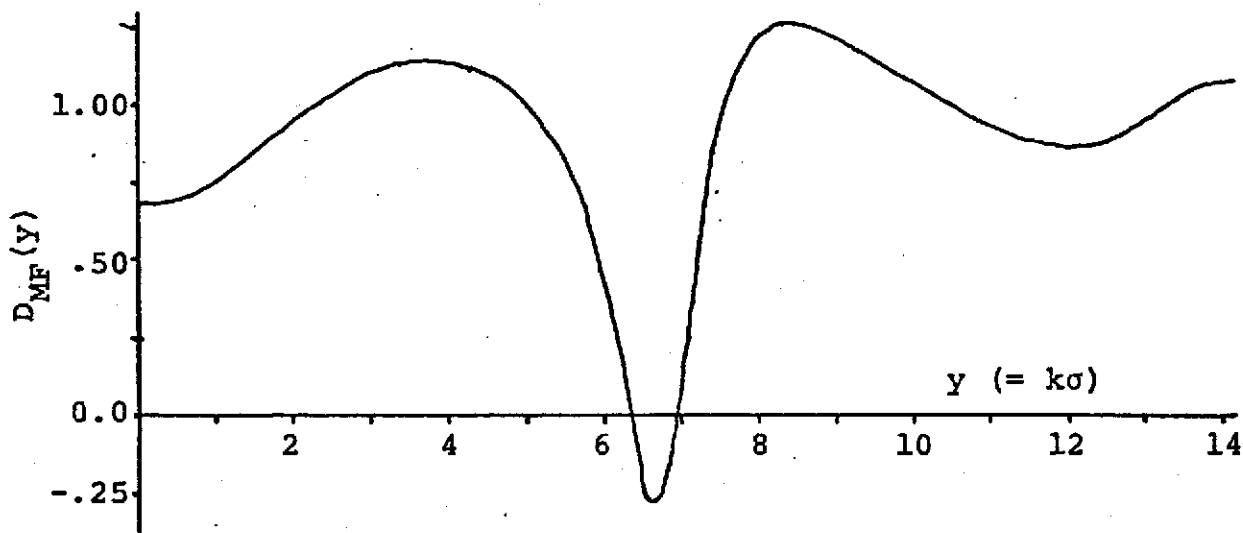
$$S(\underline{k}) = \frac{S^{\text{HC}}(\underline{k})}{1 + \beta \rho S^{\text{HC}}(\underline{k}) f^1(\underline{k})} \quad (5-18)$$

We evaluate this formula using the f_{MF}^1 of (2-16). This expression is of the same form as (5-16) and is thus similarly



4a.

$S^{HC}(y)$ in PY for $\eta = .456$.



4b.

$D_{MF}(y) = 1 + \beta \rho S^{HC}(y) f_{MF}^1(y)$ for Na at $T = 371^\circ K$.

FIGURE 4

evaluated by numerical convolution in reciprocal space.

As we have indicated in several places, a good fit to the structure of pure Na just above solidification ($T = 371^\circ\text{K}$) can be achieved with the (PY) hard sphere structure factor appropriate to $\eta = .456$ (Ashcroft and Lekner, 1966; see also Stroud and Ashcroft, 1972). This structure factor is displayed in Fig. 4a. We note the strong first peak which indicates, as discussed in section II, a strong correlated response at $k\sigma \sim 7$. Then the mean field theory at these wavelengths erroneously predicts a large effect from the perturbation v^1 . To display this effect, we calculated the expression (5-18) in the mean field approximation, taking the reference system appropriate to $\eta = .456$, and using $T = 371^\circ\text{K}$ and $v^1 = v^{\text{AL}}$ determined by $r_c^{\text{Na}} = .884 \text{ \AA}$ and $r_s^{\text{Na}} = 4.064$.* In Fig. 4b, we have displayed the resulting form of the denominator of (5-18). The strong (for these parameters, catastrophic) effect at the peak is clear.

The significance we have attributed to these mean field calculations was discussed in section II, so that no further discussion is called for here.

V-C. Pure Fluid Calculations

In this subsection, we use the theory developed in sections III and IV to calculate the structure factors of single-component fluids. These calculations are, in

*This is a bit of an error with respect to our intent to model Na. The correct value at $T = 371^\circ\text{K}$ is $r_s^{\text{Na}} = 4.045$.

themselves, of less interest than the alloy calculations to come, because the success of our theory is limited to the long wavelength regions, and it is only for the alloy case that we expect any spectacular effects. Nevertheless, these calculations do have some intrinsic interest, and they allow us to discuss many important features of our theory and calculations without the confusion which accompanies the multi-component case.

The plan of these calculations is dictated by the results of the last section and is as follows. We must calculate f^1 to insert into (5-18). We adopt the perturbation approach, expanding f^1 in a series $f^1 = a^1 + o(v^1)^2$, and truncating after the first term. We shall calculate a^1 using our only clear approximation, the form (4-25), and thus limit our investigation to small values of \underline{k} . In the next section, we shall adopt this same scheme, suitably generalized, to calculate the $S_{ij}(\underline{k})$. With a name derived from the nature of the approximation to a^1 (actually to $\rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}')$), we shall refer to this structural approximation as the "mean density approximation" (MDA).

To use (4-25), we must calculate the function $\frac{\partial^2}{\partial \rho_o^2} \rho_2^{\circ, \text{HC}}(\underline{k})$. Using the relation between ρ_2 and $S(\underline{k})$ defined by (1-6) and (1-7), we find

$$\begin{aligned} \frac{\partial^2}{\partial \rho_o^2} \rho_2^{\circ, \text{HC}}(\underline{k}) &= 2(2\pi)^3 \delta(\underline{k}) \\ &+ 2 \frac{\partial}{\partial \rho_o} S^{\text{HC}}(\underline{k}) + \rho_o \frac{\partial^2}{\partial \rho_o^2} S^{\text{HC}}(\underline{k}) . \end{aligned} \tag{5-19}$$

At this point, we face a rather difficult matter. Of the two parameters, ρ and σ , needed to specify the HC reference system, ρ is determined by the particular system under investigation, while σ is left to choice. We shall shortly have a good deal to say on the subject of the best choice of σ . The important point for now is that if σ is selected by any scheme systematically related to the potential v^{AL} , it will depend on the density through the r_g dependence of this potential. A question which might be asked is, should the density derivatives in (5-19) properly include density derivatives of this "best" σ ? This question is actually the first manifestation to this point of what is ultimately a fundamental difficulty in applying this work to metallic systems, where the notion of an ion-ion pair potential depends crucially on the accounting of conduction electron effects. We shall discuss this matter in section V-F. For now, however, we proceed from the assumption, stated in section I, that the ionic structure factors are those appropriate to a classical fluid with pair interactions v^{AL} . Then once a potential v^{AL} has been constructed, and subsequently modelled by a hard core plus tail, we shall investigate the appropriate classical structure without further consideration of the origin of these potentials. Within this view, if the parameter σ is accepted as a characteristic of the potential v^{AL} , it is a given in the problem, and the differentiations in (5-19) are performed only with respect to the explicit density dependence.

We can thus use the definition (5-9) of η to replace

$\rho_0 \frac{\partial}{\partial \rho_0}$ by $\eta \frac{\partial}{\partial \eta}$. On making this change in (5-19), and substituting into (4-25), we find

$$a^1(\underline{k}) = v^1(\underline{k}) + \frac{1}{\rho_0} \int \frac{d\underline{k}'}{(2\pi)^3} v^1(\underline{k}') \left\{ \eta \frac{\partial}{\partial \eta} S^{\text{HC}}(\underline{k}-\underline{k}') + \frac{\eta^2}{2} \frac{\partial^2}{\partial \eta^2} S^{\text{HC}}(\underline{k}-\underline{k}') \right\}. \quad (5-20)$$

We note further that since $\rho_2^{\text{HC}}(r) = 0$, identically for $r < \sigma$, we must also have $\frac{\partial^2}{\partial \rho_0^2} \rho_2^{\text{HC}}(r) = 0$, identically, for $r < \sigma$. Then (remembering that (4-25) is just the Fourier transform of (4-24)), we see that $a^1(\underline{k})$ in this approximation is explicitly independent of the form of $v^1(r)$ for $r < \sigma$. Thus, as discussed earlier, we make the replacement $v^1 = v^{\text{AL}}$. Finally, making the first order approximation $f^1 = a^1$, we have, for the mean density approximation to f^1 ,

$$f^1(\underline{k}) = v^{\text{AL}}(\underline{k}) + \frac{1}{\rho_0} \int \frac{d\underline{k}'}{(2\pi)^3} v^{\text{AL}}(\underline{k}') \left\{ \eta \frac{\partial}{\partial \eta} S^{\text{HC}}(\underline{k}-\underline{k}') + \frac{\eta^2}{2} \frac{\partial^2}{\partial \eta^2} S^{\text{HC}}(\underline{k}-\underline{k}') \right\}. \quad (5-21)$$

We note that the η derivatives of the structure factors can be given an explicit analytic form in the PY approximation, so that the expression in (5-21) is calculated by numerical integration of analytic functions.

We first specialize this calculation to the case of the absolute long wavelength limit, $k = 0$. Our interest in this case derives from two sources. First, at $k = 0$, the expression (5-20) for $a^1(0)$ is exact (for the hard core plus tail potential). Then the only approximations we make in this case

are the first order approximation, and, of course, the PY approximation for $S^{HC}(k)$. Secondly, at $k = 0$, the physical meaning of our results can be discussed using the well-known compressibility sum rule:

$$\lim_{k \rightarrow 0} S(k) = \frac{\beta}{\rho_0} \left\{ - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} \right\}, \quad (5-22)$$

where the expression in braces is the isothermal compressibility.

We have calculated $S(0)$ in the MDA for the v^{AL} appropriate to four alkali metals, Li, Na, K, and Rb, at, in each case, the temperature appropriate to melting. To specify each metallic system, we need to specify r_s , r_c , and Z . The values of r_s listed in Table I are calculated for each element from the density at melting (Smithells, 1967). The r_c value for Rb is taken from Al-II, while the other r_c values are those listed in Ashcroft and Langreth (1967C). The valence Z is unity in each case. For the hard sphere reference system, we follow the suggestion of Ashcroft and Lekner (1966) that each of these elements at melting should be characterized by the same packing fraction. We therefore take the reference fluid in each case to be a hard sphere liquid of the appropriate density with $\eta = .456$. Within the PY approximation, this yields $S^{HC}(0) = .02396$.

The results are presented in Table I. The first three entries after each element are the melting temperature T_M , r_s at melting, and r_c in Å. The next column presents the values calculated for $f^1(0)$ according to (5-21). We must say a word

$$S^{HC}(0) = .02396 \quad (\eta = .456)$$

Metal	$T_M(^{\circ}K)$	r_s	$r_c(\text{\AA})$	$f_{MDA}^1(0)$	$1+S^{HC}f^1$	$S_{MDA}(0)$
Li	453	3.318	.561	-.1965	.6342	.03778
Na	371	4.045	.884	.0872	1.133	.02114
K	337	5.017	1.132	-.0731	.9200	.02604
Rb	312	5.371	1.12	-.5247	.4587	.05223

TABLE I

Results at $k = 0$, $T = T_M$, for the pure alkalis in MDA.

C-2

about the dimensions used for the entries in this column. In this, and all subsequent reportings of f^1 , v^1 , and v^{AL} , we adopt the convention of reporting not these figures directly, but the dimensionless ratio between these figures and the quantity $4\pi Z^2 e^2 / (k_{TF})^2 = \frac{2}{3} Z E_F / \rho_0$. (Here, k_{TF} is the usual Thomas-Fermi wavenumber, or, in the notation of (5-4), just $2k_f \lambda^2$.) Thus, for example, in the column labelled $f^1(0)$, we actually quote the values of, say, $\xi(0)$, where

$$f^1(0) = \frac{4\pi Z^2 e^2}{(k_{TF})^2} \xi(0). \quad (5-23)$$

In these terms, the important quantity $\beta \rho_0 f^1(k)$ is given by $\frac{2}{3} Z \xi(k) T_F / T$, where T_F is the usual Fermi temperature. The last two columns present, from these values of f^1 , the values of the denominator in (5-18) and the resulting $S(0)$.

We note from the compressibility sum rule (5-22) and the comparison between $S(0)$ and $S^{HC}(0)$, that the compressibility can be either increased or (in the case of Na) decreased by the addition of v^1 . Numerically, this reflects the fact that the calculated values of $f^1(0)$ are of either sign. We note that, for these potentials, the mean field form $f_{MF}^1(0)$ (which is, from (2-16), just $\int_{\sigma}^{\infty} v^1(r) r^2 dr$) will not have this property, since the potentials v^1 defined here are predominantly negative for $r > \sigma$. (These potentials are displayed in AL-II. In relation to the hard sphere diameter defined by $\eta = .456$, they each take a form qualitatively like that displayed in Fig. 2.) That the correct form of $f^1(0)$ should in fact permit either sign is apparent from the fact that these negative v^1

nevertheless contain both attractive and repulsive regions. At sufficiently high density, the nearest neighbor position will be placed in the repulsive region of v^1 , so that a decrease in compressibility is expected on passing from hard core to hard core plus tail models. This is, of course, a correlation effect, since a nearest neighbor position can only be defined for correlated particles. It is instructive to note, from AL-II, that the nearest neighbor position in Na is indeed just into the repulsive part of v^1 , while in Rb, it is well into the attractive region.

