

# Theory of the Thermodynamics of Simple Liquid Metals\*

N. W. ASHCROFT

*Laboratory of Atomic and Solid State Physics and Materials Science Center, Clark Hall,  
Cornell University, Ithaca, New York*

AND

D. STROUD

*Department of Physics, Ohio State University, Columbus, Ohio*

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## I. Introduction

A liquid<sup>1-6</sup> is considered to be a condensed phase of matter. It has a density very similar to that found in the corresponding solid phase, but has a symmetry more typical of a gas. Many properties of liquids (specific heat, for example<sup>3</sup>) are not very different from those of solids at comparable temperatures, but they have generally proved much harder to calculate than either crystalline solid state or gaseous properties. Extended solids normally have both translational and point group symmetries and these lead to enormous simplifications in formulating theoretical descriptions of their various properties. In the case of dense gases, the density is a convenient parameter in terms of which expansions for the thermodynamic functions can be developed. But liquids possess neither obvious symmetry nor obvious expansion parameters, and these are serious impediments in formulating theoretical descriptions.

The behavior of liquids exhibits a variety comparable to that found in crystalline solids. For example, liquids, like solids, can be classified according to their electronic transport properties as metals, semiconductors, or insulators. Liquid metals typically have resistivities<sup>3</sup> of order 10–100  $\mu\text{ohm}\cdot\text{cm}$  and frequently a positive temperature coefficient of resistivity. Liquid semiconductors have much higher resistivities with an activated temperature dependence, and liquid insulators have very large resistivities which do not (at ordinary temperatures) show signs of thermal excitation of current carriers.

<sup>1</sup> For general references in the area of liquids and particularly liquid metals, the reader is directed to G. Busch and H.-J. Güntherodt, *Solid State Phys.* **29**, 235 (1974), and to refs. 2–6.

<sup>2</sup> J. S. Rowlinson, "Liquids and Liquid Mixtures," 2nd ed., Butterworth, London, 1971.

<sup>3</sup> T. E. Faber, "An Introduction to the Theory of Liquid Metals." Cambridge Univ. Press, London and New York, 1972.

<sup>4</sup> P. A. Egelstaff, "An Introduction to the Liquid State." Academic Press, New York, 1967.

<sup>5</sup> T. L. Hill, "Statistical Mechanics," McGraw-Hill, New York, 1956.

<sup>6</sup> J.-P. Hansen and I. R. MacDonald, "Theory of Simple Liquids." Academic Press, New York, 1976; J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids." Wiley, New York, 1954.

In solids, the distinction between metals, insulators, and semiconductors can be linked to certain features of the electronic structure. Thus insulators are found to have filled Brillouin zones and possess well-defined band gaps that are large on the scale of thermal energies, while metals have partially filled zones and possibly overlapping bands. Semiconductors have filled bands, but, because of the rather small overall gaps, admit of thermal excitation of carriers. In liquids, the disordered arrangement of the ions means that the concept of Brillouin zones is no longer useful, and consequently such a simple reciprocal space classification is not possible. Nonetheless, it is still generally the case that in liquid metals the electronic structure is characterized by a substantial density of extended electronic states at the Fermi energy, and this crudely distinguishes liquid metals from nonconducting liquids.

Rather than classifying liquids by their transport properties, one can also group them, in chemical language, according to their prevailing "intermolecular forces" or "bonds." *Simple liquids* are those composed of spherical or nearly spherical "molecules," and are characterized by predominantly two-body central bonding forces. They include *insulating fluids* such as liquid argon and even perhaps liquid methane. They also include *conducting fluids* (such as Na, Cu, liquid Si and Ge), although as we shall see the forces in these latter substances are functions of *density* as well as separation. In *homonuclear molecular liquids* such as  $H_2$  and  $N_2$ , the intermolecular forces include, in addition to a principal central component, a substantial angular part dependent upon relative molecular orientation. *Associated liquids*, such as water and glycerol, are characterized by hydrogen bonding, and *polar liquids* such as HBr and molten salts often have long-range interactions. Finally, liquids made up of large organic molecules may exhibit liquid crystalline order, that is, symmetry elements of a crystalline state while retaining other characteristics of a liquid. Except for simple liquids, all may show strong directional (or steric) effects, or are otherwise complicated by effects of anisotropy and internal degrees of freedom.

This paper is concerned with the thermodynamic properties of conducting liquids. The central problems to be dealt with are those of calculating such measurable quantities as the compressibility, specific heat, and melting curves of metals from knowledge of the fundamental interactions among the electrons and ions. In order to understand this problem, it is necessary to consider both the electronic structure and the "bonding" structure or ionic arrangement. These are closely interrelated. For example, any description of the ionic arrangement must take into account the presence of the conduction electrons. Conversely, the

electronic structure must in turn be strongly affected by the physical arrangement of the ions. The interplay between these dual aspects of liquid metals is quite complex and forms the main subject of this review.

Liquid metals may be further divided into roughly nonoverlapping classes according to their *electronic* structure. Under normal conditions these classes are broadly defined as follows:

*Simple:* These have band structures in the crystalline state that are recognizably free electronlike. Examples are Na, Mg, Al, and Pb. Their valence bands are very well separated in energy from the next lowest core-level bands.

*Transition and Noble Metals:* In varying degrees these have band structures that exhibit features both of narrow (or tight binding) bands and nearly free electron behavior. In the noble metals the tight-binding-like structure is contained below energies equal to the highest occupied level (i.e., at  $T = 0$ , the Fermi level). In the transition metals this ceases to be the case and the Fermi level lies within a principally d-electronlike band structure. In the alkaline earths the tight-binding-like bands lie just above the Fermi energy and it may not be inappropriate to refer to these examples as "near-transition" metals. (The hybridization between free electron and tight-binding-like features remains noticeable.)

*Rare Earths, Lanthanides, Actinides:* In these metals the f-bands are usually split indicating a failure of the independent particle approximation. Between split f-bands lies a set of bands roughly characterized by the atomic s and p (and in some cases, d) levels from which they derive. For certain metals there may also be densities for which mixed valences appear.

From the point of view of electron structure, the range presented by the entire class of molten metals is evidently exceedingly diverse. In the interest of presenting a coherent and relatively compact development of the theory of the thermodynamics of liquid metals, we have chosen to limit the discussion to metals (and alloys) whose band structures in the solid state are known to be very free electronlike. A large number of elements fall in this class: some, for example, Pb, Tl, etc., are heavy elements and require a description, beyond the development we shall present, which properly takes into account spin-orbit effects. In keeping with the free-electron spirit we shall also be unconcerned with the thermodynamics of the liquid metal surface, since this requires consideration of the transition from metallic liquid to nonmetallic vapor across the interface. Nor, for like reason, shall we discuss the liquid-vapor phase transition in metals. Also under the heading of apologia we note that we are concerned here with large rather than small systems, with microscopic theory rather than phenomenology, with analytic ap-

proaches rather than computer experiments, and with equilibrium rather than nonequilibrium properties.

A central question regarding liquid metals is, of course, why they form simple liquids, or equivalently, why, structurally, they have two body central forces. The answer, in the case of free-electron metals, lies in the predictions of perturbation theory as applied to an interacting electron gas. The perturbation arises from the metallic ions which carry with them, in an adiabatic way, the fundamental interaction between the electrons and ions—the pseudopotential.<sup>7</sup> The response of the electrons to this perturbation is discussed in Section II. As is described there, the original two-component medium of interacting electrons and ions can be reduced, in second order of perturbation theory, to an effective single-component system made up of ions acting under the influence of reduced (screened) interactions which are, indeed, two-body and central. There remains, however, a large volume-dependent, structure-independent term in the free energy which distinguishes simple metallic liquids from simple insulating ones like argon, and indeed dominates the binding energy of the metal.

Once the nature of the interatomic forces is known, the thermodynamics of the liquid metal can be determined by the methods of classical statistical mechanics. Some of the methods for so doing are discussed in Section III. Section IV reviews applications of these methods to various thermodynamic properties of single component liquid metals, including the liquid–solid phase transition. Section V describes the extension of these techniques to treat mixtures of liquid metals, and discusses their application to problems such as the mutual solubility of liquid metals. The problems associated with more complex systems are briefly mentioned in Section VI. Finally, in the interest of clarity, we have collected in the Appendix some of the definitions and properties of the correlation functions which are necessary for a description of liquids and particularly liquid metals.

## II. Formalism: Electrons and Ions

In a substance such as liquid argon, in which the atoms are characterized by closed electronic shells, the highest electronic levels are very tightly bound and, as far as the motion of the argon atoms is concerned, the electrons in these levels can be viewed as rigidly attached to the

<sup>7</sup> For a review of pseudopotentials, see V. Heine, *Solid State Phys.* **24**, 1 (1970), or W. A. Harrison, "Pseudopotentials in the Theory of Metals." Benjamin, New York, 1966.

nucleus. Fluctuations in the levels are, of course, important, and indeed lead, via the fluctuating dipole or van der Waals interaction, to the attraction between the pairs of atoms that are responsible for the binding of the condensed state. But once the interaction between the atoms is specified, the electronic degrees of freedom are of no further structural consequence, and an assembly of argon atoms is quite validly regarded as a one-component system in which, for dynamical purposes, the electrons and nucleus of a given atom are described by a common coordinate.

Consider now, by contrast, a liquid metal. It is composed of charged massive nuclei and light electrons in an electrically neutral admixture. In most liquid metals, some of the electrons are tightly bound to the nuclei and play only a passive role in determining the properties of the metal, much as in the case of the rigid core in argon. But the remaining electrons have degrees of freedom which must be explicitly taken into account. The elemental liquid metal is, in fact, properly to be regarded as a *two-component* mixture of interacting electrons and ions. In this section we explore the consequences of this point of view, focusing on metals which are "simple" in the sense of the Introduction. For this subclass, the two-component liquid can (for many purposes) be reduced to a quasi-one-component system with suitably redefined effective interactions between the ions. We shall carry out the required reduction and obtain an explicit expression for the effective Hamiltonian governing the dynamical entities of this one-component system. (The extension to alloys is straightforward and will be deferred to Section V.)

## 1. ELECTRON-ION INTERACTIONS: PSEUDOPOTENTIALS

The first requirement in describing a dense fluid of interacting electrons and ions is, of course, a knowledge of the interactions. We consider here the nature of the electron-ion interaction, the quantity which most clearly distinguishes simple metals from other metals. In keeping with the emphasis on simple metals, we suppose that the electrons can be unambiguously classified as "valence" or "core" electrons, the latter being so tightly bound that their degrees of freedom can be largely ignored<sup>8</sup> in calculating the thermodynamics of the liquid.

<sup>8</sup> Whether or not this approximation is reasonable will ultimately rest with the degree of polarizability of the ion: for highly polarizable ions the resulting fluctuating dipole interaction, now dynamically screened by the conduction electrons, can be expected to give noticeable corrections to the pair potentials described below. These van der Waals-like effects have been discussed by J. J. Rehr, E. Zaremba, and W. Kohn, *Phys. Rev. B* **12**, 2062 (1975); by N. W. Ashcroft, "Fundamental Aspects of Dislocation Theory" *Nat. Bur. Stan. (U.S.) Spec. Publ.* **317**, 1, 179 (1970); and by K. K. Mon, N. W. Ashcroft, and G. V. Chester (to be published).

The (unscreened) single-particle interaction between an ion and an electron in a simple metal (liquid or solid) is characterized by a potential  $V(r)$  of the form shown schematically in Fig. 1a. Typically  $V(r) \sim -Ze^2/r$  outside the core, while within it  $V(r)$  is strongly negative and nonconstant. Because of its strength  $V(r)$  is not amenable to treatment by perturbation theory, and it is thus paradoxical that the valence electrons in simple metals should behave for so many purposes like free particles. The paradox is resolved within the framework of *pseudopotential theory*, and we now summarize those aspects of the argument which are relevant for present purposes.<sup>9</sup>

Within the one-electron approximation we note first that the eigenvalue spectrum of  $T + V$  ( $T$  being the electron kinetic energy operator) contains *both* valence and core levels. But since the latter play only a passive role in determining the properties of the metal, it is desirable to eliminate them from the problem at the outset. The essence of the pseudopotential method is to replace the strong potential  $V$  by a much weaker pseudopotential  $V^p$  such that  $T + V^p$  has the *same spectrum of valence eigenvalues* as  $T + V$ , but gives rise to no eigenstates of lower energy. It proves possible to construct many pseudopotentials of this kind. Indeed, replacing  $V$  by any operator  $V^p$  having the same phase shifts at the core radius leaves the valence spectrum unchanged.

In this way it is often feasible, for the simple metals, to select a pseudopotential that is very small in the core region and is, therefore,

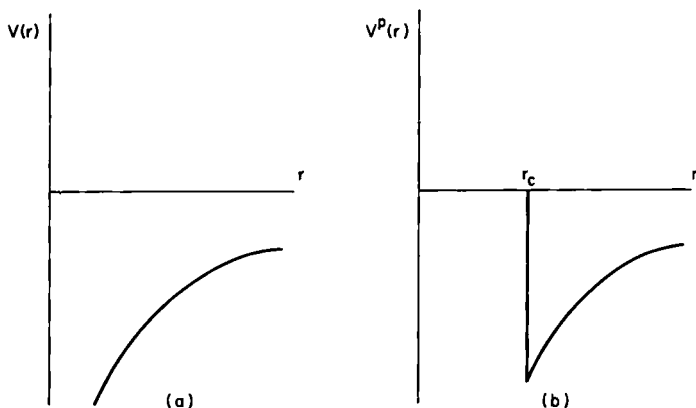


FIG. 1. (a) Schematic representation of an electron-ion potential in a simple metal. (b) Schematic representation of a local pseudopotential corresponding to this potential.

<sup>9</sup> M. L. Cohen and V. Heine, *Solid State Phys.* **24**, 38 (1970).

capable of being treated by perturbation theory, as has been extensively discussed by Heine<sup>7</sup> and by Cohen and Heine.<sup>9</sup> Such a pseudopotential is schematically drawn in Fig. 1b.

The following points should be noted about the use of a weak pseudopotential to represent the electron-ion interaction in a simple metal:

(i) The pseudopotential is not uniquely defined, as noted above. (For a discussion of this question, see Heine<sup>7</sup> and Cohen and Heine.<sup>9</sup>)

(ii) The pseudopotential is spatially nonlocal; that is, the plane wave matrix elements  $\langle \mathbf{k} + \mathbf{q} | V^p | \mathbf{k} \rangle$  depend on  $\mathbf{k}$  as well as  $\mathbf{q}$ .

(iii) The pseudopotential is, in general, energy-dependent.

(iv) While the valence *eigenvalues* of  $T + V^p$  are the same as those of  $T + V$ , the corresponding *eigenfunctions* are not. For instance, the eigenfunctions  $T + V^p$  are not orthogonal to the core wave functions. The pseudo-wave functions vary smoothly in the core, whereas the true wave functions, in order to orthogonalize themselves to the core levels, oscillate rapidly in the core.

Despite these ambiguities, we shall henceforth treat the electron-ion interaction in a simple metal as a weak, local, energy-independent pseudopotential. This approximation undoubtedly leads to some inaccuracies in the calculated thermodynamics. In the context of crystalline simple metals the corrections arising from proper inclusion of effects ii-iv noted above have been discussed by Heine and Weaire;<sup>10</sup> most of their discussion applies equally to liquid metals. They observe that nonlocality can be taken into account if one replaces the *energy-wave number characteristic* [defined in Eq. (5.4) below] by a more complicated function involving an integral over the Fermi sphere. Similarly, the effects of energy-dependence and nonorthogonality can be at least partly incorporated by renormalizing the electronic mass and the ionic charge.<sup>11</sup> But in practice some of these effects are probably included semiempirically even in the local approximation, since this, as will be seen, involves a parameter  $E_0$  which is poorly understood from first principles and usually has to be adjusted to some experimental datum.

## 2. THE HAMILTONIAN

With the caveats noted above, the full Hamiltonian appropriate to a liquid nearly free-electron metal can now be stated. Let the liquid have

<sup>10</sup> V. Heine and D. Weaire, *Solid State Phys.* **24**, 250 (1970).

<sup>11</sup> See, for example, V. Heine and D. Weaire,<sup>10</sup> pp. 326ff; R. W. Shaw, *J. Phys. C* **2**, 2335 (1969); *ibid.*, p. 2350 (1969); J. Hafner, *J. Phys. F* **6**, 1243 (1976).



volume  $\Omega$  and let it contain  $N$  ions of valence  $Z$  and  $NZ$  electrons. Then

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \frac{P_i^2}{2M} \quad (2.1)$$

$$+ \frac{1}{2} \sum_{i \neq l'} W(\mathbf{R}_i - \mathbf{R}_{l'}) + \sum_{il} V^p(\mathbf{r}_i - \mathbf{R}_l).$$

Here the  $\{\mathbf{r}_i\}$  and  $\{\mathbf{R}_l\}$  denote electronic and ionic coordinates,  $\{\mathbf{p}_i\}$  and  $\{\mathbf{P}_l\}$  the corresponding momenta,  $m$  and  $M$  the masses,  $W(R)$  is the bare ion-ion interaction, and  $V^p$  the (unscreened) electron-ion pseudopotential. At large separations  $V^p$  and  $W$  will be purely coulombic, but  $W$  will have short-range contributions arising from the van der Waals attraction and Born-Mayer repulsion between the ionic cores; at normal densities these are generally weak for metals with small cores.<sup>8</sup> In what follows we take for simplicity  $W = Z^2 e^2 / R$ , which is a reasonable replacement at the densities usually associated with simple metals.