We turn now to the results at $k \neq 0$. In Fig. 5, we present the functions $f^1(\underline{k})$ for Li, Na, and K, calculated in the MDA (that is, by (5-21)). Note that to present only $f^1(\underline{k})$, we need not present the temperature (though temperature will affect the careful selection of r_s .) As with the $k = 0$ results, we plot these functions in units of $4\pi Z^2 e^2 / (k_{TF})^2$.

The MDA is a long wavelength (first order) approximation for f^1 . We expect it to be valid for wavelengths longer than the correlation range in the reference fluid. The correlation range should be given roughly by the inverse of the width of the first peak in $S^{HC}(k)$, since this peak defines the dominant oscillation of the radial distribution function $g(r)$ (see equation (1-6)). From consideration of the HC structure factor of Fig. 4a, we expect, optimistically, that what we might call the range of "a priori validity" of the MDA should extend only out to $k\sigma \sim 1$. The interesting feature of the results presented in Fig. 5 is that, in spite of strong

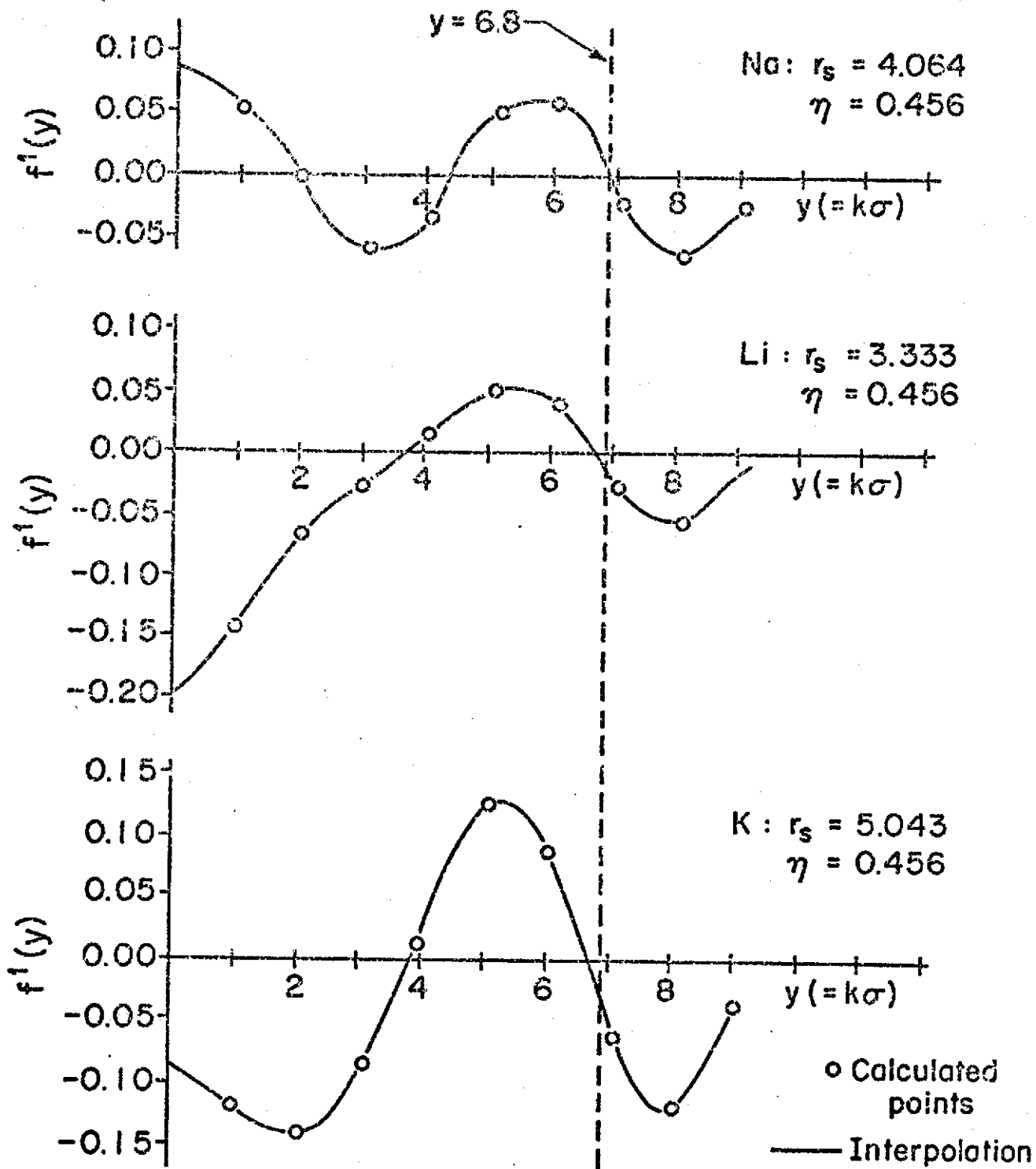


FIGURE 5

$f^1(y)$ in MDA for Na, Li, and K.

variations in the shape and amplitude of the curves, the curves all go through zero at a value of $k\sigma$ near the hard sphere peak ($k\sigma_{\text{peak}} = 6.8$). This means that for a small region around the peak, the MDA gives to $S(k)$ values which are in accord with our physical expectation that $S(k)$ should be little affected at the peak by v^1 . This region is really very narrow. In Na, the structure factor has been driven to negative values by $k\sigma = 7.0$. (Note from (1-5) that the structure factor is a positive definite quantity.) Yet the existence of such a region in each element seems to suggest that this effect may be, as discussed at the end of section IV, a manifestation of finite particle size.

Until now, we have been content to neglect the problem of selecting the hard sphere reference parameters in favor of illustrating, with simple (but not unreasonable) values, the general features of these theories. Though we shall adopt this tactic once more to make a point when we turn to the binary alloy case, we must ultimately consider the selection these parameters with care. It is convenient to begin the discussion of this matter before we leave the simpler pure fluid case.

For the pure fluid, we wish to develop a systematic procedure for selecting the "best" σ of the model potential (5-12), given the potential v^{AL} . The aim of this work is to be able, with this model, to calculate closely the structure appropriate to v^{AL} . Consideration of the physics involved

suggests that, with a good enough perturbation theory, σ could be defined through an empirical approach. The work proceeds in two stages. We first model the potential v^{AL} with the potential of (5-12), that is, with a potential which is infinite for all r less than some diameter σ , and equal to the real potential for $r > \sigma$. We then calculate the structure by a perturbation theory in which the perturbation is that part of v^{AL} which lies outside the core of diameter σ . Consider for a moment a sequence of such models for a single potential v^{AL} , arranged in order of decreasing σ . If we could sum all orders of the perturbation series, and hence calculate exactly the structure appropriate to each model potential, we should find in this sequence that the structure eventually becomes independent of σ . This will happen when v^{AL} takes on a value at $r = \sigma$ which is more than a few kT above its minimum value. Then further decreases in σ will affect the model potential only in a region which is virtually never sampled. In reality, of course, we can calculate the structure only in an approximation which is based fundamentally on the smallness of the perturbation. With decreasing σ , the perturbation becomes larger, and the approximation will eventually break down. If, however, the approximate theory works reasonably well for a perturbation of order one or two times kT , we might observe some vestige of the ideal result. That is, there might still be a small range of σ for which the calculated structure is independent of σ . This structure would clearly be the structure we are after.

To search for such a region, we repeated, for many values of η , the $S(0)$ calculation for pure liquid Na described above. A region of independence does not appear. In fact, the result is quite strongly dependent on η . At $T = 371^\circ\text{K}$ and for $r_c^{\text{Na}} = .884 \text{ \AA}$ and $r_s^{\text{Na}} = 4.064$, the values of $S(0)$ in the MDA vary almost linearly between .0335 at $\eta = .400$ and .0140 at $\eta = .500$. The result of this calculation is plotted in Fig. 6. This result provides a revealing and not too encouraging look at the adequacy of the approach.

In any case, this result means that the best we can do is try to devise an external criterion for selecting σ which will bring the calculated model structure closest to the structure appropriate to v^{AL} . It is clear that the essence of that criterion will be to select the largest hard sphere diameter consistent with a reasonable modelling of the potential. This consideration suggests an approach in the spirit of that taken by Ashcroft and Langreth (AL-II), who selected σ as that point in the core region of $v^{\text{AL}}(r)$ at which the potential has risen $\frac{3}{2} kT$ above its minimum. Such an approach seems to contain the essential physics of our problem. In more recent work (e.g. Stroud and Ashcroft, 1972) a diameter σ was selected for a different problem by a variational approach. This approach is based on the result (Lukes and Jones, 1968)

$$F \leq F^{\text{HC}} + \langle U \rangle_{\text{HC}}, \quad (5-24)$$

where F is the free energy of the fluid with internal potential $U(R)$, F^{HC} is the free energy of some hard core fluid, and

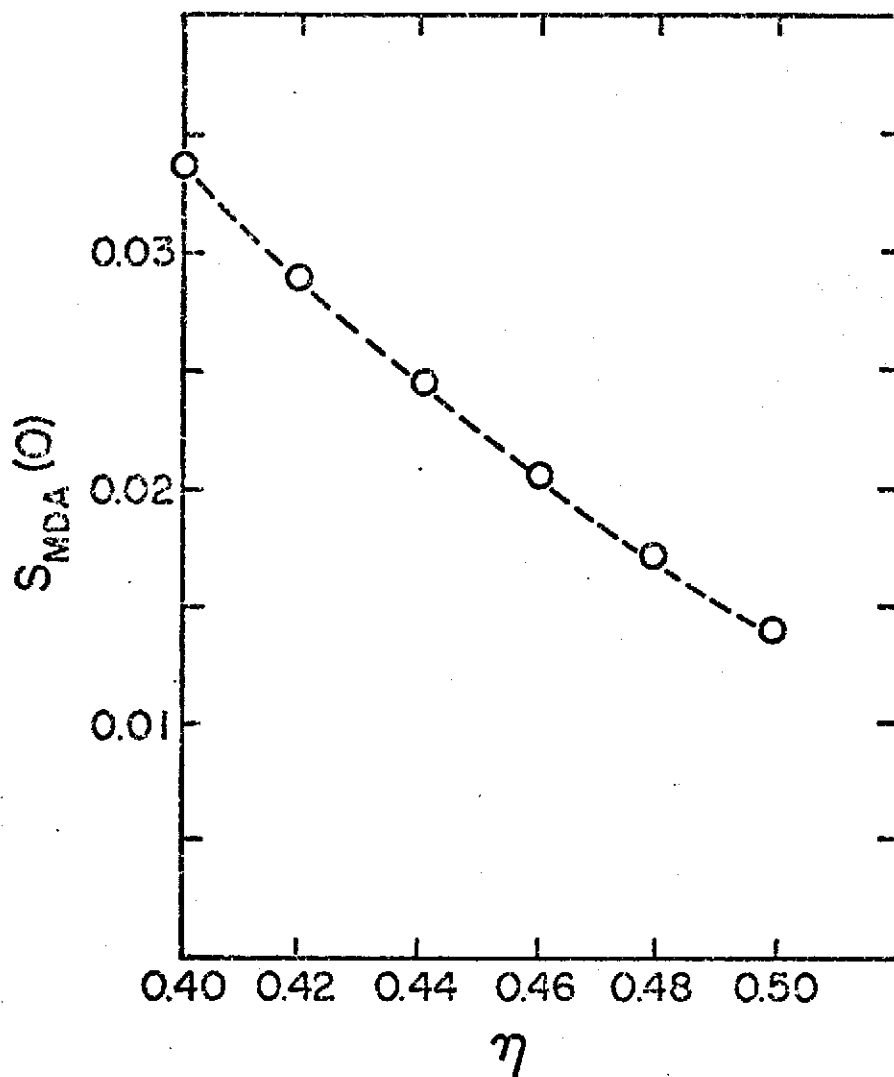


FIGURE 6

$S_{MDA}(0)$ vs. η for $r_s^{Na} = 4.064$, $r_c^{Na} = .884 \text{ \AA}$.

$\langle U \rangle_{\text{HC}}$ is the thermal average of $U(R)$ taken with the hard core distribution functions. For the case of a pure fluid with pair interaction v^{AL} , (5-24) reads

$$F \leq F^{\text{HC}} + \frac{1}{2} \int d\underline{r} d\underline{r}' v^{\text{AL}}(\underline{r}-\underline{r}') \rho_2^{\circ, \text{HC}}(\underline{r}, \underline{r}') . \quad (5-25)$$

In an effort to calculate the liquid free energy, the right side of this inequality can be minimized with respect to the hard core diameter σ . Though such an approach may seem to bear little direct relation to our problem, it, in fact, appears to contain essentially the same physics as the $\frac{3}{2} kT$ rule, for it gives very nearly the same results for both the magnitude and temperature dependence of σ . The advantage of the variational approach is that the right side of (5-25) can be simply expressed as an integral in reciprocal space and the whole procedure automated to a great extent. We make use of the generalization of this procedure for binary alloys in the next section.