The Hamiltonian (2.1) suffers from the usual divergence problems exhibited by systems with long-range interactions. These may be resolved by rearranging  $H$  so that each group of terms is finite, taking the thermodynamic limit last. (The thermodynamic limit is defined by  $N \rightarrow \infty$ ,  $\Omega \rightarrow \infty$ ,  $N/\Omega = \text{const.}$ ) Accordingly, we rewrite (2.1) as

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - E' \quad (2.2a)$$

$$+ \frac{1}{2} \sum_{i \neq l'} \frac{Z^2 e^2}{|\mathbf{R}_i - \mathbf{R}_{l'}|} + E' + E'' \quad (2.2b)$$

$$+ \sum_{il} V^p(\mathbf{r}_i - \mathbf{R}_l) - E'' \quad (2.2c)$$

$$+ \sum_i \frac{P_i^2}{2M}, \quad (2.2d)$$

where  $E'$  and  $E''$  are defined by

$$E' = \frac{1}{2} \int_{\Omega} d\mathbf{r} \int_{\Omega} d\mathbf{r}' \frac{(\rho_e e)^2}{|\mathbf{r} - \mathbf{r}'|} \quad (2.3)$$

$$E'' = \frac{1}{2} \sum_l \int_{\Omega} d\mathbf{r} \frac{Z e^2 \rho_e}{|\mathbf{r} - \mathbf{R}_l|}, \quad (2.4)$$

$\rho_e = NZ/\Omega$  being the average valence electron density. Evidently  $E'$  is the self-energy of a uniform charge density  $\rho_e|e|$ , and  $E''$  is the Coulomb interaction between the ions and such a uniform negative background.

Line (2.2a) is now the standard Hamiltonian,  $H_{\text{eg}}$ , for an interacting

electron gas embedded in a uniform compensating background. It is, of course, entirely independent of ionic coordinates. For a given ionic arrangement (2.2b) is the electrostatic energy  $U_M$  of the charged point ions in a similar neutralizing background. The remaining terms (2.2c) and (2.2d) are the electron-ion interaction and the ionic kinetic energy.

To complete the rearrangement, we rewrite (2.2) in Fourier representation. The  $\mathbf{k} = 0$  term in the sums of (2.2b) is canceled by the uniform background contribution. An analogous contribution does not fully occur in (2.2c) because of the deviation of  $V^p$  from Coulombic behavior at short range. Thus (2.2b) becomes

$$U_M = \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \frac{4\pi Z^2 e^2}{k^2} [\hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_{\text{ion}}(-\mathbf{k}) - N] \quad (2.5)$$

while (2.2c) can be written

$$H_{\text{ei}} = 1/\Omega \sum_{\mathbf{k} \neq 0} V^p(k) \hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_e(-\mathbf{k}) + NE_0 \equiv H'_{\text{ei}} + NE_0 \quad (2.6)$$

where  $\hat{\rho}_{\text{ion}}(\mathbf{k})$  and  $\hat{\rho}_e(\mathbf{k})$  are Fourier components of the ionic and the electronic density as defined in the Appendix,  $V^p(k)$  is a Fourier component of the bare electron-ion interaction or pseudopotential, and  $E_0$  is the so-called Hartree energy, given in any ensemble by

$$\begin{aligned} E_0 &= \frac{1}{\Omega} \lim_{k \rightarrow 0} \left[ \left( V^p(k) + \frac{4\pi Z e^2}{k^2} \right) \hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_e(-\mathbf{k}) \right] \\ &= \rho_e \int_{\Omega} d\mathbf{r} \left[ \frac{Z e^2}{r} + V^p(r) \right]. \end{aligned} \quad (2.7)$$

With these modifications, (2.2) takes the form

$$H = H_{\text{eg}} + U_M + H'_{\text{ei}} + NE_0 + H_K, \quad (2.8)$$

$H_K$  being the contribution to the ionic kinetic energy.

At this point we remark that  $H$  is general and applicable to any liquid metal, whether the ions are viewed as classical or as quantum (as long as the electron-ion interaction can be taken as local).

### 3. REDUCTION TO A QUASI-ONE COMPONENT FLUID

We are now in a position to show that the thermodynamics of a liquid simple metal can be approximately calculated without further explicit reference to the electronic degrees of freedom. It will be convenient at this point to work within the canonical ensemble. The Helmholtz free energy *per ion*  $F$  is then given by

$$F = -(k_B T/N) \ln Z_p \quad (3.1a)$$

where the partition function  $Z_p$  is

$$Z_p = \text{Tr} \exp (-H/k_B T), \quad (3.1b)$$

the trace running over states of the entire composite system (electrons and ions). In more explicit form  $Z_p$  may be written in terms of the ionic coordinates and momenta as

$$Z_p = \frac{1}{N! h^{3N}} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \int d\mathbf{P}_1 \cdots d\mathbf{P}_N \text{Tr}_e e^{-H/k_B T}, \quad (3.2)$$

and, making the customary adiabatic approximation, the trace now runs over a complete set of electron states appropriate to the prescribed ionic configuration.

Equation (3.2) has been obtained by viewing the ions as classical particles in the sense that the commutator  $[\mathbf{R}_i, \mathbf{P}_i]$  vanishes. The integral over ionic momenta can then be carried out with the standard result<sup>5</sup>

$$Z_p = (2\pi M/h^2)^{3N/2} Q_N \quad (3.3a)$$

where  $Q_N$  is the configurational partition function, given by

$$Q_N = \frac{1}{N!} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \exp\{-\beta(U_M + NE_0)\} [\text{Tr}_e \exp\{-\beta(H'_{ei} + H_{eg})\}]. \quad (3.3b)$$

The form (3.3b) emerges because  $U_M + NE_0$  does not involve electronic coordinates and hence may be excluded from the trace over electron states. The bracketed term is written

$$[\quad] = \exp\{-\beta NF'(\mathbf{R}_1, \dots, \mathbf{R}_N)\} \quad (3.4)$$

where  $F'(\mathbf{R}_1, \dots, \mathbf{R}_N)$  is the Helmholtz free energy per ion of an interacting electron gas *placed in the external potential described by*  $H'_{ei}$  (which corresponds to a specific ionic configuration denoted by  $\mathbf{R}_1, \dots, \mathbf{R}_N$ ). The problem of computing the thermodynamics of the liquid metal can now be broken into two parts. The first is to compute  $F'(\mathbf{R}_1, \dots, \mathbf{R}_N)$  within some approximation. Once this is achieved, the electronic degrees of freedom no longer explicitly appear and we have an essentially classical liquid-state problem of finding the configuration integral corresponding to ions moving in a mutual interaction potential described by  $U_M$  and  $NF'$ .

For the case at hand we are aided in calculating  $F'$  by the fact that the external potential  $H'_{ei}$  in which the electrons are moving is, by assumption, weak. Thus  $F'$  will only deviate slightly from  $F_{eg}$ , the Helmholtz free energy per ion of a *uniform* electron gas. The deviation can be

calculated by perturbation theory as applied to  $H'_{ei}$ . (The analysis is in fact very similar to that used to find the analogous energy in solid metals at zero temperature.<sup>10,12</sup>)

For present purposes it is convenient to start with an exact coupling-constant expression<sup>13</sup> relating  $F'$  to  $F_{eg}$ :

$$NF' = NF_{eg} + \int_0^1 \frac{d\lambda}{\lambda} \langle \lambda H'_{ei} \rangle_\lambda. \quad (3.5)$$

The subscript on the brackets here indicates that the average is to be carried out with respect to an ensemble characterized by the Hamiltonian  $H_{eg} + \lambda H'_{ei}$  (the average is calculated with the ionic configuration held fixed). Now substitution of (2.6) for  $H'_{ei}$  gives

$$\langle \lambda H'_{ei} \rangle = \frac{\lambda}{\Omega} \sum_{\mathbf{k} \neq 0} V^p(k) \hat{\rho}_{ion}(\mathbf{k}) \langle \hat{\rho}_e(-\mathbf{k}) \rangle_\lambda$$

where  $\langle \hat{\rho}_e(-\mathbf{k}) \rangle_\lambda$  is a Fourier component of the electron charge density induced by  $\lambda H'_{ei}$ . Since  $H'_{ei}$  is by hypothesis small, it is usually sufficient to calculate this induced density to *linear* order in the perturbation. This can be done immediately in terms of the density-density linear response function  $\chi^{(1)}(k)$  characteristic of the *uniform* electron gas.<sup>14</sup> This function is defined in the Appendix and its properties further discussed in the next section. From its definition it follows immediately that to linear order

$$\langle \hat{\rho}_e(-\mathbf{k}) \rangle_\lambda = \lambda \chi^{(1)}(k) V^p(-k) \hat{\rho}_{ion}(-\mathbf{k}).$$

Substituting this into (3.5) and carrying out the coupling-constant integration yields

$$\begin{aligned} NF' &= NF_{eg} + \frac{1}{2} \frac{1}{\Omega} \sum_{\mathbf{k} \neq 0} \chi^{(1)}(k) |V^p(k)|^2 \hat{\rho}_{ion}(\mathbf{k}) \hat{\rho}_{ion}(-\mathbf{k}) \\ &= NF_{eg} + U_{ei}^{(1)}. \end{aligned} \quad (3.6)$$

Evidently  $U_{ei}^{(1)}$  is precisely the electrostatic work required (at lowest order of perturbation theory) to induce the nonuniform electron density characteristic of a particular ionic configuration. The factor  $\frac{1}{2}$  in (3.6) comes from the coupling constant integration and is quite typical of calculations involving electrostatic work in linear media.

<sup>12</sup> N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **155**, 682 (1967).

<sup>13</sup> R. P. Feynman, "Statistical Mechanics." Benjamin, New York, 1972.

<sup>14</sup> See, for example, D. Pines and P. Nozières, "Quantum Liquids." Benjamin, New York, 1966. We consider only zero-frequency response, i.e.,  $\chi'(k) \equiv \chi(k, 0)$ .

Substitution of (3.6) into (3.3b) gives

$$Q_N = \frac{1}{N!} \int d\mathbf{R}_1 \cdots d\mathbf{R}_N \exp\{-\beta U(\mathbf{R}_1 \cdots \mathbf{R}_N)\}, \quad (3.7a)$$

where for fixed volume  $U$  is an effective potential energy function for the ions given by

$$U = NE_0 + NF_{eg} + U_M + U_{el}^{(1)}. \quad (3.7b)$$

With this result the electronic degrees of freedom are no longer directly displayed in the configuration partition function. The electrons' presence is, however, manifested in  $F_{eg}$ , and in  $U_{el}^{(1)}$ , the latter depending on the properties of the electron gas via  $\chi^{(1)}(k)$ .

The Helmholtz free energy per ion corresponding to (3.7) is

$$F = N^{-1}\langle U \rangle + \frac{3}{2} k_B T - T\mathcal{S}_{ion} \quad (3.8)$$

where  $\langle U \rangle$  is the average of  $U$  over ionic configurations,  $\frac{3}{2} k_B T$  is the ionic kinetic energy, and  $\mathcal{S}_{ion}$  the configurational entropy per ion. In explicit form

$$N^{-1}\langle U \rangle = F_{eg} + E_0 + E_M + E_{BS}, \quad (3.9)$$

where  $E_M = N^{-1}\langle U_M \rangle$  and  $E_{BS} = N^{-1}\langle U_{el}^{(1)} \rangle$  are, respectively, the Madelung energy and the "band structure" energy of the liquid metal. (The latter is named in analogy with the corresponding term in solid metals.<sup>12</sup>) The quantities  $E_M$  and  $E_{BS}$  are conveniently expressible in terms of the ionic structure factors defined in the Appendix:

$$E_M = \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \frac{4\pi Z^2 e^2}{k^2} [S(k) - 1] \quad (3.10)$$

$$E_{BS} = \frac{1}{2\Omega} \sum_{\mathbf{k} \neq 0} \chi^{(1)}(k) |V^p(k)|^2 S(k). \quad (3.11)$$

In practice one is usually interested in the properties of liquid metals at temperatures small compared to the Fermi degeneracy temperature. Under these conditions  $F_{eg}$  is accurately approximated by  $E_{eg}$ , the internal energy of the electrons at 0°K; the entropy of the electron gas is usually small compared to the configurational entropy of the ions (the ratio is approximately that of the electronic to the ionic specific heat). Likewise  $\chi^{(1)}$  can be approximated by its ground-state form.

## 4. RESPONSE FUNCTION AND DIELECTRIC FUNCTION

The response function  $\chi^{(1)}(k)$  appearing in (3.6) and (3.11) is closely related to the usual dielectric function  $\epsilon(k)$ . The connection between the two and the proper calculation of  $\epsilon(k)$  including exchange and correlation have been amply treated elsewhere.<sup>14,15</sup> In the present section our intent is only to summarize a few salient results.

To make connection between  $\chi^{(1)}$  and  $\epsilon$ , imagine that the electron gas is disturbed by a weak external potential  $\delta V_{\text{ext}}(k)$ . For this translationally invariant system, the induced density  $\delta\rho_{\text{ind}}(k)$  is given within linear response by

$$\delta\rho_{\text{ind}}(k) = \chi^{(1)}(k) \delta V_{\text{ext}}(k) \quad (4.1)$$

according to definition (A.17) for the response function. The *total* potential felt by a *test charge*  $-|e|$  (other than an electron) will be

$$\delta V_{\text{tot}}(k) = \delta V_{\text{ext}}(k) + V_c(k) \delta\rho_{\text{ind}}(k) \equiv \epsilon^{-1}(k) \delta V_{\text{ext}}(k) \quad (4.2)$$

where  $V_c(k) = 4\pi e^2/k^2$ . Combining (4.2) with (4.1) yields

$$\chi^{(1)}(k) = (k^2/4\pi e^2)\{[1/\epsilon(k)] - 1\}. \quad (4.3)$$

One of the simplest approximations to  $\epsilon(k)$  is the Lindhard<sup>16</sup> dielectric function, which is based on a self-consistent field approximation. In this approach, it is assumed that the electrons respond like *free particles* to the *same* total potential felt by "nonelectronic" test charge, that is, that

$$\delta\rho_{\text{ind}}(k) = \chi_0(k) \delta V_{\text{tot}}(k) \quad (4.4)$$

where  $\chi_0(k)$  is the free electron density response function given by

$$\chi_0(k) = -\frac{mk_F}{\pi^2\hbar^2} \left[ \frac{1}{2} + \frac{1}{4y} (1 - y^2) \ln \left| \frac{1+y}{1-y} \right| \right], \quad (4.5)$$

$\hbar k_F$  being the free electron Fermi momentum and  $y$  being the reduced variable  $k/2k_F$ . The combination of (4.4) with (4.3) gives the Lindhard dielectric function

$$\epsilon_L(k) = 1 - V_c(k) \chi_0(k) \quad (4.6)$$

which is plotted in Fig. 2. The Lindhard dielectric function already contains many of the central features common to more sophisticated dielectric functions. In particular, its first derivative exhibits a logarithmic

<sup>15</sup> See, for example, Pines and Nozières,<sup>14</sup> or L. Hedin and S. Lundqvist, *Solid State Phys.* **23**, 1 (1969).

<sup>16</sup> J. Lindhard, *Dan. Videnskab. Selskab. Mat. Phys. Medd.* **28**, 8, (1954).

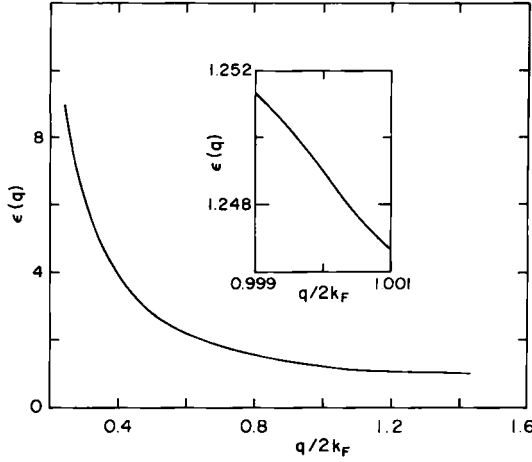


FIG. 2. Lindhard dielectric constant for  $r_s = 3.0$  ( $4\pi r_s^3/3 = n^{-1}$  is the volume per electron).

mic singularity at  $k = 2k_F$  which is responsible for the Kohn anomaly<sup>17</sup> in the phonon spectrum of metals as well as the Friedel oscillations<sup>18,19</sup> in the pairwise interactions of simple metals (as discussed below).

Equation (4.6) neglects exchange and correlation effects. These are conventionally incorporated into  $\epsilon(k)$  via a function  $G(k)$  such that

$$\epsilon(k) = 1 - \frac{V_c(k) \chi_0(k)}{1 + V_c(k)G(k)\chi_0(k)}. \quad (4.7)$$

Equation (4.7) may be viewed as the *definition* of  $G(k)$ . However, it can also be motivated by a simple, if nonrigorous, physical argument: Let  $\delta V_{\text{tot}}^e$  be the total potential felt by an *electron* when the electron gas is disturbed by  $\delta V_{\text{ext}}(k)$ . This will, of course, differ from that potential  $\delta V_{\text{tot}}(k)$  felt by any other test charge because of exchange and correlation between the "test" electron and the induced charge in the electron gas. Let us write this potential as

$$\delta V_{\text{tot}}^e(k) = \delta V_{\text{tot}}(k) + \delta V'(k) = \delta V_{\text{ext}}(k) + V_c(k) \delta \rho_{\text{ind}}(k) + \delta V'(k), \quad (4.8)$$

$\delta V'(k)$  being this extra potential felt by an *electron* test charge. Now in a linear theory  $\delta V'(k)$  will clearly be proportional to  $\delta \rho_{\text{ind}}(k)$  and so we

<sup>17</sup> W. Kohn, *Phys. Rev. Lett.* **2**, 393 (1959).

<sup>18</sup> J. S. Langer and S. H. Vosko, *J. Phys. Chem. Solids* **12**, 196 (1959).

<sup>19</sup> N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **159**, 500 (1967).

may put

$$\delta V'(k) = -G(k) V_c(k) \delta \rho_{\text{ind}}(k). \quad (4.9)$$

The electron gas then responds to  $\delta V_{\text{tot}}^e$  according to

$$\delta \rho_{\text{ind}}(k) = \chi_0(k) \delta V_{\text{tot}}^e(k). \quad (4.10)$$

Combining the last three equations with (4.1) gives

$$\chi^{(1)}(k) = \frac{\chi_0(k)}{1 - (1 - G(k)) \chi_0(k) V_c(k)}, \quad (4.11)$$

and use of the definition (4.3) for the response function then yields (4.7) for  $\epsilon(k)$ .

A number of forms for  $G(k)$  have been proposed in the literature.<sup>20</sup> Some of these are plotted in Figure 3; evidently there is a wide numerical variation in the behavior of these functions at electron densities typical of the simple metals. However, at small wave vectors all have similar behavior, this being dictated by the compressibility sum rule. For the electron gas, this rule states (see the Appendix) that

$$\lim_{k \rightarrow 0} k^2 \epsilon(k) = k_{\text{TF}}^2 (K/K_0) \quad (4.12)$$

where  $k_{\text{TF}}^2 = 4e^2 m k_{\text{F}} / \pi \hbar^2$  is the square of the Thomas-Fermi wave vector, and  $K/K_0$  is the ratio of the compressibility of interacting electron gas to that of the free (noninteracting) electron gas. Equation (4.12) implies therefore that  $G(k)$  must satisfy

$$\lim_{k \rightarrow 0} G(k)/k^2 = (1 - K_0/K)/k_{\text{TF}}^2. \quad (4.13)$$

## 5. EFFECTIVE ION-ION INTERACTIONS

The effective potential energy function  $U$  [Eq. (3.7b)] has a particularly simple interpretation in real space, as was first noted by Cohen.<sup>21</sup> Since only  $U_{\text{M}}$  and  $U_{\text{el}}^{(1)}$  depend on ionic configuration,  $U$  may be rewritten in the form

$$U(\mathbf{R}_1, \dots, \mathbf{R}_N) = U_0(\rho) + \frac{1}{2} \sum_{l \neq l'} \Phi(\mathbf{R}_l - \mathbf{R}_{l'}; \rho) \quad (5.1)$$

$$\rho = \langle \lim_{k \rightarrow 0} \hat{\rho}_{\text{ion}}(\mathbf{k}) \rangle \quad (5.1a)$$

<sup>20</sup> For a brief discussion of approximations for  $G(q)$  prior to 1970, see Hedin and Lundqvist.<sup>15</sup>

<sup>21</sup> M. H. Cohen in "Metallic Solid Solutions" (J. Friedel and A. Guinier, eds.). Benjamin, New York, 1963.



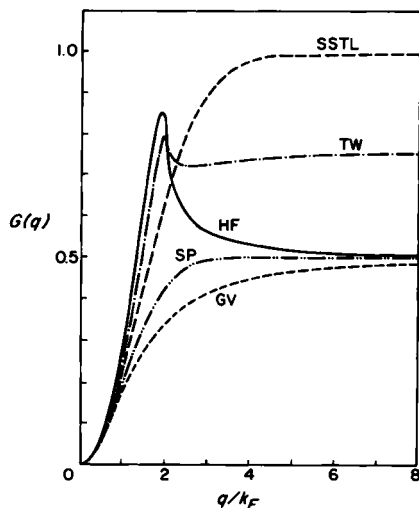


FIG. 3. The function  $G(q)$  as calculated from various approximation schemes at an electron density corresponding to liquid Na at 100°C. HF, improved Hartree-Fock [L. J. Sham, *Phys. Rev. B* 7, 4357 (1973)]; TW, Toigo and Woodruff [F. Toigo and T. O. Woodruff, *Phys. Rev. B* 2, 3958 (1970)]; SSTL, Singwi *et al.* [K. S. Singwi, A. Sjolander, M. P. Tosi, and R. H. Land, *Phys. Rev. B* 1, 1044 (1970)]; SP, Shaw and Pynn [R. W. Shaw and R. Pynn, *J. Phys. C* 2, 2071 (1969)]; GV, Geldart and Vosko [D. J. W. Geldart and S. H. Vosko, *Can. J. Phys.* 44, 2137 (1970)]. [After M. Hasegawa, *J. Phys. F* 6, 649 (1976).]

where  $U_0(\rho)$  depends only on the density of the liquid metal, and *not* on the ionic arrangement, while  $\Phi(R;\rho)$  represents an *effective pairwise interaction* between the ions.<sup>21a</sup> In terms of its Fourier transform,

$$\Phi(\mathbf{R}_l - \mathbf{R}_{l'}; \rho) = \frac{1}{\Omega} \sum_{\mathbf{k}} \Phi(k) \exp [i \mathbf{k} \cdot (\mathbf{R}_l - \mathbf{R}_{l'})] \quad (5.2)$$

where

$$\Phi(k) = \frac{4\pi Z^2 e^2}{k^2} \left\{ 1 + \left( \frac{1}{\epsilon(k)} - 1 \right) \left( \frac{V^p(k)}{4\pi Z e^2 / k^2} \right)^2 \right\} \quad (5.3)$$

$$\equiv \frac{4\pi Z^2 e^2}{k^2} + \tilde{\Phi}_{BS}(k). \quad (5.4)$$

<sup>21a</sup> The interpretation is made via Fourier transformation which, strictly speaking, requires knowledge of  $\Phi$  for *all*  $\mathbf{k}$ , including  $\mathbf{k} = 0$ . In expressing  $E_M + E_{BS}$  in terms of pairwise interactions, the  $\mathbf{k} = 0$  term must be supplied to the sum. Its negative then enters the purely volume-dependent part, as does the part corresponding to  $\mathbf{R} = \mathbf{R}'$ .

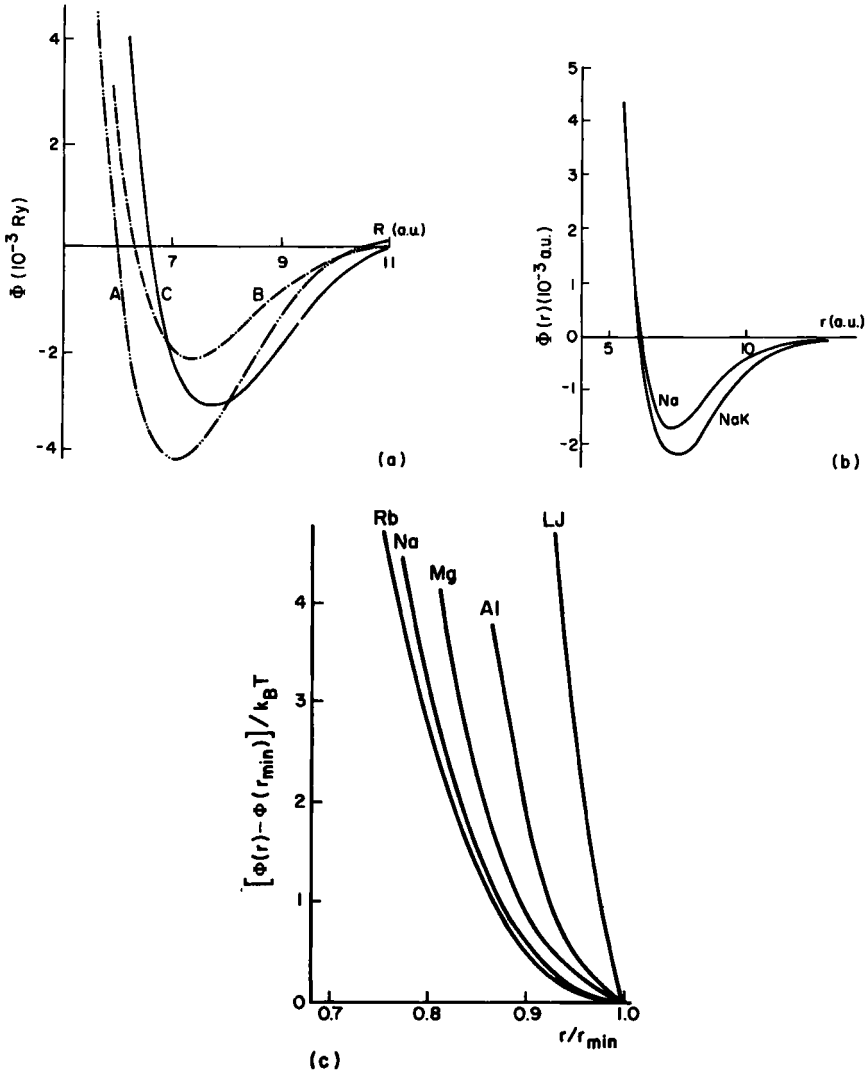


FIG. 4. (a) Pair interaction for liquid Na corresponding to several choices of local model pseudopotential, as calculated by R. Kumaravadevel and R. Evans, *J. Phys. C* **9**, 3877 (1976). (b) Pair interactions for liquid Na at densities appropriate to pure liquid Na and to liquid Na<sub>0.5</sub>K<sub>0.5</sub>, as calculated by Takeda and Watabe.<sup>24</sup> (After W. H. Young, in *Proc. Int. Conf. Liquid Met.* 3rd, 1976, p. 1.) (c) The repulsive part of the pair interactions in a number of liquid metals, compared to that of a Lennard-Jones fluid. Here  $r_{\min}$  denotes the separation at which the potential attains its principal minimum. [After R. Kumaravadevel and R. Evans, *J. Phys. C* **9**, 3877 (1976).] In Fig. 4a curves A, B, and C are as in Fig. 5.

The Fourier transform of the effective ion-ion interaction can thus be expressed in terms of the so-called energy-wave number characteristic  $\Phi_{\text{BS}}(k)$  defined in (5.4). Since  $\Phi(k)$  is radially symmetric,  $\Phi(\mathbf{R}_l - \mathbf{R}_{l'})$  is also, and it can therefore be expressed as a one-dimensional integral:

$$\Phi(R) = \frac{Z^2 e^2}{R} + \frac{1}{2\pi^2} \int_0^\infty \frac{\sin kR}{kR} \Phi_{\text{BS}}(k) k^2 dk. \quad (5.5)$$

It is of interest to compare the interactions defined by (5.4) with analogous potentials characteristic of simple insulating liquids such as argon. A typical potential for a metal is that of Na, whose form, as calculated by Kumaravadivel and Evans,<sup>22</sup> is shown in Fig. 4a for several choices of local model pseudopotential. Because of the presence of the electron dielectric function in (5.5), the pair potentials appropriate to a metal exhibit a significant density dependence which is thought to be absent from those of rare gas fluids.<sup>23</sup> This density dependence is illustrated in Fig. 4b with the pair potentials appropriate to Na at two different electron densities. These were obtained by Takeda and Watabe.<sup>24</sup>

Except for the density dependence, the pair potentials do not differ markedly from those of rare gas fluids, such as the Lennard-Jones 6-12 potential characteristic of argon. In particular, the potentials of both the metal and the insulator have a weak attractive tail, a minimum at roughly the average nearest neighbor separation, and a steeply repulsive behavior at small spacing (*not* comparable to the ionic diameter in the metallic case). The repulsion in the two cases arises from seemingly different physical origins: in rare gases, from Born-Mayer repulsion between closed shells; in metals, from the failure of electronic screening of the bare ion-ion (Coulomb) repulsion at small  $r$ .<sup>25</sup> The repulsion in the metal also tends to be less steep than in Lennard-Jones fluids.<sup>22,26</sup> This is illustrated in Fig. 4c where the repulsive parts of the potentials of several simple metals are compared to that of a Lennard-Jones fluid. At large separation the metallic potential shows a characteristic oscillation

<sup>22</sup> R. Kumaravadivel and R. Evans, *J. Phys. C* **9**, 3877 (1976).

<sup>23</sup> Actually three-body (and higher) forces can be absorbed into effective density (and temperature) dependent *pair* forces in argon as well [see Casanova *et al. Mol. Phys.* **18**, 589 (1970)].

<sup>24</sup> K. Takeda and M. Watabe, to be published.

<sup>25</sup> Both ultimately stem from the Pauli exclusion principle, however.

<sup>26</sup> See, for example, D. Schiff, "The Properties of Liquid Metals" (S. Takeuchi, ed.), p. 57. Taylor and Francis, London, 1973.

(Friedel oscillation) arising from the singularity in the screening function at  $2k_F$ . These are visible in Fig. 5 below.

Because of the presence of the dielectric function in the combination  $\epsilon^{-1}(k) - 1$ , the effective interaction just described is also quite sensitive to small changes in  $G(k)$ . (It is further affected by inclusion of nonlocality and energy dependence in the pseudopotential.) The dependence on the form of  $G$  may be seen in Fig. 5 where we plot the pair potential of Na as computed by Kumaravadivel and Evans,<sup>22</sup> using several different choices for  $G$ . For  $G = 0$  (corresponding to the Lindhard dielectric function) there is not even a minimum in the potential near the expected positions of the nearest neighbor atoms. However, this is of less concern than might be expected, because the ionic configurations at normal densities are largely determined by the repulsive cores in the effective ion-ion potential. Furthermore, it should be remembered that the pairwise interactions contribute a relatively small fraction of the *total energy*, which is dominated by the volume-dependent, structure-inde-

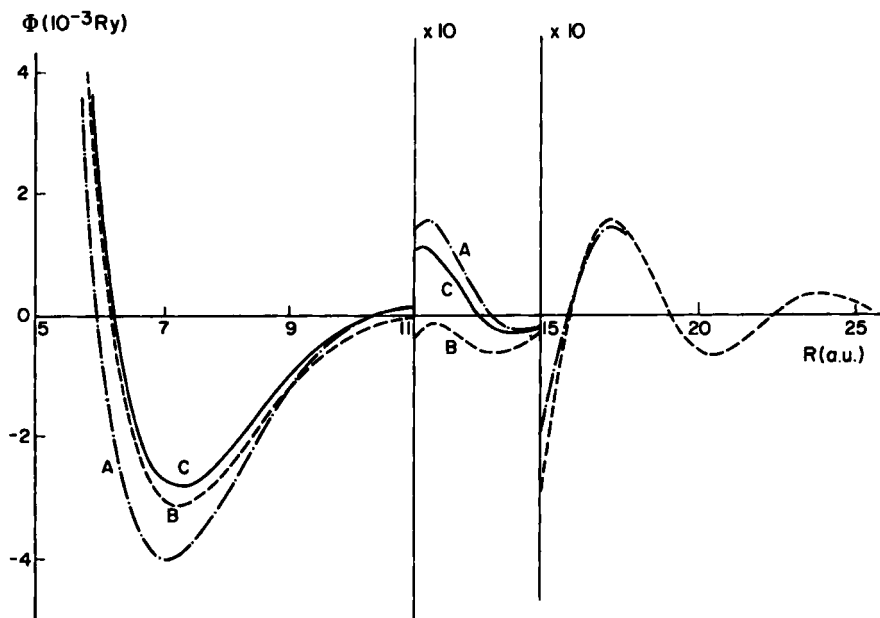


FIG. 5. Pair potentials for liquid Na, as calculated using a local model pseudopotential and several choices of  $G(q)$ . [R. Kumaravadivel and R. Evans, *J. Phys. C* **9**, 3877 (1976).] Curve A; P. Vashishta and K. S. Singwi, *Phys. Rev. B* **6**, 875 (1972); Curve B, L. Kleinman, *Phys. Rev.* **160**, 585 (1967); Curve C, Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, *Phys. Rev. B* **1**, 1044 (1970).

pendent terms (these in fact will stabilize the system in a case where liquid metal should have only repulsive interactions).