This completes the discussion of our results for pure fluids.

V-D. Binary Alloys I: The $k = 0$ Results and Phase Separation.

In this subsection, we apply the theory of sections III and IV to calculate for binary alloys the line of singularities in the x - T plane. The elements of these calculations are the same as those of the mean field calculation presented in V-B. We calculate f_{ij}^1 and search for the highest temperature at which D of (5-17) equals zero. In the present work,

however, we shall replace the mean field approximation to f_{ij}^1 by the mean density approximation, suitably generalized to the alloy case. As in the case of the pure fluid calculations, the MDA is exact in first order at $k = 0$, so that, once the hard core plus tail potentials are specified, the only approximations in the present section are the first order approximation and, as usual, the use of the PY approximation for the $S_{ij}^{HC}(\underline{k})$.

To construct the MDA for the alloy case, we consider the long wavelength approximation (4-31) to $a_{ij}^1(\underline{k})$, and proceed as we did for the pure fluid case. We can express the derivatives $\frac{\partial^2}{\partial \rho_i^0 \partial \rho_j^0} \rho_{lm}^{0,HC}(\underline{k})$ in terms of the $S_{ij}^{HC}(\underline{k})$, the reference structure factors. We differentiate only the explicit density dependence, make the replacement $v_{ij}^1 = v_{ij}^{AL}$ because the form of (4-31) is observed to be independent of $v_{ij}^1(r)$ for $r < \sigma_{ij}$, and finally make the first order approximation $f_{ij}^1 = a_{ij}^1$. The result is a set of expressions for $f_{ij}^1(\underline{k})$ which are analogous to (5-21) but more complicated. These expressions are presented in appendix D. They form the MDA to f_{ij}^1 . We note that for this case as well, the density derivatives may be given an explicit form in the PY approximation, so that the calculation of a_{ij}^1 , though by now a lengthy process, is in principle just a numerical integration over analytic functions.

For the first calculation, we sought a comparison between the mean field and mean density approximations. To do this, we use the MDA in a calculation which is otherwise identical to the mean field calculation of section V-B. That is, we set

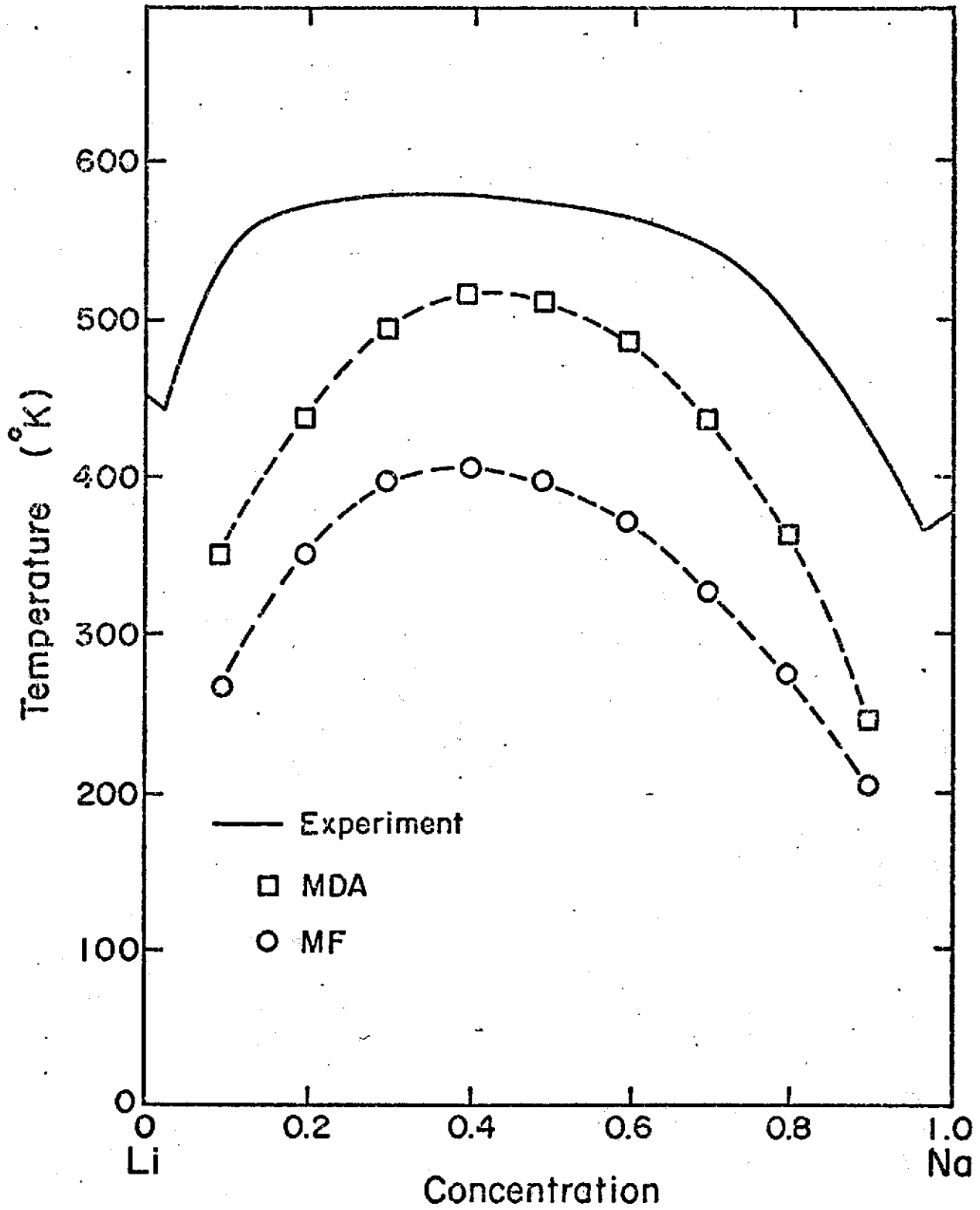


FIGURE 7

Comparison of line of singularities calculated in MF and MDA with identical parameters.

$r_s^{\text{Na}} = 4.064$, $r_s^{\text{Li}} = 3.333$, independent of temperature, and $\alpha = .8201$, $\eta = .456$, independent of temperature and concentration, solve the resulting quadratic, $D = 0$, for two roots T , and plot the higher root. The results are plotted in Fig. 7, where, for comparison, we have repeated from Fig. 3 the experimental Li-Na phase boundary and the mean field results. We can see that the asymmetry has been maintained, and that the curve has been shifted upward by about 100° in passing from mean field to MDA. That the curve has been shifted towards the experimental phase boundary is probably not important, since the selection of α and η has been quite arbitrary. This calculation shows once again that, although we originally considered correlation effects at the peak, they are of importance at long wavelengths as well. Also, the degree of success achieved by this calculation tends to support our suggestion that the lesson of the mean field success is that we should seek a consistent low order approximation to f_{ij}^1 .

To complete this comparison, we present in Table II the numerical results of these two calculations. Within our convention for reporting potentials in k-space, we list, for each concentration, the values of $v_{ij}^{\text{AL}}(0)$, $f_{ij}^1(0)$ from mean field, and $f_{ij}^1(0)$ from MDA. We also list the singularity temperatures for the two calculations. We observe that in passing from mean field to MDA, the $f_{ij}^1(0)$ are substantially changed, while their arrangement, in which f_{12}^1 lies roughly midway between f_{11}^1 and f_{22}^1 , is essentially unchanged. Perhaps the second of these observations explains why these substantial

x	$v_{AL}^1 \begin{pmatrix} 11 \\ 22 \\ 12 \end{pmatrix}$	$f_{MF}^1 \begin{pmatrix} 11 \\ 22 \\ 12 \end{pmatrix}$	$f_{MDA}^1 \begin{pmatrix} 11 \\ 22 \\ 12 \end{pmatrix}$	$T_{MF} (^{\circ}K)$	$T_{MDA} (^{\circ}K)$
.000	1.223	-.138			
	2.455	-.127			
	1.841	-.133			
.100	1.190	-.150	-.202	265	349
	2.385	-.136	-.059		
	1.787	-.144	-.168		
.200	1.156	-.161	-.204	351	434
	2.314	-.145	-.028		
	1.736	-.155	-.160		
.300	1.124	-.172	-.201	394	490
	2.256	-.153	.005		
	1.691	-.165	-.152		
.400	1.093	-.182	-.213	406	514
	2.201	-.162	.033		
	1.648	-.175	-.145		
.500	1.065	-.193	-.218	396	511
	2.151	-.170	.055		
	1.609	-.185	-.141		
.600	1.037	-.203	-.223	369	486
	2.104	-.178	.071		
	1.571	-.195	-.138		
.700	1.012	-.214	-.230	327	436
	2.059	-.186	.081		
	1.536	-.204	-.138		
.800	.987	-.224	-.236	272	358
	2.017	-.194	.085		
	1.503	-.214	-.140		
.900	.964	-.234	-.244	205	243
	1.978	-.202	.085		
	1.472	-.223	-.143		
1.000	.935	-.244			
	1.941	-.210			
	1.438	-.232			

TABLE II

Comparison of MF and MDA calculations of $f_{ij}^1(0)$ in Li-Na.

changes in the f_{ij}^1 give rise to only moderate changes in the singularity temperatures.

We must now turn to the problem of the careful selection of the reference fluid parameters α and η . The elements of the problem here are the same as in the pure fluid case, so we go straight away to the variational technique. For the binary system, the realization of (5-24) is

$$F \leq F^{HC} + \frac{1}{2} \sum_{ij} \int d\underline{r} d\underline{r}' v_{ij}^{AL}(\underline{r}-\underline{r}') \rho_{ij}^{\circ, HC}(\underline{r}, \underline{r}') . \quad (5-26)$$

The integral on the right side of (5-26) can be written as an integral in reciprocal space over $v_{ij}^{AL}(\underline{k})$ and the partial structure factors $S_{ij}^{HC}(\underline{k})$. The hard core free energy F^{HC} is known for mixtures in the PY approximation (Lebowitz and Rowlinson, 1964). The plan is to select the best values of α and η by minimizing the right side of (5-26) at each concentration and temperature.

We have applied this variational technique to the calculation of the line of singularities of the Li-Na system. The plan of the calculation is as follows. Given the concentration and a temperature T , we calculate the density of the alloy by interpolating with (5-7) between the published densities of Li and Na at T (Smithells, 1967). In this way, we make some account of the thermal expansion of the system. From the density, the three potentials $v_{ij}^{AL}(\underline{k})$ are determined as specified in V-A, and, in turn, the "best" hard sphere parameters, α and η , are determined by the variational technique. With the potentials, temperature, and α and η , the

denominator D of (5-17) can be calculated in the MDA. The calculation is then repeated for several values of T, to seek out that T for which $D = 0$.^{*} This defines an unambiguous procedure for calculating the line of singularities.

We have performed this calculation for three concentrations, .3, .4, and .5, of Na in Li, using (as always) $r_C^{\text{Na}} = .884 \text{ \AA}$ and $r_C^{\text{Li}} = .561 \text{ \AA}$. The zeroes of D are found to lie quite high, at $T = 1000^\circ\text{K}$, 1040°K , and 975°K respectively. (The experimental phase separation temperatures are 574°K , 576°K , and 560°K respectively (Schürmann, 1971).) The value calculated for α by the variational technique seems to be almost independent of concentration and temperature at .77. The values of η appropriate to the three points (x,T) presented here are .274, .271, and .284 respectively. These are not unreasonable values, since, in relation to the solidification value $\sim .45$ at 400°K for Na, they represent an average change of $-.03$ for each 100°K , precisely as suggested by Al-II (though carried to temperatures well outside the range for which that suggestion was intended.) A more complete specification of the densities and the calculated values of α and η is presented in Table III.

To round out the picture of the α and η dependence of our results, we performed a calculation of a different sort, to discover what values of α and η are required to get the "right" temperatures. Of course, we can't fit two parameters

^{*}For temperature dependent density and hard sphere parameters, the denominator is no longer a simple quadratic in T.

x	T(°K)	r_s^{Li}	r_s^{Na}	α	η	D(T)
.300	950	3.42	4.28	.770	.280	-.033
	1000	3.42	4.30	.768	.274	.005
	1050	3.44	4.32	.772	.266	.029
.400	573	3.34	4.12	.771	.351	-.608
	773	3.38	4.20	.762	.315	-.233
	900	3.40	4.25	.770	.292	-.095
	1000	3.42	4.30	.773	.277	-.020
	1040	4.43	4.32	.771	.271	.005
.500	950	3.42	4.28	.774	.288	-.015
	975	3.42	4.29	.772	.284	.000
	1050	3.44	4.32	.775	.274	.048

TABLE III

Results of the variational calculation for Li-Na. Values for r_s^{Li} and r_s^{Na} are calculated from published density data (Smithells, 1967), α and η are determined by the variational technique, and D(T) (at $k = 0$) is calculated in the MDA. The points presented were calculated in the search for T at which $D(T) = 0$.

to a single data point, but, for each concentration, there presumably exists a locus of points in the α - η plane for which $D = 0$ at the desired temperature. Then the scheme of this calculation is as follows. Given the concentration x (we choose $x = .4$, near the critical value, so that the line of singularities lies close to the phase boundary), the observed phase separation temperature is defined (575°K from Schürmann, 1971). Then the density and three potentials are calculated for this x and T as described above, and the value of D investigated as a function of α and η . In Fig. 8, we present the α - η plane for $T = 575^\circ\text{K}$ and $x = .4$. The boundary in this plane divides the region where D is greater than zero (above the boundary) from the region where D is less than zero. The boundary itself is then the desired locus of points at which $D = 0$. For comparison, the variational values assigned to α and η at this x and T are $\alpha = .772$ and $\eta = .35$.

The range of what we might consider reasonable values for α and η is determined primarily by our physical feeling for the packing fraction η . We do not want to select η much above $\sim .47$, since the experience in pure fluids suggests that the system would tend to crystallize. Since 575°K is about 125° above the melting point of Li (at $x = .4$, the mixture is Li rich), the experience of AL-II might suggest an η of .41 to .42. (The lower value obtained from the variational calculation presumably reflects both the presence of Na and the effects of thermal expansion.) For these reasons, we have chosen to exhibit in Fig. 8 the region between $\eta = .35$ and

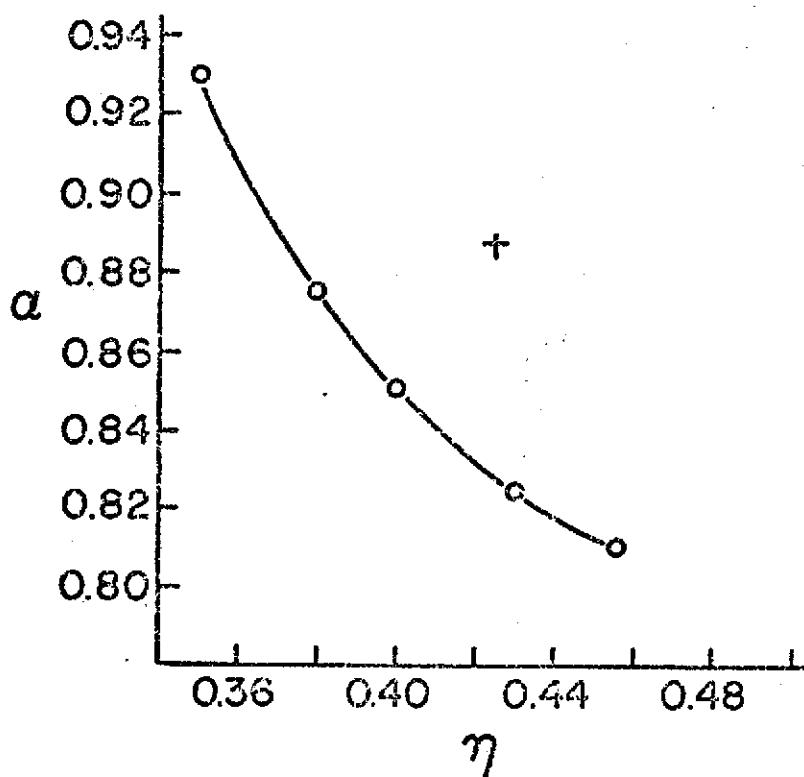


FIGURE 8

The α - η plane at $T = 575^\circ\text{K}$, $x = .4$, in Li-Na.
The denominator D is greater than zero above
the line, and less than zero below.

$\eta = .46.$

From these results, the selection of α and η emerges as one of the central difficulties in our work. It is clear that the temperature at which $D = 0$ is quite sensitive to the values of these parameters. The variational calculation, which probably has the best a priori justification, has yielded temperatures which are far too high. We have seen that the "correct" temperature can be obtained with "reasonable" values for α and η but the physical meaning of those values, indeed the physical meaning of such a fitting procedure, is unclear. The confusion at this point suggests that, while we may ultimately have learned something of the form of the structure factors near phase separation, considerably more work on the modelling of the systems (and on the theory itself) may be needed before we can predict this transition in real systems. Our difficulties here may also derive from the special problem of the metallic pair potential, to which we shall turn briefly in section V-F.

V-E. Binary Alloys II: The Results for Finite k .

We turn now to our results in the MDA for binary alloys at finite k . In the previous section, we identified points at which

$$\lim_{k \rightarrow 0} D(k) = 0, \quad (5-27)$$

where $D(k)$ is the denominator of (5-17). In this section, we examine one such point in detail, to discover the manner in

which $D(k)$ goes to zero in the MDA as $k \rightarrow 0$, and to observe the MDA structure factors themselves. Ultimately, we intend such work to form the basis of a resistivity calculation, and we conclude this section by suggesting a program for such a calculation.

We have chosen the point defined by $x = .4$, $T = 575^\circ\text{K}$, $\alpha = .825$, and $\eta = .430$. The values of α and η were estimated from earlier results to give $D(0) = 0$ in Li-Na at this concentration and temperature. These estimates are in fact slightly in error, so that the value of $D(0)$ is $-.0013$. In Table IV, we list values of $y = k/2k_F$ and the corresponding values of $D(y)$ in the MDA. These values of y were selected in another unit system, and turn out in the present units to be multiples of $.01692$, a fact which we have indicated in the second column of Table IV. In these units, the first peak of the structure factor occurs at about $y = 1.2$, so that the region in which the MDA is most to be trusted extends out to roughly $y = .2$. When these values of D are plotted vs. y on a log-log plot, they are observed to follow quite well a straight line of slope two for the small values of y , but move away from this line for the larger values (see Fig. 9). This suggests that the singularity may be of the sort

$$D = a + bk^2 . \quad (5-28)$$

This type of singularity appears in more conventional mean field theories. Because of the error in α and η , we would expect for these data to set $a = -.0013$. This suggests that we

$y(=k/2k_F)$	$y/.01692$	$D(y)$	$D(y)-D(0)$
0.00	0	-.0013	.0000
.03384	2	.0102	.0115
.05076	3	.0245	.0258
.06768	4	.0442	.0455
.08460	5	.0690	.0703
.10152	6	.0985	.0998
.11844	7	.1322	.1355
.13536	8	.1678	.1691
.16920	10	.2526	.2539
.20304	12	.3418	.3431
.25380	15	.4748	.4761
.33840	20	.6579	.6592
.50760	30	.7951	.7964
.67680	40	.8709	.8722

TABLE IV

Results in MDA for $D(y)$ at $y \neq 0$. Calculated for Li-Na at $x = .4$, $T = 575^\circ\text{K}$, $\alpha = .825$, and $\eta = .430$.

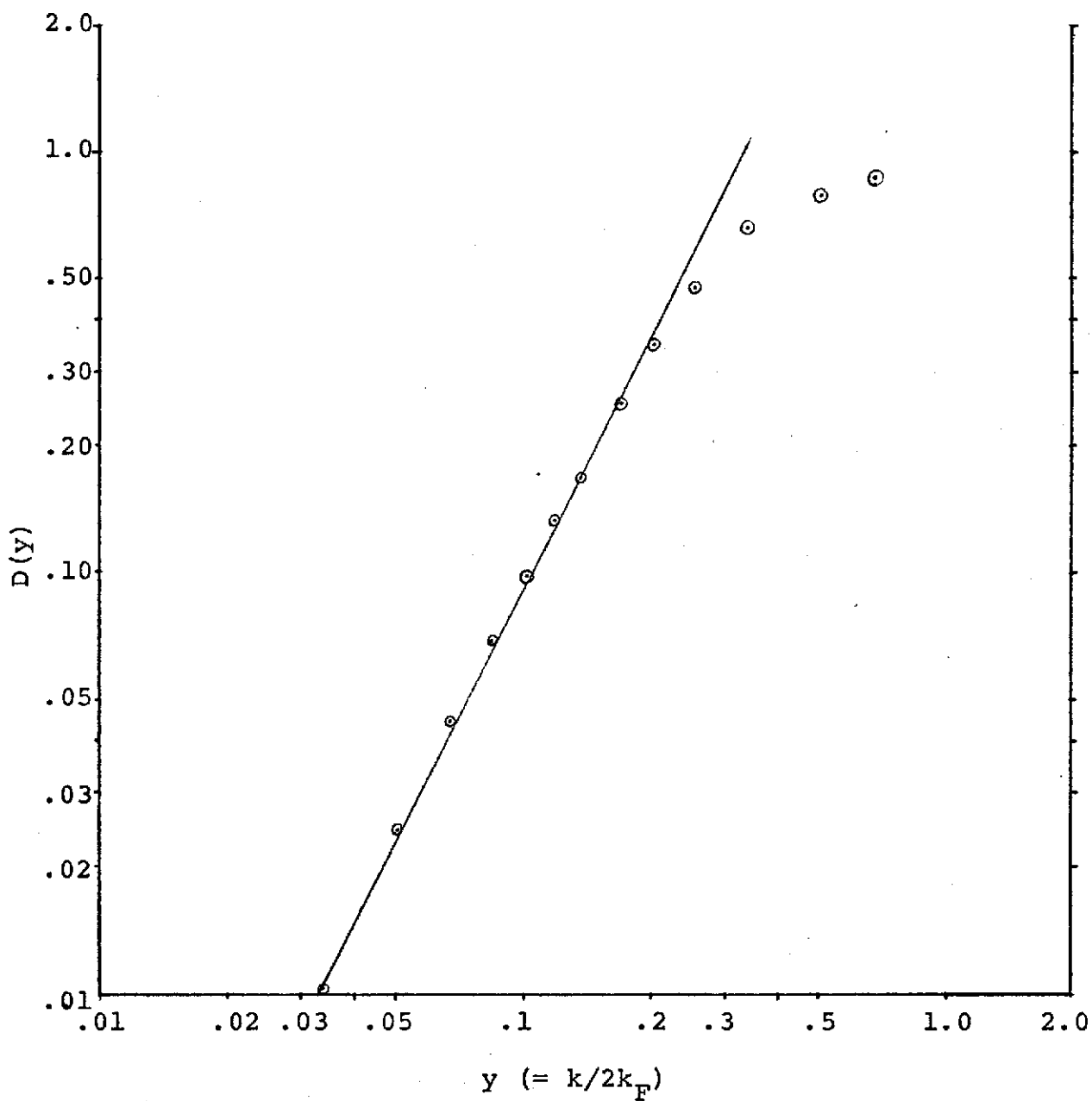


FIGURE 9

Log-log plot of $D(y)$ in MDA for Li-Na at $x = .4$, $T = 575^\circ\text{K}$, $\alpha = .825$ and $\eta = .430$. The straight line has a slope of two.

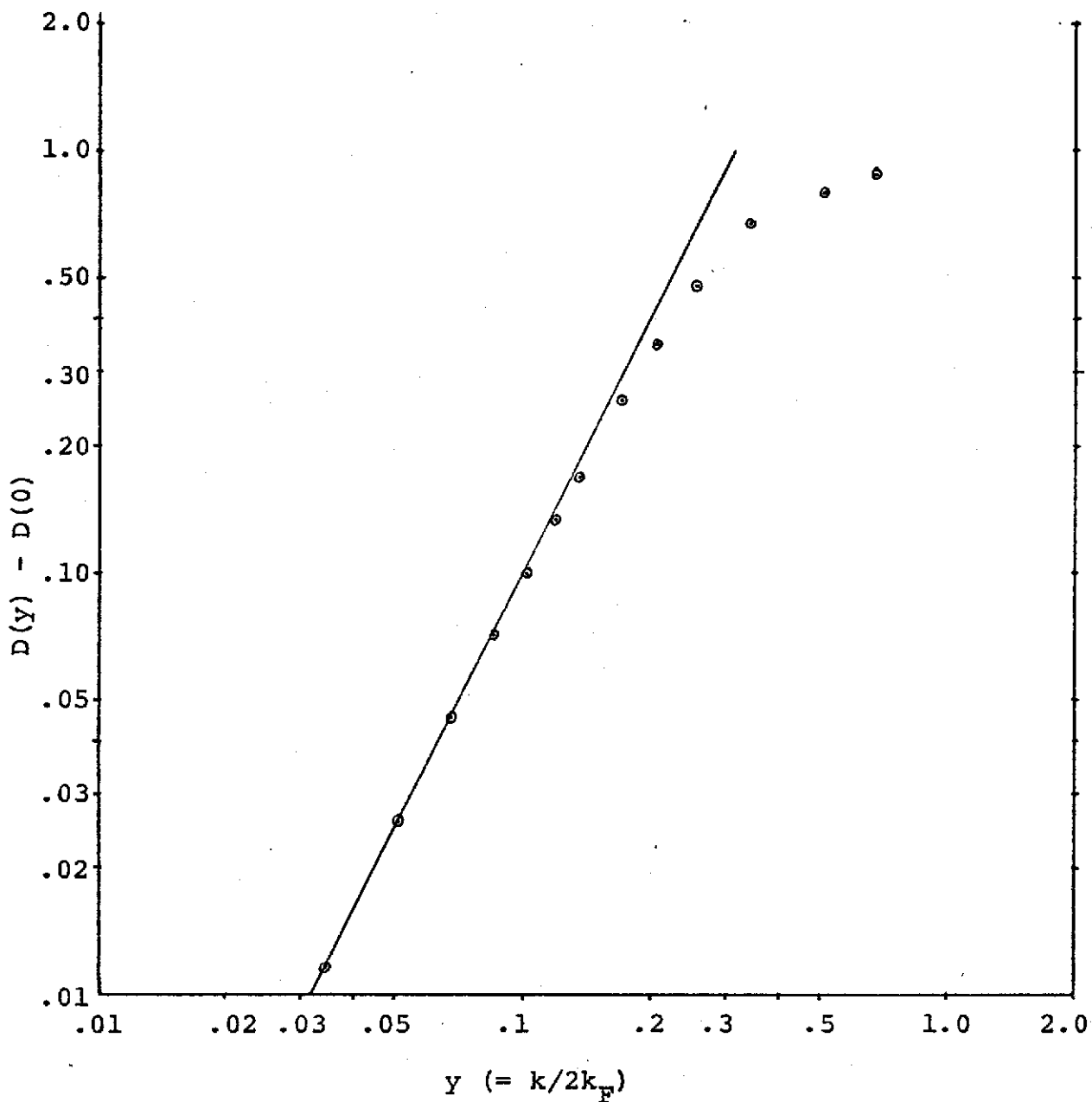


FIGURE 10

Log-log plot of $D(y) - D(0)$ in MDA for Li-Na at $x = .4$, $T = 575^\circ\text{K}$, $\alpha = .825$ and $\eta = .430$. The straight line has a slope of two.