## 6. BEYOND LINEAR RESPONSE

The discussion to this point has been based on the assumption that the electron-ion interaction in a liquid metal is a weak potential to which the electron gas responds *linearly*. The possibility of nonlinear response may, in principle, be taken into account straightforwardly. The definition given in the Appendix relating the induced density to the external potential can be generalized to read (for a *static* external potential)

$$\delta\rho(\mathbf{k}) = \chi^{(1)}(k)\delta V^{\text{ext}}(\mathbf{k}) + \sum_{\mathbf{q}} \chi^{(2)}(\mathbf{k}, \mathbf{q})\delta V^{\text{ext}}(\mathbf{q})\delta V^{\text{ext}}(\mathbf{k} - \mathbf{q}) + \dots \quad (6.1)$$

which defines the *nonlinear* response functions  $\chi^{(2)}(\mathbf{k}, \mathbf{q})$ , etc. If an expansion of this form is used to evaluate the coupling constant integral in (3.5), then it is found that the potential energy function can be written

$$U = NE_0 + F_{\text{eg}} + U_{\text{M}} + U_{\text{el}}^{(1)} + U_{\text{el}}^{(2)} + \dots \quad (6.2)$$

where, for example,<sup>27,28</sup>

$$U_{\text{el}}^{(2)} = \frac{1}{2} \frac{1}{\Omega} \sum_{\mathbf{k} \neq 0} \sum_{\mathbf{q}} \chi^{(2)}(\mathbf{k}, \mathbf{q}) V^{\text{p}}(\mathbf{k}) V^{\text{p}}(\mathbf{q}) V^{\text{p}}(-\mathbf{k} - \mathbf{q}) \cdot \hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_{\text{ion}}(\mathbf{q}) \hat{\rho}_{\text{ion}}(-\mathbf{k} - \mathbf{q}). \quad (6.3)$$

Just as  $U_{\text{el}}^{(1)}$  corresponds to effective pairwise interactions between the ions, so  $U_{\text{el}}^{(2)}$  can be related to three-body interactions, and so on. Note that  $U_{\text{el}}^{(2)}$  also contributes to two-body and one-body terms, just as the diagonal part of  $U_{\text{el}}^{(1)}$  contributes to the one-body energy. Thus  $U$  can always be written in the form

$$U = U_0(\rho) + \frac{1}{2} \sum_{l \neq l'} \Phi^{(2)}(\mathbf{R}_l - \mathbf{R}_{l'}; \rho) + \frac{1}{6} \sum_{l \neq l' \neq l''} \Phi^{(3)}(\mathbf{R}_l, \mathbf{R}_{l'}, \mathbf{R}_{l''}; \rho) + \dots \quad (6.4)$$

where the two-body, three-body, ... potentials depend on electron density via the linear and nonlinear electron gas polarizabilities.

In practice the usefulness of the structural expansion just described tends to diminish if it is carried beyond linear response. The nonlinear response functions are not as well known as their linear counterparts and must be approximated. Moreover, the presence of three-body

<sup>27</sup> P. Lloyd and C. A. Sholl, *J. Phys. C* **1**, 1620 (1968).

<sup>28</sup> J. Hammerberg and N. W. Ashcroft, *Phys. Rev. B* **9**, 409 (1974).

interactions leads to the appearance of three-body correlation functions in the liquid-free energy, and these must also be approximated, usually by relating them to two-body quantities.<sup>29</sup> For these reasons the discussion here will be based mostly on the assumption that linear response is adequate. It is worth noting, however, that in the simple metals for which the third-order terms have been calculated, their contributions to the total energy tend to be considerably smaller than the second-order terms.<sup>30</sup> On the other hand there are reasons for expecting that contributions to the energy *derivatives*, such as elastic constants, may be larger.<sup>31,32</sup>

### III. Formalism: Liquid Aspects

There are several ways of approaching the subject of liquid state thermodynamics. Including the present approach we may cite the diagrammatic expansion technique<sup>33</sup> and the method based on functional Taylor expansions.<sup>34</sup> For the present purposes it will be convenient to limit discussions largely to the integral equation method as this at least permits an immediate, if rough physical, interpretation of most of the steps of the development.

Liquid metals and alloys normally fall in the class of "simple liquids".<sup>4</sup> Simple liquids, as noted in the Introduction, are those whose appropriate dynamic units (atoms, molecules, ions, etc.) have sufficient symmetry that for fixed volume their mutual interactions can be written as functions of their mutual separations only. In the case of pairwise interactions this would mean that the pair potentials are radially symmetric. To the extent that the *structural* energy of a metal at constant volume can be resolved in terms of *effective* pair interactions between

<sup>29</sup> An alternative method of going beyond linear response is to attempt to sum all terms in the structural expansion which contribute to one-body, two-body, etc. terms in the potential energy. This can be done approximately in various ways, for example by utilizing the density functional approach of Hohenberg, Kohn and Sham [P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1963); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A133 (1965)]. For an example of renormalized pair potentials obtained by this approach, see M. Rasolt and R. Taylor, *Phys. Rev. B* **11**, 2717 (1975).

<sup>30</sup> E. G. Brovman and G. Solt, *Solid State Commun.* **8**, 903 (1970). See also Hammerberg and Ashcroft.<sup>28</sup>

<sup>31</sup> C. J. Pethick, *Phys. Rev. B* **2**, 1789 (1975).

<sup>32</sup> E. G. Brovman and M. Kagan, *Zh. Eksp. Teor. Fiz* **57** [*Sov. Phys.—JETP* **30**, 721 (1970)].

<sup>33</sup> G. Stell, *Physica* **29**, 517 (1963).

<sup>34</sup> See, for example, J. K. Percus in "The Equilibrium Theory of Classical Fluids" (H. L. Frisch and J. L. Lebowitz, eds.), pp. 11-33ff. Benjamin, New York, 1964.

metals (as discussed in Section II), we may treat liquid simple metals (and many of their alloys) as simple liquids, at least for many structural purposes. It is certainly the case that some purely "liquid" aspects of liquid metals are not dissimilar to the corresponding properties of insulating simple liquids (viscosity, for example<sup>35</sup>) and these fall well within the purview of equilibrium and nonequilibrium statistical mechanics. The purpose of this section, therefore, is to discuss briefly (insofar as the present theory presents) the structural aspects of liquids in which the electron degrees of freedom are entirely discussed in terms of effective (rather than "bare") interactions between ions. In this respect (and again, provided volume is fixed) the systems are then largely indistinguishable from classical insulating simple liquids, and it is toward the latter that the theory has mainly been directed.

## 7. DEFINITION OF DISTRIBUTION FUNCTIONS: CONNECTION BETWEEN DISTRIBUTION FUNCTIONS AND INTERPARTICLE INTERACTIONS

In the statistical theory of classical liquids at equilibrium, one generally begins by assigning to each particle of the liquid a position  $\mathbf{R}_i$  or  $\mathbf{R}_i^{(a)}$  which is taken (as in the preceding section) to commute with its momentum. The totality  $\{\mathbf{R}_i\}$  or  $\{\mathbf{R}_i^{(a)}\}$  of such positions constitute, at a given instant, a configuration of the liquid. Equilibrium properties of classical liquids then involve time-independent (or static) configurational *distribution functions*,<sup>36</sup> the latter defining the probability of occurrence of a particular arrangement of "ions" in a collection of  $N$  such ions confined to a volume  $\Omega$ . The most important of the  $n$ -particle distributions (defined in the Appendix) are the *singlet*  $\rho^{(1)}(r) \equiv \rho(r)$  and *pair* distribution,  $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ . The singlet density ( $\rho = N/\Omega$  for a pure homogeneous fluid) is clearly related to the probability of finding *any* particle in a given volume element. Likewise the pair function  $\rho^{(2)}(\mathbf{r}, \mathbf{r}')d\mathbf{r} d\mathbf{r}'$  is related to the probability of finding at the same instant *any* two different particles in  $d\mathbf{r}$  and  $d\mathbf{r}'$  and clearly satisfies, for a homogeneous fluid,

$$\int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{\Omega}. \quad (7.1)$$

In a similar way integration over one of the arguments of the  $(n+1)$ -particle functions gives, for example,

$$\int d\mathbf{r}_{n+1} \rho^{(n+1)}(\mathbf{r}_1, \dots, \mathbf{r}_{n+1}) = (N-n)\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n). \quad (7.2)$$

<sup>35</sup> N. E. Cusack, *Rep. Progr. Phys.* **26**, 361 (1963).

<sup>36</sup> For the most part we need not be concerned with the distribution of *momenta*.

Notice that if the particles are regarded as distinguishable, then in distributing them among volume elements, there can be  $N$  choices for an ion in  $d\mathbf{r}_1$  about  $\mathbf{r}_1$ ,  $(N - 1)$  in  $d\mathbf{r}_2$  about  $\mathbf{r}_2$ , and so forth. It follows that the probability function for finding a *given* selection of  $n$  ions, say  $P^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n)$ , is

$$P^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{(N - n)!}{N!} \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad (7.3)$$

which implies, for example, that

$$P^{(1)} d\mathbf{r}_1 = \frac{(N - 1)!}{N!} \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 = d\mathbf{r}_1 / \Omega$$

as expected. If the particles were uncorrelated, or if their mutual separations are *very* large then, as a further example,

$$\begin{aligned} P^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 &\rightarrow \frac{d\mathbf{r}_1}{\Omega} \frac{d\mathbf{r}_2}{\Omega}, \\ P^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 &\rightarrow \frac{d\mathbf{r}_1}{\Omega} \frac{d\mathbf{r}_2}{\Omega} \frac{d\mathbf{r}_3}{\Omega}, \text{ etc.}, \end{aligned}$$

or, in the same limits,

$$\begin{aligned} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= (N/\Omega)^2 = (\rho^{(1)})^2, \\ \rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= (N/\Omega)^3 = (\rho^{(1)})^3, \text{ etc.} \end{aligned} \quad (7.4)$$

( $N$  being typically  $\sim 10^{22}$ ). As is made explicit in the Appendix, this result is exploited in the definition of the pair or radial distribution function  $g(r)$  for a dense highly correlated fluid. It is conventional to write for a homogeneous fluid

$$\rho^{(2)}(r) = (\rho^{(1)})^2 g(r) \quad (7.5)$$

or for a mixture (see Appendix)

$$\rho_{\alpha\beta}^{(2)}(r) = \rho_{\alpha}^{(1)} \rho_{\beta}^{(1)} g_{\alpha\beta}(r) \quad (7.6)$$

(as in Section II). The significant aspect of the definition is that it shows that  $g(r) - 1$  (or  $g_{\alpha\beta} - 1$ ) expresses, for pair distributions, the *entire* effect of correlations. For this reason,

$$h(r) = g(r) - 1 \quad (7.6a)$$

is referred to as the *total* correlation function whose interpretation we shall return to shortly.



We have seen that in perturbation theory,  $g(r)$  [ or  $g(r) - 1$  via its Fourier transform<sup>37</sup>  $S(k) - 1$ ] enters into the thermodynamic functions of the liquid metal. It is also partly accessible from experiment, as is stated in the Appendix, and it is mainly for this reason that the theory of liquid structure has naturally concentrated on the pair correlation function.

In the statistical mechanical theory of the distribution functions, a principal aim is to relate  $g(r)$  to the basic interactions existing between particles, the total potential energy of the entire collection of  $N$  being, say,  $U(\mathbf{R}_1, \dots, \mathbf{R}_N)$ . Evidently the probability of finding a given configuration (say  $\mathbf{r}_1, \dots, \mathbf{r}_N$ ) of all  $N$  is then proportional, by the fundamental tenets of statistical mechanics, to  $\exp\{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)\}$  where  $\beta = (k_B T)^{-1}$ . In terms of the distribution functions we have just defined, we may therefore write

$$\rho^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = (1/Q_N) \exp\{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)\} \quad (7.7)$$

with  $Q_N$  to be determined. Successive integration over the coordinates then gives immediately

$$\rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{1}{(N-n)!} \frac{1}{Q_N} \int d\mathbf{r}_{n+1} \dots \int d\mathbf{r}_N \exp\{-\beta U\} \quad (7.8)$$

and in particular

$$\rho^{(1)} = \frac{N}{\Omega} = \frac{1}{(N-1)!} \frac{1}{Q_N} \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \exp\{-\beta U\}$$

from which it follows that  $Q_N$ , the configurational partition function for the ions, can be written

$$Q_N = \frac{1}{N!} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \exp(-\beta U(\mathbf{r}_1 \dots \mathbf{r}_N)),$$

a result already used in Section 3.

As an example of (7.8), we note that

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{(N-2)!} \frac{1}{Q_N} \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N \exp(-\beta U). \quad (7.9)$$

For a liquid metal we can separate  $U$  into (see Section II)

$$U(\mathbf{R}_1, \dots, \mathbf{R}_N) = U_0(\rho) + U_s(\mathbf{R}_1, \dots, \mathbf{R}_N; \rho)$$

where<sup>3</sup>  $U_0(\rho)$  expresses the volume-dependent part of the energy entirely

<sup>37</sup> This is usually called the *structure factor*, a term apparently originating with von Laue and other early workers on X-ray diffraction from *solids*.

independent of structure and  $U_s(\mathbf{R}_1, \dots, \mathbf{R}_N; \rho)$  is the structure- and volume-dependent remainder. Notice that in the determination of the distribution functions only  $U_s$  enters.<sup>2,3,38</sup> [If this is set zero, then  $\rho^{(2)} = (\rho^{(1)})^2$  as before.]

If the structure-dependent part of the potential energy can be written in a pair approximation with pair potential  $\Phi(r; \rho)$ , then it is plausible (and indeed easy to show) that the mean configurational energy can be written

$$U = U_0(\rho) + \frac{1}{2} \rho^{(1)2} \int dr 4\pi r^2 g(r) \Phi(r; \rho) \quad (7.10)$$

where  $\rho = \rho^{(1)}$  is the mean ionic density. By using the standard scaling argument<sup>2,39</sup> it is also straightforward to show from (7.10) that the pressure can be written<sup>40</sup>

$$p = \beta^{-1} \rho + \rho \frac{dU_0}{d\rho} - \frac{1}{2} (\rho^{(1)})^2 \int dr 4\pi r^2 g(r) \left\{ \frac{r}{3} \frac{\partial \Phi}{\partial r} - \rho \frac{\partial \Phi}{\partial \rho} \right\} \quad (7.11)$$

which is the analog, for a metal, of the familiar result for insulating fluids

$$p = \beta^{-1} \rho^{(1)} - \frac{1}{6} (\rho^{(1)})^2 \int dr 4\pi r^2 g(r) r \Phi'(r) \quad (7.11a)$$

the quantity  $r\Phi'(r)$  being the interparticle virial.

## 8. APPROXIMATIONS TO $g(r)$ BASED ON DECOUPLING SCHEMES

The equilibrium properties of fluids are therefore closely related to pair potentials and pair distributions. But the distribution functions themselves, and in particular  $g(r)$ , are also closely related to the interactions between particles. This is most easily seen by starting with (7.9), writing the structural part of  $U$  as a sum over pair interactions, and taking the gradient of the equation with respect to  $\mathbf{r}_1$ . This gives

$$(N-2)! \nabla_1 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \nabla_1 \Phi(\mathbf{r}_{12}) (-\beta)(N-2)! \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ + (-\beta)(N-2) \int d\mathbf{r}_3 \nabla_1 \Phi(r_{13}) \int d\mathbf{r}_4 \dots d\mathbf{r}_N \exp(-\beta U) \quad (8.1)$$

and since the last term clearly contains the 3-particle distribution function, we have

$$k_B T \nabla_1 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) + \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \nabla_1 \Phi(r_{12}) = - \int d\mathbf{r}_3 \rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \nabla_1 \Phi(r_{13}). \quad (8.2)$$

<sup>38</sup> C. A. Croxton, "Liquid State Physics—A Statistical Mechanical Introduction." Cambridge Univ. Press, New York and London, 1974.

<sup>39</sup> H. S. Green, "Molecular Theory of Fluids." Wiley (Interscience), New York, 1952.

<sup>40</sup> M. Hasegawa and M. Watabe, *Proc. Second Int. Conf. Liquid Met.*, 1975, p. 439.

This is an example of a hierarchy equation relating  $n$ -particle distribution functions to  $(n + 1)$ -particle distributions. The closure of such equations, that is, the imposition of an additional physical approximation relating higher correlation functions to lower, results in integrodifferential equations containing a single distribution function.<sup>41</sup> If, for example, it is held that the probability density  $\rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  is proportional to the products of the probability densities for finding the particle in *pairs*, i.e.,

$$\rho^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = (\rho^{(1)})^{-3} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho^{(2)}(\mathbf{r}_2, \mathbf{r}_3) \rho^{(2)}(\mathbf{r}_3, \mathbf{r}_1) \quad (8.3)$$

(the constant being fixed by examining  $\rho^{(3)}$  as a function of large mutual separation), then on writing  $\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$  and  $\mathbf{r}_1 - \mathbf{r}_3 = \mathbf{r}'$  (8.2) becomes

$$\begin{aligned} \frac{d}{dr} \{ \log g(r) + \beta \Phi(r) \} &= -\beta \rho^{(1)} \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}') g(\mathbf{r}') \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}' \Phi'(\mathbf{r}') \\ &= -\beta \rho^{(1)} \int d\mathbf{r}' g(\mathbf{r}') (g(\mathbf{r} - \mathbf{r}') - 1) \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}' \Phi'(\mathbf{r}') \end{aligned} \quad (8.4)$$

which is commonly referred to as the Born–Green equation.<sup>42</sup> Through the use of a subsidiary function

$$E(x) = \beta \int_x^\infty dy g(y) \Phi'(y). \quad (8.5)$$

Bogolyubov<sup>43</sup> and Rushbrooke<sup>44</sup> have shown that (8.4) can be once integrated to give

$$\begin{aligned} \log g(r) + \beta \Phi(r) &= \rho^{(1)} \int d\mathbf{r}' (g(\mathbf{r} - \mathbf{r}') - 1) E(|\mathbf{r}'|), \\ &= \rho^{(1)} \int d\mathbf{r}' h(\mathbf{r} - \mathbf{r}') E(|\mathbf{r}'|), \end{aligned} \quad (8.6)$$

an equation that has been subjected to extensive numerical study.<sup>45</sup> Many other schemes have been devised to effect closure of the hierarchy equations; in one way or another they rely on some approximation<sup>38</sup> to the higher correlation functions in terms of the sought-for  $g$ .

<sup>41</sup> The right-hand side of (8.2) vanishes if  $\rho^{(3)}$  is replaced by its ideal gas (uncorrelated) value. The solution is then  $g(\mathbf{r}_1, \mathbf{r}_2) = \exp - \Phi(r_1, r_2)/k_B T$  which can only be expected to be reasonable at small values of  $|\mathbf{r}_1 - \mathbf{r}_2|$ .

<sup>42</sup> Or Born–Green–Yvon equation; see Hirschfelder *et al.*,<sup>6</sup> or J. Yvon, "Actualités Scientifiques et Industrielles," p. 203. Hermann and CIE, Paris, 1935.

<sup>43</sup> N. N. Bogolyubov, *J. Phys. (Moscow)* **10**, 257 (1946).

<sup>44</sup> G. S. Rushbrooke, *Physica* **26**, 259 (1960).

<sup>45</sup> See, for example, R. O. Watts in "Specialist Periodical Reports." Statistical Mechanics, Vol. 1, p. 1. The Chemical Society, 1973.

The validity of these assumptions is generally most easily established in low density systems rather than at densities appropriate to real liquids.

Given a solution to (8.6) for  $g(r)$ , it is clear from (7.11a) (that is, for an insulating liquid) that the equation of state of the fluid is then determined. Where comparison with computer experiment is possible (in which the fiction of only pairwise interactions between particles can be made a reality), the equation of state, perhaps as expected, is in reasonable agreement only at low density.<sup>45</sup>

## 9. APPROXIMATIONS TO $g(r)$ BASED ON THE DIRECT CORRELATION FUNCTION

It is evident from the preceding discussion that a truly consistent approximation to  $g(r)$  must proceed by a method other than the various hypotheses just described. Indeed, far better agreement with computer experiment has been achieved with pair distribution functions obtained using an approach which is quite different from closure of the hierarchy equations. It proceeds by defining (as first did Ornstein and Zernike,<sup>46</sup> in 1914) a function  $c(r)$  or  $c(\mathbf{r}_1, \mathbf{r}_2)$  intended to express the effects of *direct* correlation between pairs of particles in the fluid. Recall from (7.6a) that in terms of the distribution of *pairs* of particles, the quantity  $h(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_1, \mathbf{r}_2) - 1$  expresses the entire effect of correlations in the fluid. In physical terms we can think of separating this into two parts, namely, the *direct* effect of two particles present at  $\mathbf{r}_1$  and  $\mathbf{r}_2$  that is to be augmented by the totality of *indirect* pair effects mediated by a third particle, itself physically correlated with the original two. The direct correlation function  $c(r)$  is then defined by the Ornstein-Zernike integral equation

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + \rho^{(1)} \int d\mathbf{r}_3 c(\mathbf{r}_1, \mathbf{r}_3) h(\mathbf{r}_3, \mathbf{r}_2). \quad (9.1)$$

or in a homogeneous system

$$h(r) = c(r) + \rho^{(1)} \int d\mathbf{r}' c(r') h(\mathbf{r} - \mathbf{r}'). \quad (9.2)$$

This last equation can be iterated to give

$$\begin{aligned} h(r) = c(r) + \int \rho^{(1)} d\mathbf{r}' c(r') c(\mathbf{r} - \mathbf{r}') \\ + \int \rho^{(1)} d\mathbf{r}' \int \rho^{(1)} d\mathbf{r}'' c(\mathbf{r} - \mathbf{r}') c(\mathbf{r}' - \mathbf{r}'') c(r'') + \dots \end{aligned}$$

As described above, this evidently sums up *direct* correlations and those transmitted *indirectly* through the fluid. Structure in  $h(r)$  is generally of much longer range than that of  $\Phi(r)$ : the point of introducing  $c(r)$  is in

<sup>46</sup> L. S. Ornstein and F. Zernike, *Proc. K. Ned Akad. Wet. Ser.* 17, 793 (1914).

fact to seek a function expressing the effect of correlations in pair functions, but one which has a range representative of  $\Phi$  rather than  $h$ .

The direct correlation function is simply related, via its Fourier transform  $c(k)$ , to the structure factor  $S(k)$ : since the Fourier transform of  $h(r) = g(r) - 1$  is proportional to  $S(k) - 1$  we have, from (9.2),

$$S(k) = [1 - \rho^{(1)}c(k)]^{-1}. \quad (9.3)$$

It can also be used in an alternative statement of the compressibility sum rule: from the Appendix we have for a single component fluid

$$k_B T \left( \frac{\partial \rho^{(1)}}{\partial p} \right)_T = 1 + \rho^{(1)} \int d\mathbf{r} h(\mathbf{r}) \quad (9.4)$$

which from (9.2) can be written

$$\left( \frac{\partial p}{\partial \rho^{(1)}} \right)_T = k_B T \left( 1 - \rho^{(1)} \int d\mathbf{r} c(r) \right). \quad (9.5)$$

The latter is particularly interesting because once  $c(r)$  and its density dependence is known, we may obtain  $p$  as a function of  $\rho^{(1)}$  by integration. On the other hand, if  $c(r)$  is known, then (in principle) so is  $g(r)$  [via the convolution (9.2)] and thus the equation of state itself, once again, from (7.11a). The *two* equations of state obtained this way will surely agree if  $g(r)$  and  $c(r)$  are known *exactly*: the extent to which they *disagree* must therefore be a measure of the quality of the physical approximation made in determining either one. We have briefly considered an approximation to  $g(r)$  resulting from closure of the hierarchy equations: we now consider approximations to structure resulting from physical statements made about  $c(r)$ , but we first note in this context a very suggestive way of recasting the Born–Green equation.

Keeping in mind its origin via the superposition approximation, the Born–Green equation, in the form given in (8.6), is

$$\log(g(r)e^{\beta\Phi(r)}) = \rho^{(1)} \int d\mathbf{r}' h(\mathbf{r} - \mathbf{r}') E(|\mathbf{r}'|), \quad (9.6)$$

where

$$E(r) = \int_r^\infty dy g(y) \frac{d}{dy} \left( \frac{\Phi}{k_B T} \right).$$

Now  $E$  can be manipulated as follows:

$$\begin{aligned} E(r) &= \int_r^\infty dy g(y) \frac{d}{dy} (\log g(y) e^{\beta\Phi(y)}) - \int_r^\infty dy g(y) \frac{d}{dy} (\log g(y)) \\ &= h(r) + \int_r^\infty dy g(y) \frac{d}{dy} (\log g(y) e^{\beta\Phi(y)}), \end{aligned}$$

or

$$h(r) = E(r) + \int_{\infty}^r dy g(y) \frac{d}{dy} (\log g(y) e^{\beta\Phi(y)}). \quad (9.7)$$

But to the extent that the *integrated effect* of the structure in  $g(y)$  can be neglected, (9.7) immediately reduces to

$$h(r) \doteq E(r) + \log (g(r) e^{\beta\Phi(r)}) \quad (9.8)$$

or, using (9.6) itself,

$$h(r) \doteq E(r) + \rho^{(1)} \int d\mathbf{r}' h(\mathbf{r} - \mathbf{r}') E(|\mathbf{r}'|). \quad (9.9)$$

Comparison of (9.9) with the Ornstein-Zernike relation shows that  $E(r)$  evidently bears some relation, albeit approximate, to the direct correlation function  $c(r)$ . Since

$$E(r) = -g(r) \frac{\Phi(r)}{k_B T} - \int_r^{\infty} dy \left( \frac{\Phi}{k_B T} \right) \frac{d}{dy} g(y)$$

and  $g' = (d/dy)g(y)$  is oscillatory, the major contribution to  $E(r)$  evidently comes from  $-\beta g\Phi$  and its range is therefore expected to be a reflection of the range of  $\Phi$ , in keeping with the physical idea underlying the very introduction of  $c(r)$ . Equation (9.8) therefore suggests an example of the sought for relationship between  $c(r)$  and  $g(r)$ , namely

$$c(r) = h(r) - \log [g(r) e^{\beta\Phi(r)}], \quad (9.10)$$

that may be taken together with

$$h(r) = c(r) + \rho^{(1)} \int d\mathbf{r}' h(\mathbf{r} - \mathbf{r}') c(\mathbf{r}') \quad (9.11)$$

to give a coupled set of equations for  $c$  or  $g$ . At this point (9.10) might only be regarded as a plausible physical approximation subject to test via the compatibility relation. It has, however, been derived by a completely different argument and is known as the hypernetted chain approximation (HNC).<sup>47,44</sup> The name reflects its origin in an alternative approach to the theory of structure of fluids based on an expansion<sup>48</sup> of, in particular,

$$\rho^{(2)} = \frac{1}{(N-2)!} \frac{1}{Q} \int d\mathbf{r}_N \exp \left( -\beta \sum_{i < j} \Phi_{ij} \right).$$

<sup>47</sup> J. M. J. van Leeuwen, J. Groeneveld, and J. de Boer, *Physica* 25, 792 (1959).

<sup>48</sup> Questions of convergence in such dense systems are serious. The point is, however, that the *structure* of various groupings of the terms emerging in the expansion give a guide to the possible forms the sought for functions may take.

A diagrammatic language has been developed to deal with the burdensome combinatorial problem arising in the expansion of this expression, and the hypernetted chain approximation, in this parlance, amounts to the neglect of certain classes of diagrams.<sup>49</sup> Comparison of the equations of state (resulting from an application of the compatibility relations) for a hard sphere system shows substantial discrepancies at higher densities.<sup>50</sup>

Thus the trial approximation (9.10) is not entirely satisfactory. The precise connection between  $c$  and  $g$ , although arrived at by reasonable arguments, is evidently somewhat remote from reality for dense systems. It remains possible, however, that a relation between  $c(r)$  and  $g$  having a structural similarity to (9.10) may lead to improvements. For example, for small interparticle separation we expect (from 8.2) that  $g(r)e^{\beta\Phi(r)}$  is close to unity. Certainly for large separation this will be also the case, and these two observations combine to suggest the modification of (9.10):

$$c(r) \doteq h(r) [g(r)e^{\beta\Phi(r)} - 1]$$

or

$$c(r) = g(r)[1 - \exp(\beta\Phi(r))]. \quad (9.12)$$

In the brief development sketched here, it would appear that (9.12) is lacking in detailed physical justification. The compatibility test, however, turns out to be often far better satisfied than the hypernetted chain approximation and to some extent the sequence of approximations leading to (9.12) must be mutually annulling. The approximation (9.12) is known as the Percus–Yevick (PY) approximation. In the diagrammatic approach, the neglected higher terms of the approximation must also be of less importance. Certainly the Percus–Yevick approximation (though originally introduced<sup>51</sup> by an argument different both from the one given here and from its derivation via diagrammatic analysis<sup>49</sup>) exploits the notion of Ornstein and Zernike that there should exist a function describing direct correlations with a range comparable to  $\Phi(r)$ . Beyond a certain range  $\Phi(r)$  is usually negligible: the factor  $1 - e^{\beta\Phi}$  insures a similar behavior in  $c(r)$ .

## 10. APPLICATION TO A MODEL SYSTEM: THE HARD-SPHERE LIQUID

In order to make concrete some of the points just discussed, it will be convenient to consider a model system that has proved of great utility in

<sup>49</sup> D. Ruelle, *Rev. Mod. Phys.* **36**, 580 (1964).

<sup>50</sup> Cf. Rowlinson,<sup>2</sup> p. 285.

<sup>51</sup> J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958).

the theory of liquids, both as a limiting case of a liquid characterized strongly repulsive interparticle forces, and as a reference or zeroth-order system for a perturbation treatment of more realistic liquids, both insulating and conducting. This is a one component system with *hard-sphere* interactions:

$$\begin{aligned}\Phi_{\text{HS}}(r) &= 0, & r > \sigma; \\ \Phi_{\text{HS}}(r) &\rightarrow \infty, & r < \sigma.\end{aligned}$$

The Percus–Yevick approximation just described is particularly suited to treating the hard-sphere liquid. The reason is that since  $\Phi_{\text{HS}}$  vanishes for  $r > \sigma$ , then within the PY equation the direction correlation function  $c(r)$  does also.<sup>52</sup> Indeed, for this case,  $c(r)$  can be obtained exactly.<sup>53,54,55</sup> The solution is

$$c(r) = -\alpha + \beta(r/\sigma) + \gamma(r/\sigma)^3 \quad (10.1)$$

where

$$\begin{aligned}\alpha &= (1 - 2\eta)^2/(1 - \eta)^4 \\ \beta &= -6\eta(1 + \tfrac{1}{2}\eta)^2/(1 - \eta)^4 \\ \gamma &= \tfrac{1}{2}\eta/(1 - \eta)^4 \\ \eta &= (\pi/6)\rho^{(1)}\sigma^3.\end{aligned}$$

The last quantity is the *packing fraction*, that is, the ratio of volume occupied in the fluid by hard-spheres to the total volume. For the present purposes, two points concerning (10.1) are particularly noteworthy. The first is that if we apply the compatibility test, then from the virial equation we get

$$p/(\rho^{(1)}k_{\text{B}}T) = (1 + \eta + \eta^2 - 3\eta^3)/(1 - \eta)^3 \quad (10.2)$$

while from the compressibility

$$p/(\rho^{(1)}k_{\text{B}}T) = (1 + \eta + \eta^2)/(1 - \eta)^3. \quad (10.3)$$

Dense fluids, near melting, have corresponding values of  $\eta$  in the neighborhood of 0.4 and so the difference in these two results is therefore quite small, as was already noted in the previous section;

<sup>52</sup> Analytic solutions have also been given for the sticky hard-sphere potential; see, for example, J. Jelinck and I. Nezbeda, *Physica* **84A**, 175 (1976).

<sup>53</sup> E. Thiele, *J. Chem. Phys.* **39**, 474 (1963).

<sup>54</sup> M. S. Wertheim, *Phys. Rev. Lett.* **10**, 321 (1963); *J. Math. Phys.* **8**, 927 (1964).

<sup>55</sup> Quantum effects in these systems have been discussed by J. Chihara, *Prog. Theor. Phys.* **50**, 1156 (1973).



indeed as Caranahan and Starling<sup>56</sup> have observed, a simple interpolation between (10.2) and (10.3)

$$p/(\rho^{(1)}k_B T) = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 \quad (10.3a)$$

fits the machine generated data for hard spheres very well. Second (10.1) admits, via (9.3), of a completely analytic solution<sup>57</sup> for the structure factor  $S(k)$  whose form is shown in Fig. 6 and compared there with an accurate measurement of  $S_{ii}(k)$  for sodium and aluminum.<sup>58</sup> The agreement is seen to be substantial over a wide range of wave vectors, attesting, evidently, not only to the quality of the Percus–Yevick equation, but to the hard-sphere interaction as an adequate model (for structural purposes) of the interaction between atoms in a liquid metal. This is the main conclusion we want to draw here.