construct a log-log plot of $(D + .0013)$ vs. y . This has been done, and is presented in Fig. 10. The straight line in this figure also has a slope of two, and now appears more properly as an asymptote. This observation lends support to the proposed form (5-28), viewed as a limit.

There are two points to be made about these results. First, they coincide with the physical expectation that the singularity at $k = 0$ is the first (highest temperature) of the possible long wavelength singularities. This must be true on physical grounds, since any singularity will render the system unstable, while real alloy systems of critical concentration are stable down to the critical temperature, at which point the structure factors diverge at $k = 0$. Secondly, while we can present no direct evidence for a k^{-2} singularity, we must have a singularity which occurs less rapidly than k^{-4} in order that the resistivity integral (1-1) converge at the lower limit. That our long wavelength approximation conforms to both these physical expectations, despite the complexity of the binary alloy formulas, is a gratifying result.

In Figure 11, we present the structure factors $S_{ij}(k)$ calculated at this point in the MDA. They have been formed using (3-40) for the χ_{ij} and the relation (3-5) between χ_{ij} and S_{ij} . In the same figure, we have presented for comparison the (PY) structure factors of the underlying hard core reference mixture (the mixture defined by $x = .4$, $\alpha = .825$, and $\eta = .430$). The MDA structure factors appear to join rather smoothly with the HC structure factors at point roughly midway

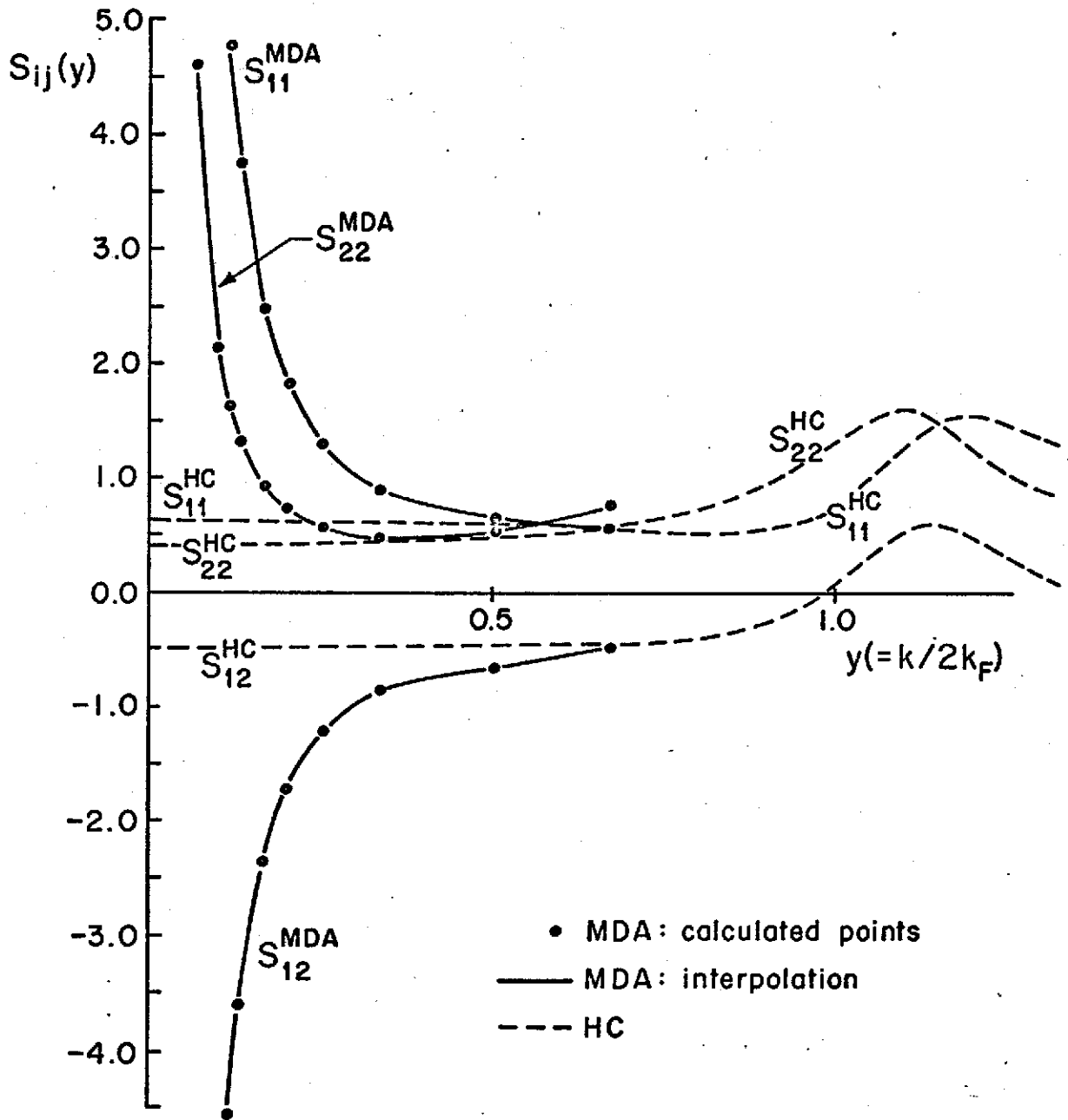


FIGURE 11

Partial structure factors for Li-Na at $x = .4$, $T = 575^\circ\text{K}$, $\alpha = .825$, and $\eta = .430$. The solid lines represent the structure in the MDA, and the dashed lines represent the structure of the hard sphere reference system.

between the origin and the first peaks. This fact is in accord with our physical expectation for these systems, and, as discussed below, might be put to good use in a resistivity calculation. However, the MDA is expected to be valid only for small k ($y \lesssim .2$) so that the ultimate meaning of this observation is unclear.

This completes the report on the calculations we have performed for metallic systems. Although we have stopped short of a resistance calculation, we can at least indicate the shape that such a calculation may take. We are interested in shedding some light on the conjecture, discussed in section I, that the resistivity anomaly observed by Schürmann and Parks in Li-Na is a long wavelength effect. As indicated in (1-1), what we need for a resistance calculation is the form of the $S_{ij}(k)$ for $0 \leq k \leq 2k_F$. What we have is an approximation valid for small k ($0 \leq k \lesssim 2k_F/7$) and the physical idea that the structure factors $S_{ij}(k)$ should remain substantially unchanged around the peaks as we pass from hard core to hard core plus tail model potentials. It is immediately clear that we are in no position to do any serious quantitative calculation. Yet we might still imagine a calculation which could lend qualitative support to the long wavelength hypothesis. We might, for instance, simply calculate the contribution to the resistivity from that part of the integral in (1-1) for which the MDA is valid. More completely, we might calculate the structure in the MDA at small wavelengths, and join the results smoothly to the HC structure factors around the peaks,

thus incorporating what we expect will be the essential features of $S_{ij}(k)$ near phase separation. (As noted above, the MDA, somewhat inexplicably, seems to be doing this job for us.)

The trick in any such calculation, of course, is going to be to get the T-dependence right (since we are looking for a temperature dependent effect.) This involves understanding both the "normal" (that is, linear) and the anomalous parts of the resistivity. We might, however, simplify a first calculation by supposing that the "normal" part is ultimately attributable to the hard cores, that is, could be dealt with by a HC structural model of sufficiently subtle temperature dependence. (In view of the successful resistivity calculations of AL-II, this may not be an unreasonable assumption.) Under such an assumption, the plan of a first simple calculation would be to ignore the temperature dependence of the density and the "best" hard sphere model, and study only the remaining T dependence of the difference $\rho_{elec}^{MDA} - \rho_{elec}^{HC}$. We plan to undertake such a calculation in the near future.

V-F. The Metallic Pair Potential

In these calculations for metallic liquids, we have several times encountered the conceptual difficulty arising from the density dependence of the pair potential. We have also encountered a great deal of difficulty in getting our calculated results to agree in more than general form with the experimental results for the real systems. It seems to us in

retrospect that these difficulties may be traceable to an incorrect assumption made at the outset, namely, that the ionic structure is precisely that appropriate to (classical) particles interacting via the pair potential v^{AL} . We have not undertaken a detailed and careful investigation of this problem. Yet it seems to us that there is, within the tradition which gave rise to the effective potential v^{AL} , a certain contradiction in usage which suggests that the potential v^{AL} is incorrectly used to calculate the structure factors at small k . Whether this is in fact the case is a difficult (and still open) question.

The difficulty appears in the following way. Our calculations are based on an approximate accounting of energy in simple metallic systems (Ashcroft and Langreth, 1967C, and Harrison, 1966). For this discussion, the essential features of this approximation are contained in the form

$$E(\rho_0, R) = E_1(\rho_0) + E_2(\rho_0, R) . \quad (5-29)$$

The terms belonging to $E_1(\rho_0)$ depend only on the average density $\rho_0 = N/V$. The terms belonging to $E_2(\rho_0, R)$ depend on the explicit ionic positions R as well as on ρ_0 . When E_2 is calculated within a linear screening approximation, the result can be cast as a sum over an effective ion-ion pair potential. With the choices of dielectric function and pseudopotential specified in V-A, this potential becomes v^{AL} .

Without going further into the origins and form of this expression, we can make the important points here by consid-

ering and contrasting how it has been used in the calculation of the compressibility and structure of simple metals. In each of these calculations, we are considering the effects of density variations. To calculate the compressibility, we consider variations in the average density ρ_0 . A calculation of $S(k)$, however it proceeds, must be equivalent to considering spatially varying densities, since $S(k)$ is the density linear response function. Viewed in this way, the two calculations differ only in that the appropriate density variations are of infinite wavelength in the first, and of finite wavelength in the second. Yet the customary use of (5-29) in these calculations requires a fundamental distinction between these two cases, hence, between infinite and finite wavelength density variations. Good values of the compressibility are obtained if one considers all of the ρ_0 dependence in (5-29). On the other hand, the structure factor is calculated ignoring $E_1(\rho_0)$ entirely, and also ignoring the density dependence of $E_2(\rho_0, R)$, that is, of v^{AL} . (Of course, $\rho_0 = N/V$ is constant in the canonical ensemble. Our question will be, is this always the correct density to use in calculating the energy?) This reduces the structural problem to the problem of a classical liquid with pair interaction v^{AL} , and, as discussed in I-D, places the hard sphere success on a good foundation.

The point we wish to make is that, whatever its successes, this procedure rests on too sharp a distinction between finite and infinite wavelength. Indeed, for long wavelengths, the distinction is blurred. This must be so because the correla-

tions (both ionic and electronic) in the liquid are of only finite range. Then a density variation with a wavelength much longer than the range of correlations must have effects which are locally indistinguishable from those of a change in ρ_0 , which gives the same local density. With this blurring of the distinction between finite and infinite wavelengths comes an ambiguity in the structure calculation at long wavelength. In our calculations, we have followed the traditional method of ignoring the ρ_0 dependence and treating v^{AL} as a valid pair potential at all finite wavelengths. Yet it seems from this discussion as if, at long wavelengths, we must discover how to include the effects of $E_1(\rho_0)$ and the ρ_0 dependence of v^{AL} , presumably by evaluating these somehow at the local density. It is not clear which view (if either) is correct.

We remark that this discussion is confined to the consideration of long wavelengths. With respect to these matters, the existing short wavelength calculations seem to be less in doubt. A density variation of wavelength much shorter than the range of ionic or electronic correlations will look over this range nothing at all like a change in ρ_0 . We expect the existing pair potential approximation to be valid for such wavelengths. These wavelengths will include the first peak in $S(k)$. Then, in particular, the success of the hard sphere model, which means primarily the ability of this model to reproduce the experimental first peak, is probably still attributable to the form of v^{AL} .

Clearly, a careful and systematic investigation of this

matter is required before we can remove the ambiguity at long wavelengths, and define a consistent procedure. We mention that efforts are being made (Watabe and Hasegawa, 1972A,B) to treat the structural and thermodynamic properties of pure metallic liquids by considering these systems from the outset as binary systems composed of ions and electrons. We suggest here that one fruitful line of study for the particular problem at long wavelength (and in the present tradition) might be to consider calculating the energy of the metal in a perturbation theory that begins, not with the uniform electron gas, but with the non-uniform electron gas studied by Hohenberg and Kohn (1964) and Kohn and Sham (1965).

We note finally that if careful investigation of the long wavelength problem proves our calculations to be wrong, they may still be viewed as model calculations, which illustrate the form of the structure factors near phase separation (and thus may still give us a qualitative understanding of the resistive anomaly). The developments of sections III and IV, although carried out with metallic systems in mind, stand quite independently of these systems within the tradition of classical liquid theory.

VI. Discussion, Conclusions, and Suggestions for Further Work

This work has been divided into two parts: the development of the perturbation theory of the hard core plus tail mixture, and the application to the metallic liquids and alloys. Although some items to be discussed relate to results from both parts, we shall adopt this same division in this last section.

VI-A. The Perturbation Theory

We have cast our study of structure in terms of the functions $f_{ij}(\underline{k})$, which we may take as defined by (3-33). These functions are closely related to the more familiar direct correlation functions of Ornstein and Zernike (1914) (see equation (3-35)). Perhaps our most important result for these functions is the equation (3-75), which shows that to calculate these functions to first order in the perturbing potentials v_{ij}^1 , we must calculate $\rho_{ij}^{\rho, \text{ref}}(\underline{r}, \underline{r}')$, the two body function in the non-uniform reference fluid, to second order in $\delta\rho_i(\underline{r})$. This observation leads directly to the long wavelength approximation (4-31). As indicated at the close of section IV, a successful approximation for short wavelengths may possibly be developed by a carefully chosen analogy to crystalline solids.

In this effort, we have produced a theory which retains many of the virtues of the "simplest" mean field theory of the

phase transition itself (that is, the theory defined by (4-9) and used by Stroud (1973) in his study of phase separation), but which is, in principle at least, a reasonable theory of structure (which the simplest mean field theory is not.) It incorporates, in principle, the hard sphere successes, and is in the spirit of the most successful of the present theories of simple liquids, the perturbation theories on a HC reference system.

We note here that, while our effort has concentrated on the structure factors, we have actually been doing thermodynamic perturbation theory as well. To make this point, we consider the form of the Zwanzig expansion of the free energy F (in the absence of external fields.) Writing $U(R) = U^{\text{ref}} + U^1(R)$, where $U^1(R)$ is defined by (3-68), specializing to pure fluids, and introducing an expansion parameter λ by replacing v^1 by λv^1 , we find quickly (from (3-1) with $\phi(R) = 0$)

$$\frac{\partial F_\lambda}{\partial \lambda} = \langle U^1(R) \rangle_\lambda = \frac{V}{2} \int d\underline{r} v^1(\underline{r}) \rho_2^{\circ, \lambda}(\underline{r}), \quad (6-1)$$

where $\langle \rangle_\lambda$ and $\rho_2^{\circ, \lambda}(\underline{r})$ are evaluated from the distribution function determined by $U(R) = U^{\text{ref}}(R) + \lambda U^1(R)$. Then

$$\frac{\partial^2 F_\lambda}{\partial \lambda^2} = \frac{V}{2} \int d\underline{r} v^1(\underline{r}) \frac{\partial}{\partial \lambda} \rho_2^{\circ, \lambda}(\underline{r}). \quad (6-2)$$

Using (6-1) and (6-2) in a λ expansion of F_λ about $\lambda = 0$ and setting $\lambda = 1$, and writing $\rho_2^{\circ, \lambda=0}(r)$ ($= \rho_2^{\circ, \text{ref}}(r)$) in terms

of $S^{\text{ref}}(\underline{k})$ by (1-6) and (1-7), we find eventually

$$\begin{aligned}
 F &= F^{\text{ref}} + \frac{N\rho_0}{2} \{v^1(0) + \frac{1}{\rho_0} \int \frac{d\underline{k}}{(2\pi)^3} v^1(\underline{k}) (S^{\text{ref}}(\underline{k}) - 1)\} \\
 &+ \frac{N\rho_0}{4} \left\{ \frac{1}{\rho_0} \int \frac{d\underline{k}}{(2\pi)^3} v^1(\underline{k}) (S^{\text{ref}}(\underline{k}))^2 (-\beta\rho_0 a^1(\underline{k})) \right\} \quad (6-3) \\
 &+ o(v^1)^3 .
 \end{aligned}$$

where a^1 (as defined in (3-73)) is the first order term in the λ expansion of f^1 . That is, the second order term in the Zwanzig expansion of (2-2) may be calculated knowing S^{ref} , v^1 , and a^1 . At the present level of our work, of course, in which we have only a long wavelength approximation to $a^1(\underline{k})$, we are not yet able to perform a sensible approximate calculation of this second order term in F . Perhaps with better approximations to ρ_2^{ref} this situation will change. We note that this second order term is, of course, the term studied by Barker and Henderson (1967A, 1967B). In this sense, our MDA appears similar in spirit (though not identical) to the "macroscopic compressibility" and "local compressibility" approximations introduced (and later abandoned) by these authors (1967A, 1972).

To proceed beyond the lowest order term in f^1 , we note again that f^1 is a well-defined, if inaccessible, sum in the conventional perturbation series. Perhaps further progress can be made by combining our view of f^1 with the perturbation series approach. As a simple (and possibly important)

example, we know from the perturbation series for a pure fluid that, whenever a single term $\beta v^1(\underline{r})$ appears, we can perform a partial summation of higher order terms by replacing that $\beta v^1(\underline{r})$ with $\{1 - e^{-\beta v^1(\underline{r})}\}$. (See, for example, Brout, 1965, or Andersen and Chandler, 1972.) Then we may use (3-75) to generate a further approximation to f^1 specified by*

$$\begin{aligned}
 & -\frac{1}{\beta} \int d\underline{r} \int d\underline{r}' e^{-\beta v^1(\underline{r}-\underline{r}')} \{ \rho_2^{\rho, \text{ref}}(\underline{r}, \underline{r}') - \rho_2^{\circ, \text{ref}}(\underline{r}, \underline{r}') \} \\
 & = \int d\underline{r} \int d\underline{r}' \delta \rho(\underline{r}) \delta \rho(\underline{r}') f^1(\underline{r}-\underline{r}') + o(\delta \rho)^3.
 \end{aligned}
 \tag{6-4}$$

(The generalization to multi-component systems is presumably straightforward.) The approximation represented by (6-4) must represent a valid summation in the perturbation series, and goes beyond any we have used in this work. Such an approximation will clearly affect the T-dependence of the results. (Since, for the metallic systems, we have v^1 explicitly only in reciprocal space, the generalization of (3-75) to (6-4) introduces non-trivial computational problems.) Direct extension of our approach to higher order seems all but out of the question, since the expansion leading to (3-75) involves, in the next term, the three and four body distribution functions of the non-uniform fluid.

Now consider the adequacy of the overall approach, that is, of the approach which calculates the structure by

*The constant term in $\{1 - e^{-\beta v^1(\underline{r})}\}$ vanishes from (6-4) by the sum rule on ρ_2 . (See Appendix A, equation (A-8)).

calculating f^1 in first order. We note that, in view of the objection raised in the discussion of the metallic potentials, our metallic calculations may not have provided a test of the theory. It may be that the only test we have run on this theory is the calculation of $S^{\text{MDA}}(0)$ for Na parameters and several values of η . While the results of this test were not encouraging, it is clearly incomplete and insufficient to stand as the only test of the adequacy of the theory. More complete and careful testing of this theory on model potentials is clearly called for.

Application of this work to Lennard-Jones fluids will require a little care, since the work finds its most natural expression in reciprocal space. We will thus not be able to use the full potential as the perturbation on the hard core as we could for metals. Since, however, these results are explicitly independent of the form of $v^1(r)$ for $r < \sigma$, we are at liberty to give to v^1 a form inside the core which makes Fourier transform of v^1 possible. This is the approach taken by Chandler et al. (1972) in their "optimized" RPA. Direct application of this work to molecular liquids must be held pending an understanding of the importance of the assumption $v^1(r) = v^1(-r)$, which has apparently been required in several places. The essentials of the approach, however, that is, the view which takes the densities rather than the potentials as the basic variables, may, in suitably generalized form, have wide application in the theory of both simple and molecular (insulating) liquids.

VI-B. Application to Metallic Liquids

We have used the results of sections III and IV to define a long wavelength structural approximation which we have called the mean density approximation (MDA). In application to potentials modelled for the pure alkali metals, this approximation yields, at $k = 0$, results consistent with our expectations for the compressibility. At values of k around the reference (HC) peak, the results in the MDA seem to give some indication of a finite particle size effect. At $k = 0$ in the binary case, a simple model calculation of the line of singularities reproduces quite well the asymmetry and position of the Li-Na phase boundary in the x - T plane. Because the correct line of "hypothetical" singularities lies below the phase boundary at all points but the critical point, we expect qualitatively the more rounded shape we observe in the calculated curve. The selection of the hard sphere reference parameters emerges as a central problem. This problem, however, was studied almost entirely with respect to metallic potentials and real systems, so that, in view of the difficulty with the metallic potential, we clearly need to do more work in the spirit of the test at $S(0)$, that is, in the spirit of calculations for model systems. The nature of the singularity as $k \rightarrow 0$ was investigated, and appears asymptotically to be of the form $(a + bk^2)^{-1}$ (a gratifying result in view of the complexity of the MDA formulas), a form which insures the convergence of the resistivity integral (1-1) at the lower limit. The partial structure factors in the MDA were calculated and

plotted vs. k for one combination of parameters. Suggestions were made for a simple resistivity calculation which might shed some light on the nature and origin of the anomaly observed by Schürmann and Parks. Finally, a possible difficulty of the metallic potential at long wavelength was noted and suggestions made for work on the problem.

These calculations tend to support the hypothesis that the separation transition is driven primarily by the tail of the potential. This suggests that the study of such phase transitions could ultimately yield useful experimental information on this long range part of the potential. Such information has been difficult to extract from the structure factors themselves, since these tend to be dominated by the geometric effects of the repulsive cores. It is obvious, however, that an enormous amount of theoretical progress is still required. A certain amount of pessimism may be justified.

A question which remains unanswered is why some metallic binaries separate and others do not. One need only consider Na-K, rather than Li-Na, to find a binary system in which the uniform phase is stable at all concentrations for any temperature above solidification. Our physical understanding of this matter is that phase separation (a long wavelength ordering) and freezing (a short wavelength ordering) must in each system be competing transitions. A calculation of sufficient subtlety should show that, in Li-Na, the separation transition occurs at a higher T than a (hypothetical) freezing transition, while the converse is true in Na-K. It remains to be

seen whether such a calculation can be performed successfully with present techniques.

The theory of the phase transition implicit in the MDA is, of course, essentially mean field, so that we do not expect this work to shed any light on the usual problems encountered in the study of critical exponents (Fisher, 1964). The critical exponents in this problem are defined by Schürmann (1971), to whose work the interested reader is referred. We have paid little attention to this view of the problem and its necessary introduction of Ising type models, in favor of an approach directly through the structural results and calculations of classical liquid theory.

The structural work has been presented with a resistivity calculation ultimately in view. The work, of course, will have application near the phase transition to other properties of liquid metals which depend on the structure (e.g. the thermopower, thermal conductivity, optical absorption, ultrasonic absorption). Before such problems can be studied with any confidence, however, it seems that we must resolve the difficulty of the pair potential approximation at long wavelength.