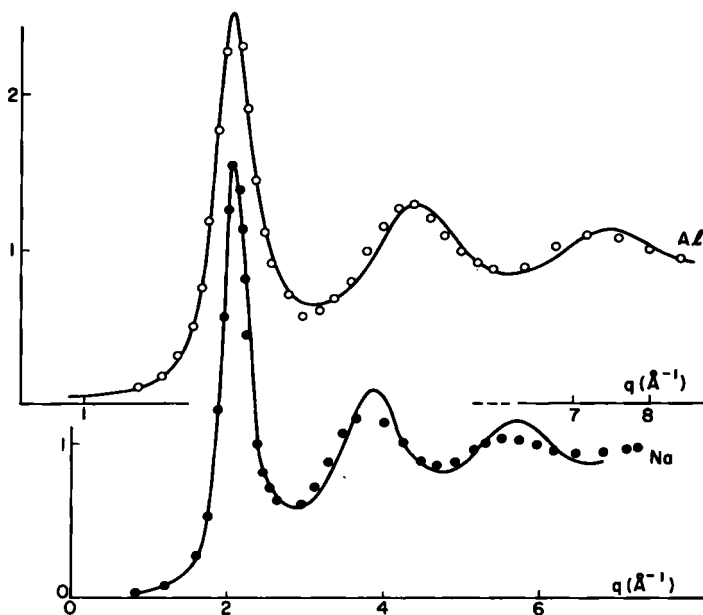


FIG. 6. Structure factors for Na at 373 K and Al at 943 K. Also shown (full lines) are corresponding Percus–Yevick hard-sphere structure factors with  $\eta = 0.475, 0.45$ , respectively. The values of  $\eta$  were chosen to match the height of the first peaks. (From W. H. Young, in *Proc. Int. Conf. Properties Liquid Met.* 3rd, 1976, p. 1.)

<sup>56</sup> N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969); **53**, 600 (1970).

<sup>57</sup> N. W. Ashcroft and J. Lekner, *Phys. Rev.* **165**, 83 (1966).

<sup>58</sup> Quoted by W. H. Young, *Proc. Third Int. Conf. Liquid Met.* 1976, p. 1.

These attributes of the PY form for the hard sphere  $S(k)$  make its use attractive to the study of thermodynamics of liquid metals. We have seen already that the pair potentials in liquid metals possess repulsive short-range parts which, though not as repulsive as the corresponding potential in molecular fluids, nonetheless can exceed a few  $k_B T$  within a short inter-ionic excursion. The ubiquity of the measured  $S(k)$  in simple liquids reflects a remarkable insensitivity of this function to the long-range part of the interaction. Accordingly, for a variety of simple liquids, including liquid metals, it suffices for many structural purposes to regard the constituents as interacting by means of hard-sphere interactions.

## 11. VARIATIONAL METHOD FOR CALCULATING THE FREE ENERGY OF LIQUID METALS

In view of the discussion of the preceding sections, we now wish to write down an explicit prescription for calculating the Helmholtz free energy of a simple liquid metal, taking advantage, insofar as is possible, of the resemblance between the liquid structure factor and that of an assembly of hard spheres. In this section we describe a variational method that has been found to be particularly convenient for the purpose.

As we have seen, simple metals can be viewed as a mixture of ions and electrons, the interaction between the two being described by a weak pseudopotential. We have already indicated that this system, unlike an insulating fluid, is dominated by long-range forces and other volume-dependent terms. We shall continue to view the ions as classical particles (their momenta and positions therefore commuting) so that the kinetic energy of the ions can be considered separately. We shall also calculate the free energy per particle (i.e., per ion) and always have in mind an appropriate thermodynamic limit. The Hamiltonian for the system can be written

$$H_{\text{eff}} = H_{\text{eg}} + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{N}{\Omega} \frac{4\pi Z^2 e^2}{k^2} \left\{ \frac{1}{N} \hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_{\text{ion}}(-\mathbf{k}) - 1 \right\} \\ + \frac{1}{\Omega} \sum_{\mathbf{k} \neq 0} \hat{\rho}_{\text{ion}}(\mathbf{k}) \hat{\rho}_e(-\mathbf{k}) V^p(\mathbf{k}) + NE_0 \quad (11.1)$$

(the terms being defined earlier) and the free energy per ion at second order is

$$F \doteq N^{-1} U_0 + E_{\text{kin}} - TS_{\text{ion}} + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} \{S_H(k) - 1\} \Phi(k). \quad (11.2)$$

In (11.2)  $\Phi(k)$  is the Fourier transform of the effective interaction between ions,  $U_0$  is the sum of *all* structure independent terms of (3.7b), and  $E_{\text{kin}}$  is the kinetic energy per ion treated, as we have said, classically. The problem is therefore to calculate (11.2) (or its equivalent for a two-component system such as a liquid alloy) and the difficult term, of course, is the entropy. But, we shall see that we can evaluate this in closed form for a model hard-sphere system. The problem is then to relate this system to the liquid metal: this is the task which the variational method is designed to accomplish.

The variational approach we describe,<sup>59</sup> is based on an exploitation of the so-called Gibbs–Bogolyubov inequality.

*Gibbs–Bogolyubov Inequality:* Suppose we have a liquid (at a certain density) whose particles have potential energy function  $U$  and free energy  $NF$ . We agree to call this the “real system.” Consider another system, at the same density, in which the potential energy is  $\bar{U}$  and the free energy is  $N\bar{F}$ : we shall call this the “reference” system. Then the inequality states that

$$NF \leq N\bar{F} + \langle U - \bar{U} \rangle_{\bar{v}}, \quad (11.3)$$

which means that  $F$  is bounded above by the free energy of the reference system augmented by the potential difference averaged with respect to the distributions of the reference system.<sup>60</sup> Evidently the appellations “real” and “reference” are immediately interchangeable in the application of (11.3), so we must also have

$$N\bar{F} \leq NF + \langle \bar{U} - U \rangle_U \quad (11.4)$$

or

$$\bar{F} + N^{-1}\langle U - \bar{U} \rangle_U \leq F \leq \bar{F} + N^{-1}\langle U - \bar{U} \rangle_{\bar{v}}, \quad (11.5)$$

which is a powerful result, particularly if the distribution functions of the reference system are known to be close to those of the real system. If the potentials  $U$  and  $\bar{U}$  can be described in terms of *pair* interactions alone, then only pair distributions are involved in computing the averages in (11.5) and, as we have remarked, these mainly reflect the highly repulsive part of the interparticle potential. Then (11.5) rather closely sandwiches  $F$ . Accordingly, let us take as reference system one whose free energy can be written in the form (11.4) in which the ionic distributions are those of a hard-sphere system (of diameter  $\sigma$ ) at the

<sup>59</sup> G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969); J. Rasaiah and G. Stell, *Mol. Phys.* **18**, 249 (1970).

<sup>60</sup> See, for example, ref. 13, p. 67; A. Isihara, *J. Phys. A* **1**, 539 (1968); D. J. Edwards and J. Jarzynski, *J. Phys. C* **5**, 1745 (1972).

same density. In a hard-sphere system we necessarily have  $g_{\text{HS}}(r) = 0$  for  $r < \sigma$ , and it follows that we may take, for the difference in potentials appearing in  $\langle U - \bar{U} \rangle_{\text{HS}}$ , the *entire* effective interaction between ions. In Fourier space this means

$$F \leq F^{\text{HS}} + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} \{S^{\text{HS}}(\eta, k) - 1\} \Phi(k), \quad (11.6)$$

where for a metal  $F^{\text{HS}}$  also contains the volume-dependent terms discussed in Section II. Here  $\eta = (\pi/6)\rho^{(1)}\sigma^3$ , there being substantial empirical evidence<sup>57</sup> as already noted that  $\sigma$  can be chosen to give good agreement between the Percus-Yevick form of  $S(k)$  and experiment. It follows from (11.4) and (11.6) that if  $\mathcal{S}_{\text{HS}}(\eta)$  is the hard-sphere entropy, then

$$F \leq N^{-1}U_0 + E_{\text{kin}} - T\mathcal{S}_{\text{HS}}(\eta) + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} \{S^{\text{HS}}(\eta, k) - 1\} \Phi(k), \quad (11.7)$$

where  $U_0$  is the sum of all structure-independent terms in  $F$ . Equation (11.7) now gives a method for variationally determining  $\eta$  (or  $\sigma$ ) as a function of  $T$ ; i.e.,

$$\partial F / \partial \eta = 0 \rightarrow \sigma = \sigma(T).$$

The term

$$\frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} [S^{\text{HS}}(k) - 1] \Phi(k)$$

can be separated as

$$\begin{aligned} \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} [S^{\text{HS}}(k) - 1] \frac{4\pi Z^2 e^2}{k^2} \\ + \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} (S^{\text{HS}}(k) - 1) \frac{4\pi^2 e^2 (V^p)^2}{k^2 V_c^2} \left( \frac{1}{\epsilon(k)} - 1 \right) \end{aligned} \quad (11.8)$$

as originally expressed. (Here  $V^c = 4\pi Z^2 e^2 / k^2$ .) Computationally it is quite advantageous to do this because the second term in (11.8) converges rapidly, while the first (the Madelung energy) can be obtained, within the Percus-Yevick approximation, entirely in closed form. This was shown by Jones<sup>61</sup> and his result can be written

$$\begin{aligned} E_M &= \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{1}{\Omega} [S^{\text{HS}}(k) - 1] V^c(k) \\ &= NZ \frac{e^2}{2a_0} \frac{Z^{2/3}}{r_s} (-6\eta^{2/3}) \left[ \frac{1 - (\eta/5) + (\eta^2/10)}{1 + 2\eta} \right] \end{aligned} \quad (11.9)$$

where  $a_0$  is the Bohr radius and  $\frac{4}{3}\pi r_s^3 = \Omega/Z$  as before. An analogous

<sup>61</sup> H. Jones, *J. Chem. Phys.* **55**, 2640 (1971). The result is misprinted in the original.

result for binary systems within the PY approximation, now parameterized by a packing function  $\eta$  and hard-sphere ratio  $\alpha = \sigma_1/\sigma_2$ , has been obtained by Ross and Seale<sup>62</sup> and used by Stroud,<sup>63</sup> Umar *et al.*,<sup>64</sup> and Stevenson<sup>65</sup> (see Section V).

The remaining term in (11.7) is the entropy term  $T\mathcal{S}_{\text{HS}}(\eta)$  which can also be obtained in closed form. From the PY virial equation of state (10.2) and the Maxwell relation  $(\partial p/\partial T)_V = (\partial \mathcal{S}/\partial V)_T$  it is readily shown, for example, that the excess entropy per atom is

$$\frac{(\mathcal{S} - \mathcal{S}_{\text{gas}})}{k_B} = -2 \log(1 - \eta) - 6 \left( \frac{1}{1 - \eta} - 1 \right), \quad (11.10)$$

while from (10.3) we find

$$\frac{(\mathcal{S} - \mathcal{S}_{\text{gas}})}{k_B} = \log(1 - \eta) - \frac{3}{2} \left( \frac{1}{(1 - \eta)^2} - 1 \right), \quad (11.11)$$

and finally, from the empirical<sup>56</sup> equation of state (10.3a), we find

$$\frac{(\mathcal{S} - \mathcal{S}_{\text{gas}})}{k_B} = -\eta \frac{4 - 3\eta}{(1 - \eta)^2}, \quad (11.12)$$

$\mathcal{S}_{\text{gas}}$  being the ideal gas entropy per ion. These functions are compared in Fig. 7, where it will be clear that at real liquid densities ( $\eta \sim 0.45$ ) the differences between them are quite small.

The variational prescription for evaluating the free energy is thus (a) minimize the right-hand side of (11.7) with respect to  $\eta$ , evaluating the various terms by the methods described, and (b) let the resulting minimum upper bound be viewed as an approximation to  $F(T)$ .

In addition to the method just described, there exist a variety of other perturbation schemes for finding the free energy of a liquid in terms of some underlying reference system. One scheme, developed by Weeks, Chandler, and Anderson<sup>66</sup> and since used by a number of workers,<sup>67-74</sup> is

<sup>62</sup> M. Ross and D. Seale, *Phys. Rev. A* **9**, 396 (1974).

<sup>63</sup> D. Stroud, *Phys. Rev. B* **7**, 4405 (1973).

<sup>64</sup> I. H. Umar, A. Meyer, M. Watabe, and W. H. Young, *J. Phys. F* **4**, 1691 (1974).

<sup>65</sup> D. J. Stevenson, ref. 74.

<sup>66</sup> J. D. Weeks, D. Chandler, and H. C. Anderson, *J. Chem. Phys.* **54**, 5237 (1971).

<sup>67</sup> J. D. Weeks, D. Chandler, and H. C. Anderson, *J. Chem. Phys.* **55**, 5422 (1971).

<sup>68</sup> K. E. Gubbins, W. R. Smith, M. K. Tham, and E. W. Toppel, *Mol. Phys.* **22**, 1089 (1971).

<sup>69</sup> J. A. Barker and D. Henderson, *Phys. Rev. A* **4**, 806 (1971).

<sup>70</sup> L. Verlet and J.-J. Weis, *Phys. Rev. A* **5**, 939 (1972).

<sup>71</sup> H. C. Anderson, D. Chandler, and J. D. Weeks, *J. Chem. Phys.* **56**, 3812 (1972).

<sup>72</sup> H. C. Anderson and D. Chandler, *J. Chem. Phys.* **57**, 1918 (1972).

<sup>73</sup> S. Sungard and D. Chandler, *Phys. Rev. A* **9**, 1688 (1974).

<sup>74</sup> D. J. Stevenson, *Phys. Rev. B* **12**, 3999 (1975).

particularly close in spirit to the variational method just described. In this approach, one considers a system characterized by the standard repulsive core and attractive tail. The free energy is then expressed in terms of the distribution functions and free energy of a reference system characterized by the repulsive ion part of the pair potential only. The reference free energy and pair distribution function are then in turn expressed in terms of those of a hard-sphere system, the hard-sphere diameter being chosen according to a variational principle. Methods have also been developed for modifying this approach to include the effects of the attractive tail on  $g(r)$ .<sup>71</sup> A recent review of the theory, in the general context of the variational approach we have described here, has been given by Barker and Henderson.<sup>75</sup>

#### IV. Applications to Pure Liquid Metals

We now turn to applications of the methods of the preceding sections to the properties of pure liquid metals, focusing, for simplicity, on the variational approach described above.

##### 12. PURE LIQUID METALS: THERMODYNAMIC FUNCTIONS

We suppose, to begin with, that the free energy as given by (11.7) has been minimized with respect to variations in  $\eta$ . This gives  $\eta$  as a function of  $T$  or, equivalently,  $T$  as a function of  $\eta$  where

$$T(\eta) = \frac{\partial E_{BS}/\partial\eta + \partial E_M/\partial\eta}{\partial \mathcal{S}_{HS}/\partial\eta}. \quad (12.1)$$

The denominator in (12.1) can be calculated explicitly either within the PY equation or via integration of the empirical equation of state. The entropies obtained from these various approaches [Eqs. (11.10)–(11.12)] are, as noted, quite similar, as are the corresponding derivatives and for the denominator in (4.1) it is therefore sufficient to use (11.12),

$$\frac{1}{k_B} \frac{\partial \mathcal{S}_{HS}}{\partial\eta} = - \frac{2(2 - \eta)}{(1 - \eta)^3}, \quad (12.2)$$

which is plotted in Fig. 7. Notice that when  $\eta \sim 0.45$  (the value common to most liquids just above their solidification points) the derivative has a value  $\sim -20$ . We can also obtain an analytic expression for  $\partial E_M/\partial\eta$  by using (11.9).

<sup>75</sup> J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).

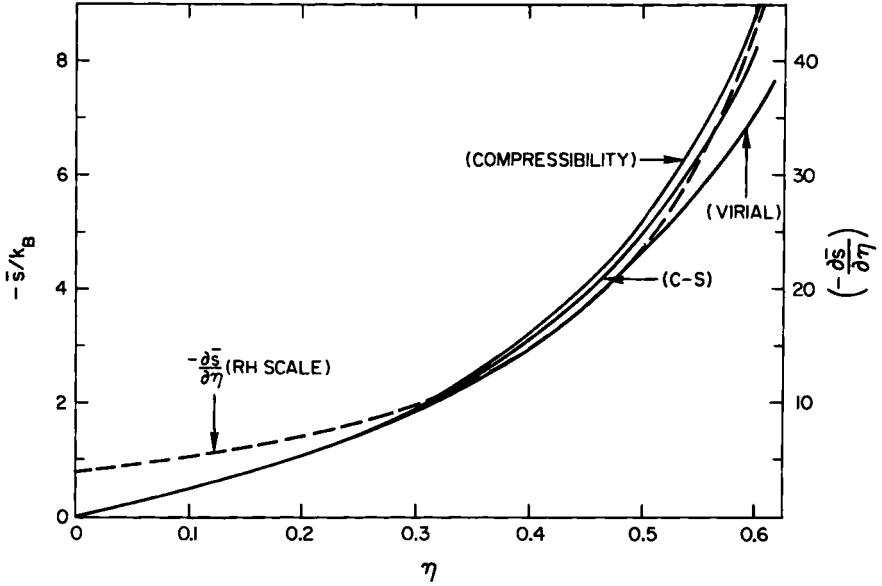


FIG. 7. Excess entropy per particle for a hard-sphere fluid, as a function of packing fraction. Solid lines correspond to Eqs. (11.10), (11.11), and (11.12), with  $\bar{s} = S - S_{\text{gas}}$ . The derivative  $-\partial\bar{s}/\partial\eta$  is calculated from the Carnahan–Starling form for the entropy [Eq. (11.12)].

As a somewhat artificial example of the use of the method (but one with applications in a different context), we consider the problem of determining the thermodynamic functions of a classical one component plasma.<sup>76</sup> This might be regarded as a high-density limiting case of a liquid metal in which the electron system constitutes an essentially uniform background, and whose volume dependent contributions to the total energy need not be explicitly considered. Then from (11.9), (12.1), and (12.2) we find immediately

$$k_B T = \frac{Z^2 e^2}{2r_{\text{WS}}} \left\{ \eta^{-1/3} \left( \frac{2 + \eta}{2 - \eta} \right) \frac{(1 - \eta)^5}{(1 + 2\eta)^2} \right\} \quad (12.3)$$

where  $r_{\text{WS}} = Z^{1/3} r_s$ . In terms of the quantity  $\Gamma = Z^2 e^2 / k_B T r_{\text{WS}}$ , the conventional scaled parameter describing the plasma, Eq. (12.3) may be rewritten

$$\Gamma = 2\eta^{1/3} \left( \frac{2 - \eta}{2 + \eta} \right) \frac{(1 + 2\eta)^2}{(1 - \eta)^5}, \quad (12.4)$$

<sup>76</sup> D. Stroud and N. W. Ashcroft, *Phys. Rev. A* **13**, 1660 (1976).

which is plotted in Fig. 8. The corresponding free energy per ion in excess of the ideal gas value is [from (11.7) with  $\Phi_{\text{eff}} = 4\pi Z^2 e^2/k^2$ ]

$$f(\eta) = \left( \frac{Z^2 e^2}{2r_{\text{ws}}} \right) \frac{\eta^{2/3}}{1 + 2\eta} \left\{ \left( \frac{2 + \eta}{2 - \eta} \right) \frac{(4 - 3\eta)(1 - \eta)^3}{(1 + 2\eta)} - 6(1 - \eta/5 + \eta^2/10) \right\} \quad (12.5)$$

and is plotted in Fig. 9. By combining  $f = f(\eta)$  and  $\Gamma = \Gamma(\eta)$  we can obtain  $f = f(\Gamma)$  which is compared in Fig. 10 with Hansen's<sup>77</sup> computer simulation results. Over a considerable range of temperatures, from the observed crystallization upward, it can be seen that (12.5) is in substantial agreement with experiments. This remains true for the excess specific heat<sup>76</sup> and the thermodynamics of the plasma can therefore be

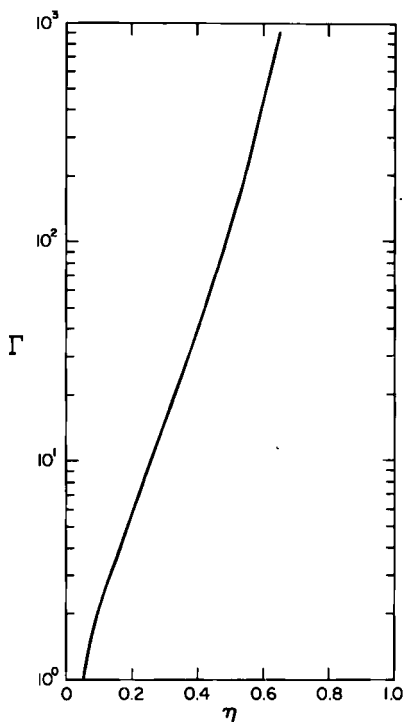


FIG. 8.  $\Gamma(\eta)$  as calculated for a classical one-component plasma in the variational approach.

<sup>77</sup> J.-P. Hansen, *Phys. Rev. A* **8**, 3096 (1973).



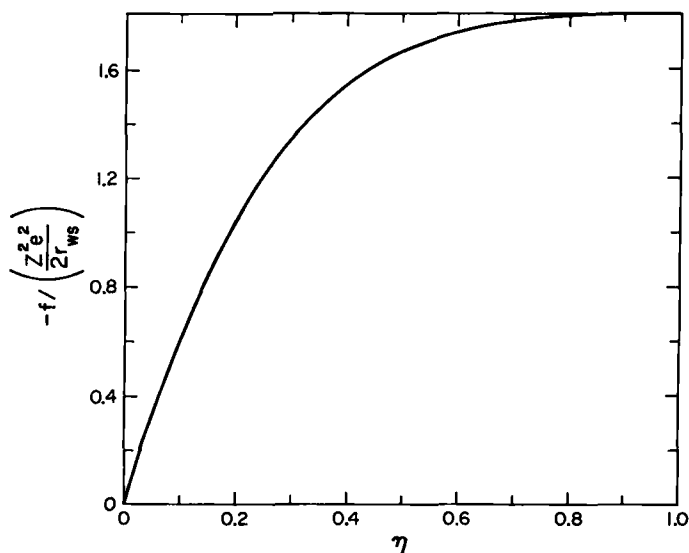


FIG. 9. Excess free energy  $\tilde{f}(\eta)$  of a one-component plasma, as calculated within the variational approach.

described in a simple parametric fashion. The description is most accurate where fluctuations in the potential energy are expected to be small compared with the mean potential energy itself. Since the *average* distance of closest approach is taken as  $\sigma$ , the corresponding fluctuation

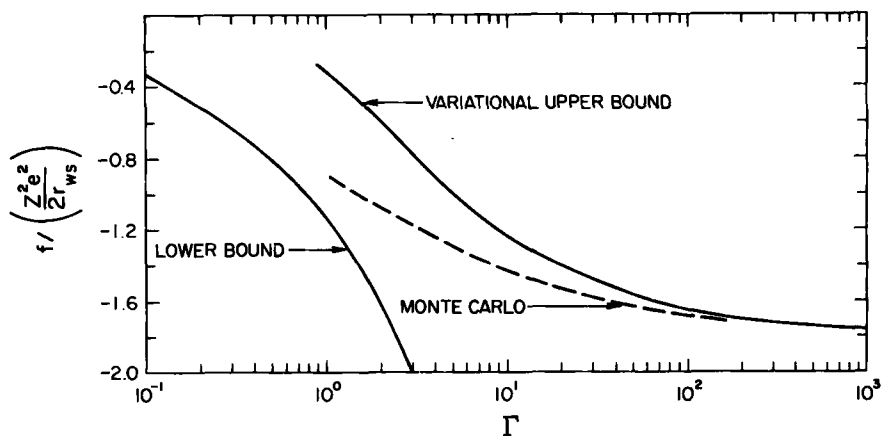


FIG. 10. Excess free energy plotted against  $\Gamma$ . Dashed lines, Monte Carlo results of Hansen [J. P. Hansen, *Phys. Rev. A* 8, 3096 (1973)]. Upper line, variational upper bound. Lower line, Debye-Hückel lower bound.

$\Delta r$  will approximately satisfy  $E(\sigma - \Delta r) - E(\sigma) = (3/2) k_B T$  where  $E(r) = Z^2 e^2 / r$ . It follows immediately that  $\Delta r / \sigma \sim (3/\Gamma) \eta^{1/3}$ , which is indeed smallest at large  $\Gamma$ .

Note that the variational method does not require the ratio of mean potential to mean kinetic energy to be small: it only requires that fluctuations in the potential energy be small. Nor is it strictly necessary (as this example shows) for there to be a physical similarity between the interactions of the system under consideration and the underlying reference system. As we have seen, however, in real simple liquid metals, the effective interaction between ions does display a hard-core character so that the bounds represented by (11.5) are expected to be quite close. In applying the variational method to such systems, it is clear from (12.1) that the quantity  $\partial E_{BS} / \partial \eta$  must be determined. For a general pseudopotential this must be carried out numerically, a task which presents little technical difficulty since the integral in  $E_{BS}$  is quite convergent. For the appropriate minimum value of  $\eta$  (say  $\bar{\eta}$ ), we may write the internal energy of the liquid metal as

$$U(\bar{\eta}) = NZ \left\{ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + E_{\text{corr}}(r_s) \right\} + \frac{1}{2} \frac{N}{\Omega} \sum_{\mathbf{k} \neq 0} \frac{4\pi Z^2 e^2}{k^2} [S_{ii}(\bar{\eta}, k) - 1] \\ + \frac{N}{\Omega} \sum_{\mathbf{k} \neq 0} \chi^{(1)}(k) |V^p(k)|^2 S_{ii}(\bar{\eta}, k) + \dots \quad (12.6)$$

which, in the liquid state, is the equivalent of the expression used by Ashcroft and Langreth,<sup>12</sup> Harrison,<sup>7</sup> and Heine and Weaire<sup>10</sup> as the starting point for calculations, in crystals, of the compressibility of simple metals. [Note that in a Bravais lattice, as we show below,  $\langle \hat{\rho}_i(\mathbf{k}) \hat{\rho}_i(-\mathbf{k}) \rangle = N^2 \delta_{\mathbf{k}, \mathbf{K}}$ ,  $\mathbf{K}$  being a reciprocal lattice vector.] Hasegawa and Watabe<sup>78</sup> have applied (12.6) to calculate the compressibility of several simple metals with satisfactory results, as can be seen from Fig. 11. As in the case of their crystalline counterparts, there is some sensitivity to the choice of the electron gas polarizability  $\chi^{(1)}(k)$  as well as to the pseudopotential, particularly in the high-valence metals. The calculation of the compressibility also requires  $S_{ii}(k)$ , which Hasegawa and Watabe took from neutron diffraction measurements. Near melting (as we have seen), these functions are very close to the hard-sphere functions with  $\eta \sim 0.45$ . Equation (11.9) gives a very good account of the sensitivity of the Madelung energy to changes in structure as represented by variations in fraction  $\eta$ . For  $\eta \sim 0.45$ , as can be seen from Fig. 12, the Madelung energy is fairly flat and differences anticipated in the use of measured rather than hard sphere structure factors are therefore expected to be small.

<sup>78</sup> M. Hasegawa and M. Watabe, *J. Phys. Soc. Jpn.* **32**, 14 (1972).

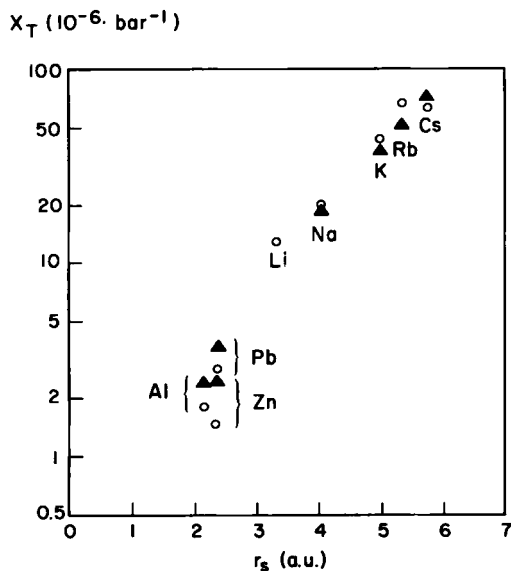


FIG. 11. Compressibility of various liquid metals near their melting points.  $r_s$  is the conventional parameter characterizing electron density and is defined in terms of electron density  $n$  by  $n^{-1} = (4\pi/3)r_s^3$ . (From Hasegawa and Watabe.<sup>78</sup>) (O) calculated; (Δ) experimental.

We comment now on the last term  $E_{BS}$  of (3.9) and its sensitivity to  $\eta$ . This can be seen in Fig. 13, for the case of Na, where  $E_{BS}$  is plotted as a function of volume (per ion) for several hard-sphere packing fractions.<sup>79</sup> As expected physically, the band structure energy is less negative than the corresponding crystalline result and its absolute value reduces progressively (for fixed volume) as the correlation in the liquid is correspondingly reduced.

It is also of interest to compare the predictions of the variational method with the experimentally observed entropies of liquid metals. As has been noted by Silbert *et al.*,<sup>80</sup> the entropy can be written

$$\mathcal{S}/k_B = - \left[ \frac{\partial}{\partial T} F(T, \rho, \eta(T))_{\rho, \eta} + \frac{d\eta}{dT} \frac{\partial}{\partial \eta} F(T, \rho, \eta(T))_{\rho, T} \right]. \quad (12.7)$$

But since the last term vanishes by virtue of the minimum principle, we have simply

$$\mathcal{S}(T) = \mathcal{S}_{HS}[\eta(T)]. \quad (12.8)$$

<sup>79</sup> D. Stroud and N. W. Ashcroft, *Phys. Rev. B* **5**, 371 (1972).

<sup>80</sup> M. Silbert, I. H. Umar, M. Watabe, and W. H. Young, *J. Phys. F* **5**, 1262 (1975); see also I. H. Umar and W. H. Young, *J. Phys. F* **4**, 525 (1974).

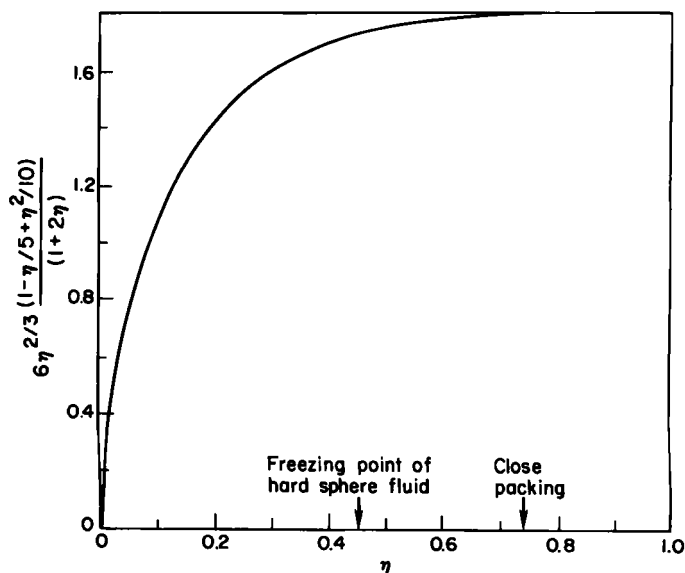


FIG. 12. Madelung constant for the hard-sphere fluid, as calculated in the Percus-Yevick approximation. The point at which the hard-sphere fluid is found to freeze in Monte Carlo calculations is also indicated, as is the packing fraction corresponding to a close-packed solid.

The entropies of a number of simple liquid metals at melting have been computed in this way by Kumaravadev and Evans;<sup>22</sup> these (and the corresponding values of  $\eta$ ) are shown in Table I, where it is seen that the agreement with experiment is very good. Those metals for which the calculated entropy lies *above* experiment (Cd, Ga, Sn) have slight anomalies in the measured structure factors (in particular a shoulder on the high- $k$  side of the first peak in the structure factor<sup>81</sup> as discussed by Mon *et al.*<sup>8</sup>).

### 13. APPLICATION TO MELTING IN SIMPLE METALS

In the context of homogeneous<sup>82</sup> melting the quantity of central importance is the melting curve obtained as the locus of  $p$  and  $T$  arising

<sup>81</sup> Such shoulders are described, e.g., by Waseda.<sup>126</sup>

<sup>82</sup> For recent reviews of the theory of melting of simple liquids, including discussion of machine results, see W. G. Hoover and M. Ross, *Contemp. Phys.* 12, 339 (1971); S. M. Stishov, *Sov. Phys.—Usp. (Engl. Transl.)* 17, 625 (1975). The melting of *semiconductors* such as Si and Ge (which are metals in the liquid phase) has been treated by G. L. Warren and W. E. Evenson, *Phys. Rev. B* 11, 2979 (1975).

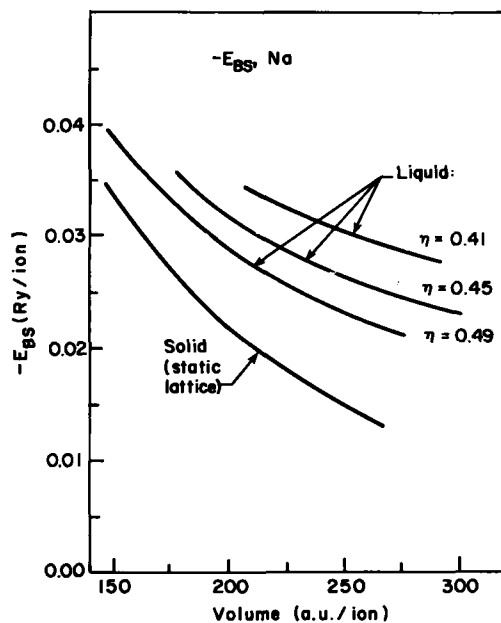


FIG. 13. Band-structure energies for solid and liquid Na, from Stroud and Ashcroft.<sup>79</sup>

TABLE I. PACKING FRACTIONS  $\eta$ , EFFECTIVE HARD-SPHERE DIAMETERS  $d$ , AND EXCESS ENTROPIES  $S_E$  CALCULATED BY THE VARIATIONAL METHOD<sup>a,b,c</sup>

Metal	$T(K)$	$d(a.u.)$	$\eta$	$-S_E/k_B$	$-S_E/k_B$ (experiment)
Na (empty core)	373	6.23	0.45	3.94	3.45
Cs	303	9.14	0.48	4.54	3.56
Rb	313	8.35	0.47	4.33	3.63
K	338	7.88	0.48	4.54	3.45
Cd	623	5.00	0.42	3.42	4.00
Mg	948	5.41	0.47	4.33	3.29
Zn	723	4.64	0.47	4.33	3.78
Ga	353	4.83	0.46	4.13	4.62
Al	1000	4.77	0.45	3.94	3.49
Sn	523	5.31	0.41	3.26	4.08

<sup>a</sup> The electronic contribution will reduce the calculated values of  $-S_E/k_B$  by about 0.05 for Na and about 0.11 for Al. These estimates are calculated for the noninteracting electron gas.