Appendix A: The Distribution Functions

We shall define the distribution functions for a pure fluid. The generalization to mixtures is straightforward but cumbersome. We consider a system of N particles in a volume V at temperature T , and evaluate thermal averages in a canonical ensemble. We define the N particle distribution function

$$P_N(\mathbf{R}) = e^{-\beta U(\mathbf{R})} e^{-\beta \Phi(\mathbf{R})} / \left(\int d\mathbf{R} e^{-\beta U(\mathbf{R})} e^{-\beta \Phi(\mathbf{R})} \right) \quad (\text{A-1})$$

(just as in (3-9)). This function satisfies

$$\int d\mathbf{R} P_N(\mathbf{R}) = 1. \quad (\text{A-2})$$

In terms of this function, the thermal average of some quantity $A(\mathbf{R})$ is calculated, just as in (3-63), by

$$\langle A(\mathbf{R}) \rangle = \int d\mathbf{R} A(\mathbf{R}) P_N(\mathbf{R}). \quad (\text{A-3})$$

The n -body distribution function is defined by

$$\begin{aligned} \rho_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \\ = \frac{N!}{(N-n)!} \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; \mathbf{r}_{n+1}, \dots, \mathbf{r}_N). \end{aligned} \quad (\text{A-4})$$

For $n = 1$,

$$\rho_1(\underline{\mathbf{r}}) = N \int d\underline{\mathbf{r}}_2 \dots d\underline{\mathbf{r}}_N P_N(\underline{\mathbf{r}}, \underline{\mathbf{r}}_2, \dots, \underline{\mathbf{r}}_N), \quad (\text{A-5})$$

is just the single particle density. This function clearly satisfies the sum rule

$$\int d\underline{\mathbf{r}} \rho_1(\underline{\mathbf{r}}) = N. \quad (\text{A-6})$$

For $n = 2$,

$$\rho_2(\underline{r}, \underline{r}') = N(N-1) \int d\underline{r}_3 d\underline{r}_4 \dots d\underline{r}_N P_N(\underline{r}, \underline{r}', \underline{r}_3, \dots, \underline{r}_N) \quad (\text{A-7})$$

is the two body distribution function which plays the important role in our work. It has the meaning that $\rho_2(\underline{r}, \underline{r}') d\underline{r} d\underline{r}'$ is the probability of finding a particle in $d\underline{r}$ about \underline{r} and another in $d\underline{r}'$ about \underline{r}' . It satisfies the sum rule

$$\int d\underline{r} d\underline{r}' \rho_2(\underline{r}, \underline{r}') = N(N-1) . \quad (\text{A-8})$$

Now consider the role of these functions in a thermal average, using (A-3). First consider the thermal average of the sum on single particle potentials $\phi(R)$ defined, as in (3-2), by

$$\phi(R) = \sum_{i=1}^N \phi(\underline{r}_i) . \quad (\text{A-9})$$

Then

$$\langle \phi(R) \rangle = \sum_{i=1}^N \int d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_N \phi(\underline{r}_i) P_N(\underline{r}_1, \dots, \underline{r}_N) . \quad (\text{A-10})$$

Because P_N is a symmetric function of its arguments, we may make in each integral in (A-10) the change of variables $\underline{r}_i \rightarrow \underline{r}_1$, and $\underline{r}_1 \rightarrow \underline{r}_i$. Since all N integrals are then seen to be equivalent, we have

$$\langle \phi(R) \rangle = N \int d\underline{r}_1 \phi(\underline{r}_1) \int d\underline{r}_2 \dots d\underline{r}_N P_N(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) . \quad (\text{A-11})$$

By (A-5), this is just

$$\langle \phi(R) \rangle = \int d\underline{r} \phi(\underline{r}) \rho_1(\underline{r}) . \quad (\text{A-12})$$

Next calculate the thermal average of the sum of pair potentials $U(R)$ defined, as in (3-42), by

$$U(R) = \frac{1}{2} \sum_{i \neq j} v(\underline{r}_i - \underline{r}_j) . \quad (A-13)$$

Then

$$\langle U(R) \rangle = \frac{1}{2} \sum_{i \neq j} \int d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_N v(\underline{r}_i - \underline{r}_j) P_N(\underline{r}_1, \dots, \underline{r}_N) . \quad (A-14)$$

We use the symmetry of $P_N(R)$ to make, in each integral of (A-14), the changes of variable $\underline{r}_i \rightarrow \underline{r}_1$, $\underline{r}_1 \rightarrow \underline{r}_i$, $\underline{r}_j \rightarrow \underline{r}_2$, and $\underline{r}_2 \rightarrow \underline{r}_j$. Then all $N(N-1)$ integrals in (A-14) are seen to be equivalent, and we have

$$\begin{aligned} \langle U(R) \rangle & \\ & = \frac{1}{2} N(N-1) \int d\underline{r}_1 d\underline{r}_2 v(\underline{r}_1 - \underline{r}_2) \int d\underline{r}_3 \dots d\underline{r}_N P_N(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) , \end{aligned} \quad (A-15)$$

so that, by (A-7), we find

$$\langle U(R) \rangle = \frac{1}{2} \int d\underline{r} d\underline{r}' v(\underline{r} - \underline{r}') \rho_2(\underline{r}, \underline{r}') . \quad (A-16)$$

Finally, consider the thermal average of the density operator $\hat{\rho}(\underline{k})$ defined by (1-3). In real space, this operator is

$$\hat{\rho}(\underline{r}) = \sum_i \delta(\underline{r} - \underline{r}_i) . \quad (A-17)$$

Then

$$\langle \hat{\rho}(\underline{r}) \rangle = \sum_i \int d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_N \delta(\underline{r} - \underline{r}_i) P_N(\underline{r}_1, \dots, \underline{r}_N) . \quad (A-18)$$

Using the symmetry of $P_N(R)$, we make, in each integral of

(A-18), the changes of variable $\underline{r}_i \rightarrow \underline{r}_1$ and $\underline{r}_1 \rightarrow \underline{r}_i$, so that all N integrals in (A-18) are seen to be equivalent, and we have

$$\begin{aligned} \langle \hat{\rho}(\underline{r}) \rangle &= N \int d\underline{r}_1 \delta(\underline{r}-\underline{r}_1) \int d\underline{r}_2 \dots d\underline{r}_N P_N(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \\ &= \rho_1(\underline{r}) , \end{aligned} \tag{A-19}$$

by (A-5). Then $\hat{\rho}(\underline{r})$ is, as stated in section I, the operator whose thermal average is the single particle density. Similar arguments will establish the relations, given in (1-6) and (1-7), between $S(k)$ defined in terms of $\hat{\rho}(\underline{k})$ (in (1-2)) and the two body distribution function $\rho_2(\underline{r}, \underline{r}')$.

Appendix B: Phase Separation and Singularities in the $S_{ij}(k)$.

Here we wish to elaborate on the conclusions stated in section I concerning the relation between phase separation and singularities in the partial structure factors $S_{ij}(k)$ in the limit as $k \rightarrow 0$.

The analysis concerns the form of the Gibbs energy per particle, $g(x)$, plotted as a function of x at constant T and p . For some $T_1 < T_C$, this isotherm will have a form like that presented schematically in Figure B-1. This curve exhibits regions where it is concave upward and regions where it is concave downward. In the region where the curve is concave downward, between the points labelled C and D, we have

$$\left(\frac{\partial^2 g(x)}{\partial x^2} \right)_{T,p} < 0, \quad (B-1)$$

so that the system is unstable against concentration fluctuations. The points A and B are defined (uniquely) by constructing a line tangent to this curve at two points. A straightforward calculation of the Gibbs energies involved (bearing in mind particle number conservation) shows that, for any concentration between x_A and x_B (say x_E), the Gibbs energy of the uniformly mixed phase is higher than that of some separated phase, and that the separated phase with the lowest Gibbs energy is that defined by x_A and x_B . On the other hand, for concentrations outside this region, $x \leq x_A$ or $x \geq x_B$, the Gibbs energy of the uniform phase is lower than that of any separated phase. Then the concentrations x_A and x_B mark the

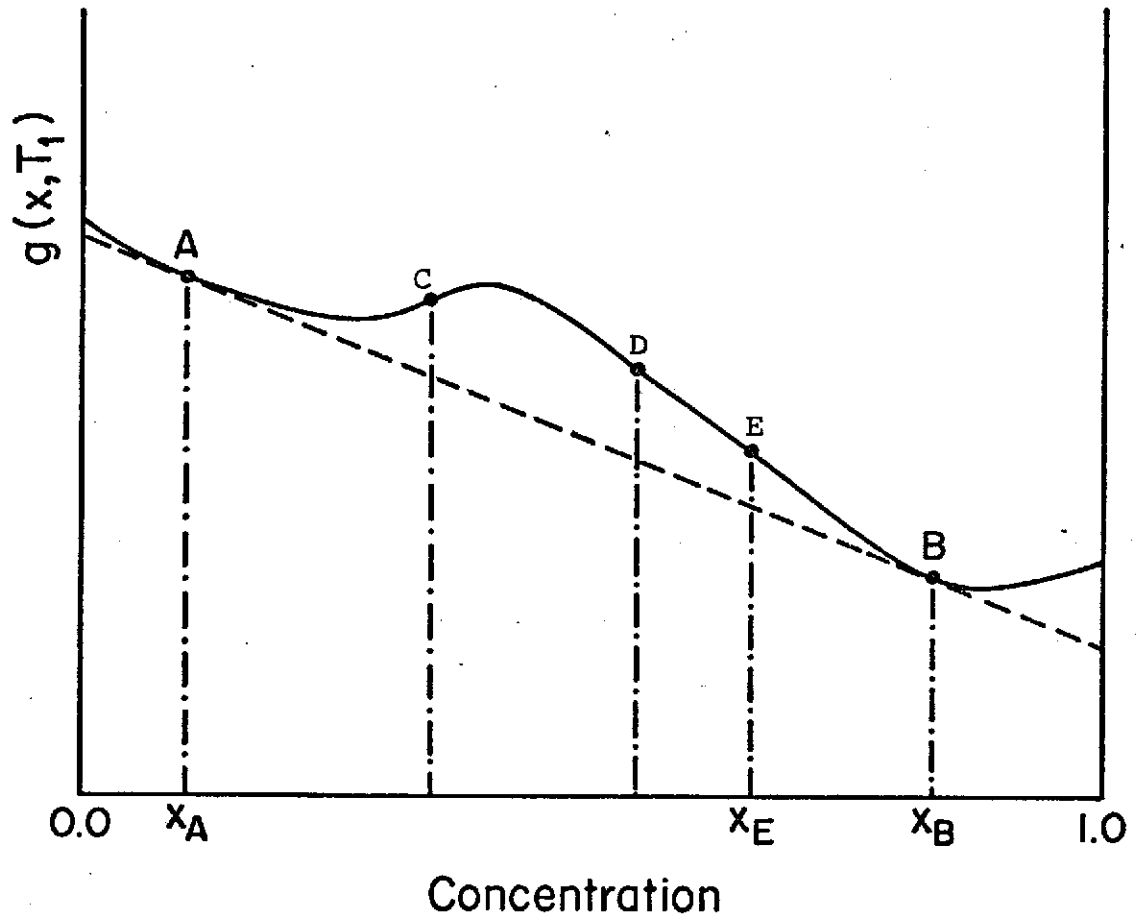


FIGURE B-1

Gibbs energy per particle as a function of concentration at $T = T_1 < T_C$.

points in the x-T plane at which the line $T = T_1$ intersects the phase boundary. (Refer to the discussion in section I-A.) As the temperature is raised, these points move closer together, until, at the critical temperature T_C , they coincide. For all $T > T_C$, the curve is everywhere concave upward. Then a common tangent may not be constructed, and the uniform alloy is stable in all concentrations.

Our concern is with the inflection points C and D, at which

$$\left(\frac{\partial^2 g(x)}{\partial x^2} \right)_{T,p} = 0 . \quad (B-2)$$

Bhatia and Thornton (1970) have shown that these are the points at which the partial structure factors of the uniform alloy diverge in the limit as $k \rightarrow 0$. It is clear that, at the temperature T_1 represented by the isotherm in Figure B-1, these points are not accessible. They must lie below the phase boundary in the x-T plane. As the temperature is increased towards T_C , however, these inflection points will move closer together until, at T_C , the inflection points and the common tangent points coincide. It is thus only at the critical point that the singularity is fully realized at separation. Then the line of singularities in the x-T plane lies below the phase boundary in general, but joins it at the one point which is the critical point.

Appendix C: The $k = 0$ result (4-32).

We note from (1-2) and (1-3) that

$$S_{ij}(0) = (N_i N_j)^{-\frac{1}{2}} \langle N_i N_j \rangle - (N_i N_j)^{\frac{1}{2}} . \quad (C-1)$$

We evaluate $\langle N_i N_j \rangle$ in a grand canonical ensemble at constant T , V , and chemical potentials μ_i . Consider the pure fluid case, for which

$$\langle N \rangle = \frac{\sum_N N \frac{1}{N!} e^{\beta \mu N} \int dR e^{-\beta U(R)}}{\sum_N \frac{1}{N!} e^{\beta \mu N} \int dR e^{-\beta U(R)}} \quad (C-2)$$

Then we find

$$\left(\frac{\partial}{\partial \mu} \right)_{T,V} \langle N \rangle = \beta (\langle N^2 \rangle - \langle N \rangle^2) . \quad (C-3)$$

Then

$$\frac{1}{\beta} \frac{1}{\langle N \rangle} \left(\frac{\partial}{\partial \mu} \right)_{T,V} \langle N \rangle = \frac{1}{\langle N \rangle} \langle N^2 \rangle - \langle N \rangle = S(0) . \quad (C-4)$$

That is

$$S(0) = \frac{1}{\beta \rho} \left(\frac{\partial \rho}{\partial \mu} \right)_{T,V} , \text{ where } \rho = \frac{\langle N \rangle}{V} . \quad (C-5)$$

In a multi-component system, this result generalizes readily to

$$S_{ij}(0) = \frac{1}{\beta \sqrt{\rho_i \rho_j}} \left(\frac{\partial \rho_i}{\partial \mu_j} \right)_{T,V,\mu'} , \quad (C-6)$$

where the prime indicates that all μ 's are held fixed except

the one explicitly appearing in the derivative. By (3-5), this result is

$$X_{ij}(0) = -\left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} \quad (C-7)$$

Now, if ρ_i is considered a function of all the μ 's, and μ_j is considered a function of all the ρ 's, we have

$$d\rho_i = \sum_j \left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} d\mu_j ; d\mu_j = \sum_\ell \left(\frac{\partial \mu_j}{\partial \rho_\ell}\right)_{T,V,\rho'} d\rho_\ell \quad (C-8)$$

which gives

$$d\rho_i = \sum_{j\ell} \left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} \left(\frac{\partial \mu_j}{\partial \rho_\ell}\right)_{T,V,\rho'} d\rho_\ell \quad (C-9)$$

This yields

$$\sum_j \left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T,V,\mu'} \left(\frac{\partial \mu_j}{\partial \rho_\ell}\right)_{T,V,\rho'} = \delta_{i,\ell} \quad (C-10)$$

or

$$P = U^{-1} \quad (C-11)$$

where P is the matrix whose elements are $(\partial \rho_i / \partial \mu_j)_{T,V,\mu'}$, and U is the matrix whose elements are $(\partial \mu_j / \partial \rho_\ell)_{T,V,\rho'}$. Introducing the matrices X and F from (3-33), we then have, from (C-7) and (C-11),

$$X = -P = -U^{-1} = -F^{-1} \quad (C-12)$$

so that F = U, or

$$f_{ij}(0) = \left(\frac{\partial \mu_i}{\partial \rho_j}\right)_{T,V,\rho'} \quad (C-13)$$

From thermodynamics, this is

$$f_{ij}(0) = \frac{1}{V} \left(\frac{\partial^2 F}{\partial \rho_i \partial \rho_j} \right)_{T, V, \rho} , \quad (C-14)$$

where F now denotes the free energy of the system. To arrive at (4-32), we expand f_{ij} and F in powers of the perturbation v_{ij}^1 . We introduce an expansion parameter λ by replacing v_{ij}^1 with λv_{ij}^1 , and expand f_{ij} as in section III:

$$f_{ij}(0) = f_{ij}^{\text{ref}}(0) + \lambda a_{ij}^1(0) + o(\lambda)^2 . \quad (C-15)$$

For the expansion of F , we simply insert the Zwanzig expansion, which, as we saw in the argument to (3-75), is just

$$F = F^{\text{ref}} + \lambda \langle U^1(R) \rangle_{\circ, \text{ref}} + o(\lambda)^2 . \quad (C-16)$$

On writing $\langle U^1(R) \rangle_{\circ, \text{ref}}$ in terms of $\rho_{ij}^{\circ, \text{ref}}(\underline{r}, \underline{r}')$, just as in (3-71), and substituting into (C-14), the desired result, (4-32), follows immediately.

We note that this result is also (plausibly) consistent with a certain limiting case studied by Lebowitz and Penrose (1966). These authors replace $v^1(r)$ with the form

$$v^1(r) = \lambda^3 \phi(\lambda r) , \quad (C-17)$$

and study the form of the free energy in the thermodynamic limit and in the limit as $\lambda \rightarrow 0$. In this limit, the potential v^1 becomes very weak and very long range. The limiting result for the free energy is

$$F(\rho) = F^{\text{ref}}(\rho) + \frac{1}{2} \rho^2 \phi_0 , \quad (C-18)$$

where $F(\rho)$ now denotes the free energy per unit volume, and

$$\phi_0 = \int d\underline{r} \phi(\underline{r}) = \int d\underline{r} \lambda^3 \phi(\lambda \underline{r}) \quad , \quad \text{for all } \lambda. \quad (\text{C-19})$$

This result is made plausible by consideration of (C-16), which reads, for this choice of v^1 ,

$$F(\rho) = F^{\text{ref}}(\rho) + \frac{1}{2} \int d\underline{r} \lambda^3 \phi(\lambda \underline{r}) \rho_2^{\circ, \text{ref}}(\underline{r}) + o(\phi)^2. \quad (\text{C-20})$$

(Note that between (C-16) and (C-20), both F and λ have been redefined.) If the dimensions of the system are much greater than the range of $\lambda^3 \phi(\lambda \underline{r})$, we can change variables in the integral to write

$$F(\rho) = F^{\text{ref}}(\rho) + \frac{1}{2} \int d\underline{r} \phi(\underline{r}) \rho_2^{\circ, \text{ref}}(\underline{r}/\lambda) + o(\phi)^2. \quad (\text{C-21})$$

If we now take the thermodynamic limit and the limit as $\lambda \rightarrow 0$ (in that order, so that the dimensions of the system are always much greater than the range of $\lambda^3 \phi(\lambda \underline{r})$), we see that the region of integration in which $\rho_2^{\circ, \text{ref}}(\underline{r}/\lambda)$ differs from ρ^2 will shrink to zero. Then (C-18) will follow if, as seems reasonable for this weak form of $v^1(\underline{r})$, the higher order terms may be neglected.

The result (C-18) yields, through (C-14), the mean field result

$$f^1(0) = \phi_0 = \int d\underline{r} v^1(\underline{r}). \quad (\text{C-22})$$

This result can be obtained directly from (4-32) by a similar plausibility argument. For this potential, (4-32) reads

$$\begin{aligned}
 f^1(0) &= \frac{1}{2} \int d\underline{r} \ v^1(\underline{r}) \ \frac{\partial^2}{\partial \rho^2} \ \rho_2^{\circ, \text{ref}}(\underline{r}) \ + \ o(v^1)^2 \\
 &= \frac{1}{2} \int d\underline{r} \ \phi(\underline{r}) \ \frac{\partial^2}{\partial \rho^2} \ \rho_2^{\circ, \text{ref}}(\underline{r}/\lambda) \ + \ o(\phi)^2 \ ,
 \end{aligned}
 \tag{C-23}$$

where, for the last step, we again require that the dimensions of the system be much larger than the range of $\lambda^3 \phi(\lambda \underline{r})$. If we perform the same limiting steps described above, the region where $\frac{1}{2} \frac{\partial^2}{\partial \rho^2} \rho_2^{\circ, \text{ref}}(\underline{r}/\lambda)$ differs from unity is seen to shrink to zero, so that (C-22) follows from the neglect of higher order terms.

Appendix D: The MDA to $f_{ij}^1(\underline{k})$ for a Two-component Fluid.

Let $x_1 = \rho_1^\circ/\rho$ and $x_2 = \rho_2^\circ/\rho$, where ρ_1° and ρ_2° are the densities of species one and two respectively, and $\rho = \rho_1^\circ + \rho_2^\circ$. Define the partial packing fractions η_1 and η_2 by $\eta_i = \pi \rho_i^\circ \sigma_i^3/6$, where σ_i is the hard core diameter associated with the i^{th} species. Then the MDA for f_{ij}^1 for a binary alloy is

$$\begin{aligned}
f_{11}^1(\underline{k}) &= v_{11}^{\text{AL}}(\underline{k}) \\
&+ \frac{1}{x_1 \rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{11}^{\text{AL}}(\underline{k}') \left\{ \frac{\eta_1^2}{2} \frac{\partial^2}{\partial \eta_1^2} S_{11}^{\text{HC}}(\underline{k}-\underline{k}') + \eta_1 \frac{\partial}{\partial \eta_1} S_{11}^{\text{HC}}(\underline{k}-\underline{k}') \right\} \\
&+ \left(\frac{x_2}{x_1^3} \right)^{\frac{1}{2}} \frac{1}{\rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{12}^{\text{AL}}(\underline{k}') \left\{ \eta_1^2 \frac{\partial^2}{\partial \eta_1^2} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') - \frac{1}{4} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') \right. \\
&\quad \left. + \eta_1 \frac{\partial}{\partial \eta_1} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') \right\} \\
&+ \frac{x_2}{x_1^2} \frac{1}{\rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{22}^{\text{AL}}(\underline{k}') \left\{ \frac{\eta_1^2}{2} \frac{\partial^2}{\partial \eta_1^2} S_{22}^{\text{HC}}(\underline{k}-\underline{k}') \right\},
\end{aligned} \tag{D-1}$$

$$\begin{aligned}
f_{12}^1(\underline{k}) &= v_{12}^{\text{AL}}(\underline{k}) \\
&+ \frac{1}{x_2 \rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{11}^{\text{AL}}(\underline{k}') \left\{ \frac{\eta_1 \eta_2}{2} \frac{\partial^2}{\partial \eta_1 \partial \eta_2} S_{11}^{\text{HC}}(\underline{k}-\underline{k}') + \frac{\eta_2}{2} \frac{\partial}{\partial \eta_2} S_{11}^{\text{HC}}(\underline{k}-\underline{k}') \right\} \\
&+ \frac{1}{\sqrt{x_1 x_2}} \frac{1}{\rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{12}^{\text{AL}}(\underline{k}') \left\{ \eta_1 \eta_2 \frac{\partial^2}{\partial \eta_1 \partial \eta_2} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') + \frac{1}{4} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') \right. \\
&\quad \left. + \frac{\eta_1}{2} \frac{\partial}{\partial \eta_1} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') + \frac{\eta_2}{2} \frac{\partial}{\partial \eta_2} S_{12}^{\text{HC}}(\underline{k}-\underline{k}') \right\} \\
&+ \frac{1}{x_1 \rho} \int \frac{d\underline{k}'}{(2\pi)^3} v_{22}^{\text{AL}}(\underline{k}') \left\{ \frac{\eta_1 \eta_2}{2} \frac{\partial^2}{\partial \eta_1 \partial \eta_2} S_{22}^{\text{HC}}(\underline{k}-\underline{k}') + \frac{\eta_1}{2} \frac{\partial}{\partial \eta_1} S_{22}^{\text{HC}}(\underline{k}-\underline{k}') \right\}.
\end{aligned}$$

The form of $f_{22}^1(\underline{k})$ may be obtained from the form of $f_{11}^1(\underline{k})$ by replacing all subscripts '1' with subscripts '2', and vice versa.

The η_i derivatives of the S_{ij} may be given explicit forms in the PY approximation. If these forms are to be derived from the published expressions (AL-II), care must be taken that the right variables are held constant as the differentiations are performed. The structure function S_{ij} is a function of k , ρ_1^0 , ρ_2^0 , σ_1 , and σ_2 . We stipulate, just as in the pure fluid case, that the σ_i are held fixed. Then, for example, some of the necessary derivatives in (4-31) take the form

$$\left(\frac{\partial S_{ij}}{\partial \rho_1^0} \right)_{k, \rho_2^0, \sigma_1, \sigma_2} \quad (D-2)$$

The following discussion of the variables will be valid as well for the more complicated derivatives derived from (4-31), but we shall take the expression (D-2) as the simplest example.

From the definition of the η_i , it is clear that we may trade the five variables above for k , η_1 , η_2 , σ_1 , and σ_2 . We then have

$$\rho_1 \left(\frac{\partial S_{ij}}{\partial \rho_1^0} \right)_{k, \rho_2^0, \sigma_1, \sigma_2} = \eta_1 \left(\frac{\partial S_{ij}}{\partial \eta_1} \right)_{k, \eta_2, \sigma_1, \sigma_2} \quad (D-3)$$

Further, since S_{ij} is unchanged when we scale all lengths by the same amount, we have

$$S_{ij}(k, \eta_1, \eta_2, \sigma_1, \sigma_2) = S_{ij}(\lambda^{-1}k, \eta_1, \eta_2, \lambda\sigma_1, \lambda\sigma_2) \quad (D-4)$$

so that S_{ij} may be considered a function of only the four

variables $k\sigma_1$, $k\sigma_2$, η_1 , and η_2 . Then the expression (D-3) becomes

$$\eta_1 \left(\frac{\partial S_{ij}}{\partial \eta_1} \right)_{k\sigma_1, k\sigma_2, \eta_2} \quad (D-5)$$

If we now trade $k\sigma_1$ and $k\sigma_2$ for $\alpha \equiv \sigma_1/\sigma_2$ and $k\sigma_2$, we arrive finally at the result

$$\rho_1^0 \left(\frac{\partial S_{ij}}{\partial \rho_1^0} \right)_{k, \rho_2^0, \sigma_1, \sigma_2} = \eta_1 \left(\frac{\partial S_{ij}}{\partial \eta_1} \right)_{k\sigma_2, \alpha, \eta_2} \quad (D-6)$$

where S_{ij} is now considered a function of $k\sigma_2$, α , η_1 , and η_2 . Then the form quoted in AL-I must be rewritten, since the variables in AL-I are $k\sigma_2$, α , x , and η .

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