<sup>b</sup>  $T$  denotes temperature.

<sup>c</sup> From Kumaravadeivel and Evans.<sup>22</sup>

from the solution to

$$G_s(p, T) = G_L(p, T) \quad (13.1)$$

where  $G_s$  and  $G_L$  are, respectively, the Gibbs free energies per ion for solid and liquid phases

$$G = F + pv,$$

$v$  being the specific volume per ion. In practice it is convenient to work with  $F$ , subsequently arriving at the pressure (and hence  $pv$ ) from  $p = (-\partial F/\partial v)_{T,N}$ .

When a solid is warmed, the motion of the ions (as gauged by, say, the rms ionic displacement) increases; vacancies and other defects are also formed, although their concentration even at the melting point is rather small. If the solid (for  $T < T_{\text{melting}}$ ) is indeed crystalline on average, then the average force on any one ion must be *self-consistently* periodic. Thus, as first noted by Lindemann,<sup>83</sup> there is the possibility that in the presence of large thermal motion the self-consistent average crystalline arrangement can be destroyed. When this happens, the underlying lattice ceases to have a meaning in the sense that a given atom can any longer be assigned to a given crystal site, and a physically appealing measure of this is afforded by the Lindemann parameter  $\gamma = \rho_0^2/R_{nn}^2$ , which is the mean-square ionic displacement expressed as a fraction of the square of the nearest neighbor-lattice separation. For many classes of solids, and metals in particular, values of  $\gamma$  in the neighborhood of  $10^{-2}$  are typical.

What we have just described is the possibility that self crystallization of a solid can be cooperatively destroyed, an idea that has been extensively discussed by Choquard.<sup>84</sup> The instability reflects a single phase view of a phase transition, a complete description of which requires the solution of (13.1). The Gibbs energy for the liquid phase follows, for example, from an application of the variational principle as just discussed. For the dynamic solid, it is also possible, again through the use of a variational principle, to obtain a bound to the free energy, provided that the excursion of the ions from their crystalline sites can be described as a linear combination of phonon coordinates.

The free energy per ion of the solid takes the form

$$F_{\text{solid}} \doteq E_{\text{eg}} + E_0 + E_M + E_{\text{BS}} + E_{\text{kin}}^{\text{solid}} - TS^{\text{solid}} \quad (13.2)$$

where  $E_{\text{kin}}^{\text{solid}}$  is the kinetic energy of the solid and is expressible as a sum

<sup>83</sup> F. A. Lindemann, *Z. Phys.* **11**, 609 (1910).

<sup>84</sup> P. F. Choquard, "The Anharmonic Crystal." Benjamin, New York, 1967.

over the Brillouin zone of phonon frequencies  $\omega_{q\lambda}$  to be determined shortly:

$$E_{\text{kin}}^{\text{solid}} = \frac{1}{2N} \sum_{q\lambda} \hbar \omega_{q\lambda} (n_{q\lambda} + \frac{1}{2}) \quad (13.3)$$

where  $n_{q\lambda}$  is the phonon occupation number for phonons of wave vector  $\mathbf{q}$  and polarization  $\lambda$ . In (13.2)  $\mathcal{S}^{\text{solid}}$  is the entropy in the phonon system:

$$-T\mathcal{S}^{\text{solid}} = \frac{1}{N} \sum_{q\lambda} \{ [k_B T \ln [1 - \exp(-\hbar \omega_{q\lambda}/k_B T)] - \hbar \omega_{q\lambda} [\exp(-\hbar \omega_{q\lambda}/k_B T)] \}. \quad (13.4)$$

It remains, therefore, to calculate  $E_M$  and  $E_{BS}$  for a solid disturbed by phonons. Both involve

$$S(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}\mathbf{R}'} \langle \exp(i\mathbf{k} \cdot \mathbf{R} - i\mathbf{k} \cdot \mathbf{R}') \rangle \quad \mathbf{k} \neq 0$$

where the average is taken over the state of a harmonic solid for which we may write

$$\mathbf{R} = \mathbf{R}_l + \mathbf{u}_l. \quad (13.4a)$$

Here  $\mathbf{R}_l$  are the site vectors in a Bravais lattice and  $\mathbf{u}_l$  are the displacements of the ions from those sites (we take one atom per unit cell). Then

$$S(\mathbf{k}) = \frac{1}{N} \sum_{l'l''} \exp[i\mathbf{k} \cdot (\mathbf{R}_l - \mathbf{R}_{l'})] \langle \exp(i\mathbf{k} \cdot \mathbf{u}_l) \exp(-i\mathbf{k} \cdot \mathbf{u}_{l'}) \rangle \quad (13.5)$$

and since the  $\mathbf{u}_l$  can be written as a linear combination of phonon operators (13.5) can be rewritten as<sup>85,86</sup>

$$S(\mathbf{k}) = \sum_l \exp(i\mathbf{k} \cdot \mathbf{R}_l) \exp[-\frac{1}{2} \sum_{\mu\nu} k_\mu k_\nu \lambda_{\mu\nu}(\mathbf{R}_l)] \quad (13.6)$$

where for ions of mass  $M$

$$\lambda_{\mu\nu} = \frac{\hbar}{MN} \sum_{q\lambda}^{(BZ)} (1 - \cos \mathbf{q} \cdot \mathbf{R}_l) e_{\mu\lambda}(\mathbf{q}) e_{\nu\lambda}(\mathbf{q}) \frac{\coth \frac{1}{2} \beta \hbar \omega_{q\lambda}}{\omega_{q\lambda}}, \quad (13.7)$$

the  $e_{\mu\lambda}(\mathbf{q})$  being the components of the polarization vectors in mode  $\lambda$ . At this point the frequencies  $\omega_{q\lambda}$  may simply be regarded as a set of

<sup>85</sup> Cf., e.g., N. W. Ashcroft and N. D. Mermin, "Solid State Physics," p. 791. Holt, New York, 1976.

<sup>86</sup> This is easily generalized to the case of a lattice with a basis.

variational parameters, determined by requiring (13.2) to be a minimum for each choice ( $q\lambda$ ). The minimization condition then leads immediately to

$$M\omega^2\mathbf{e}(q) = D(q)\mathbf{e}(q) \quad (13.8)$$

where

$$D(q) = - \sum_{l \neq 0} (1 - \cos q \cdot \mathbf{R}_l) \sum_{\mathbf{k} \neq 0} \mathbf{k} \mathbf{k} e^{i\mathbf{k} \cdot \mathbf{R}_l} \Phi(\mathbf{k}) \exp \left[ -\frac{1}{2} \sum_{\mu\nu} k_\mu k_\nu \lambda_{\mu\nu}(\mathbf{R}) \right] \quad (13.9)$$

with  $\Phi(\mathbf{k})$  being the Fourier transform of the effective pair interaction. The elements of the dynamic matrix  $D(q)$  contain the required frequencies  $\omega_{q\lambda}$  and polarizations  $\mathbf{e}_\lambda(q)$ , and in general must be solved for self-consistently. Evidently the solution requires detailed evaluation of the same sums given in (13.7), a procedure which can be carried out quite expeditiously by exploiting the special point methods.<sup>87-90</sup> Certain aspects of the problem can, however, be illuminated by assuming that the phonon frequencies are independent of polarization. In this case (13.8) and (13.9) give

$$3M\omega_q^2 = \sum_{l \neq 0} \left( - \sum_{\mathbf{k} \neq 0} k^2 \exp(i\mathbf{k} \cdot \mathbf{R}_l) \exp(-k^2 \rho_l^2) \Phi(\mathbf{k}) (1 - \cos q \cdot \mathbf{R}_l) \right) \quad (13.10)$$

which represents the trace of the dynamic matrix averaged over ionic positions, and for this polarization-independent model is a simple formulation of the self-consistent phonon approximation.<sup>84,91</sup> The self-consistency condition is most easily demonstrated by invoking a Debye approximation for the phonon frequencies ( $\omega_{q\lambda} = cq$ ,  $\omega_D = ck_D = k_B \theta_D / \hbar$ ). Then summing both sides of (13.10) over an entire zones gives<sup>79</sup>

$$\frac{3}{2} M (k_B \theta_D)^2 = \sum_{\mathbf{k} \neq 0} \sum_{l \neq 0} k^2 \exp(i\mathbf{k} \cdot \mathbf{R}_l) \exp(-k^2 \rho_l^2) \Phi(\mathbf{k}) \quad (13.11)$$

where, in the same approximations (degenerate phonon branches with linear dispersion), we have

$$\rho_l^2 / (\hbar^2 / 2M) = \frac{3}{2} [k_B T / (k_B \theta_D)^2] J(\theta_D / T; \mathbf{R}_l)$$

where

$$J(x, \mathbf{R}_l) = \frac{1}{x} \int_0^x dt \, t \coth \frac{1}{2} t \left( 1 - \frac{\sin t \mu_l}{t \mu_l} \right)$$

<sup>87</sup> A. Baldereschi, *Phys. Rev. B* **7**, 5212 (1973).

<sup>88</sup> D. J. Chadi and Marvin L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).

<sup>89</sup> H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

<sup>90</sup> D. M. Straus and N. W. Ashcroft, *Phys. Rev. B* **14**, 448 (1976).

<sup>91</sup> N. S. Gillis, N. R. Werthamer, and T. R. Koehler, *Phys. Rev.* **165**, 951 (1968).



TABLE II. DATA FOR SOLID AND LIQUID PHASES OF Na ALONG THE MELTING CURVE<sup>a,b,c</sup>

$p$	$T$	$V_s$	$V_l$	$S_s/k_B$	$S_l/k_B$	$V_l - V_s$	$(S_l - S_s)/k_B$	$\eta$	$3\rho_0^2/R_{nn}^2$
0.0 <sup>c</sup>	390[370]	275	289	6.9	8.1	14	1.2[0.85]	0.41/0.42	0.0152
1.0	400[376]	272	286	6.9	8.1	14	1.2	0.41/0.42	0.0151
6.0	450[414]	255	265	7.0	8.2	9	1.2	0.41/0.42	0.0146
11.1	500[442]	240	249	7.1	8.2	9	1.1	0.41/0.42	0.0142
18.1	550[473]	223	231	7.1	8.3	8	1.2	0.42	0.0137
31.4	600[510]	203	203	7.0	8.0	0	1.0	0.42/0.43	0.0128

<sup>a</sup> The columns are, from left to right, pressure (kbar), temperature (°K), solid and liquid volumes (a.u./ion), solid and liquid entropy per ion, difference between liquid and solid volumes, difference between liquid and solid entropies, liquid packing fraction, and solid Lindemann ratio. Experimental values are in brackets.

<sup>b</sup> From Stroud and Ashcroft.<sup>79</sup>

<sup>c</sup> Data at zero pressure extrapolated from 1 kbar.

TABLE III. MODEL DEPENDENCE OF PROPERTIES OF LIQUID SODIUM NEAR THE MELTING POINT ( $p = 0$ )<sup>a,b</sup>

Model		$T_m$	$\rho_{\text{liq}}$		$A$	$S$	$L$	$dp/dT$
$g_0(r)$	$A_0$	(K)	(g/cm <sup>3</sup> )	$\Delta V/V_{\text{sol}}$	(cal/g)	(cal/g·K)	(cal/g)	(kbar/K)
PY	V	270	0.933	0.027	-6529	0.5390	22	0.121
PY	CS	346	0.901	0.048	-6566	0.6366	40	0.093
PY	OZ	372	0.890	0.056	-6581	0.6650	45	0.085
VW	CS	395	0.879	0.064	-6593	0.6869	49	0.076
Experiment		371	0.905	0.205	-6420	0.7125	27	0.113

<sup>a</sup> The models are: PY (Percus-Yevick), VW (Verlet-Weis), V (Virial theorem), CS (Carnahan-Starling), and OZ Ornstein-Zernike).  $A$ ,  $S$ , and  $L$  are the free energy, entropy, and latent heat.  $dp/dT$  is the slope of the melting curve.

<sup>b</sup> As calculated by Jones.<sup>92</sup>

and

$$\mu_l = k_D R_l / x = (k_B \theta_D / c \hbar x) R_l.$$

For low and moderate temperatures (where the mean excursions of ions are a small fraction of all dimensions) the physically acceptable solutions of (13.11) for  $\theta_D$  are smoothly varying (roughly constant) functions of the temperature  $T$ . The dependence on density, through  $r_s$ , is relatively weak. As Jones<sup>92</sup> has pointed out, some care is required in identifying possible solutions to (13.11) which correspond physically, and at low temperatures, to states in which the overlap of *ionic* wave functions in neighboring cells, is substantial. For such states the assertion that a given ion can always be assigned a unique site vector [see (13.4a)] is untenable, and the basis for the variational calculation fails. However, for the other set of solutions, the corresponding overlap between ionic wave functions is very small. It was found by Stroud and Ashcroft<sup>79</sup> that the temperatures above which no solution for  $\theta_D$  can be found *at all* are extremely high and quite remote from the actual melting temperature.

The procedure for determining the melting temperature is straightforward, though numerically very demanding since the purely structural parts of the energies of simple metals are a small fraction of the whole. Table II shows results for sodium taken from Stroud and Ashcroft<sup>79</sup> and Table III shows the results of Jones<sup>92</sup> for sodium; these results show the

TABLE IV. MODEL DEPENDENCE OF CALCULATED PROPERTIES FOR LIQUID SODIUM<sup>a,b</sup>

	Model				Experiment
	CS/VW	CS/PY	OZ/PY	V/PY	
$T_m$ (K)	395	346	372	270	371
$\rho_L$ (g/cm <sup>3</sup> )	0.878	0.901	0.889	0.933	0.927
$1/K_T$	47.9	50.6	49.0	55.4	52.3
$c_p$ (cal/mole·K)	7.68	7.93	7.80	8.42	7.61
$C$ (m/sec)	2506	2527	2511	2569	2526
$10^4 \alpha$ (K <sup>-1</sup> )	2.93	3.00	2.96	3.11	2.44
$c_p/c_v$	1.152	1.137	1.145	1.111	1.099

<sup>a</sup>  $T_m$ ,  $\rho_L$ ,  $K_T$ ,  $c_p$ ,  $c_v$ ,  $C$ , and  $\alpha$  are, respectively, the calculated melting temperature, liquid density, isothermal compressibility, specific heats at constant pressure and volume, sound speed, and linear expansion coefficient. The CS, OZ, and V refer, respectively, to the Carnahan-Starling, Ornstein-Zernike, and Virial equations for the hard-sphere free energy  $A_0$ . The PY and VW refer, respectively, to the Percus-Yevick and Verlet-Weis approximations to the hard-sphere radial distribution function. In every case, properties are calculated at the theoretically determined melting point shown.

<sup>b</sup> As given by Jones.<sup>92</sup>

<sup>92</sup> H. Jones, *Phys. Rev. A* **8**, 3215 (1973).

TABLE V. INPUT PARAMETERS AND THE CALCULATED AND EXPERIMENTAL LATENT HEATS IN MILLIRYDBERGS PER ION<sup>a,b</sup>

	density (g/cm <sup>-3</sup> )	$\frac{\Delta\Omega_0}{\Omega_0}$ (solid)	$r_c$ (a.u.)	$T_m$ (K)	$\theta_D$ (k)	L, theor. (mRy/ion)	L, exp. (mRy/ion)
Li	0.519	0.015	1.40	452	335	-1.12	3.49
Na	0.928	0.025	1.69	371	156	1.48	1.98
K	0.825	0.024	2.226	337	91.1	1.69	1.82
Rb	1.475	0.025	2.40	312	55.5	1.88	1.166
Cs	1.84	0.026	2.62	302	39.5	1.88	1.160
Mg	1.572	0.042	1.38	924	370	9.7	6.37
Zn	6.92	0.069	1.27	693	235	6.2	5.08
Cd	8.02	0.047	1.405	594	143	6.6	4.73
Al	2.38	0.066	1.117	933	428	15.5	8.25
Tl	11.29	0.032	1.033	576	78.5	4.3	3.28
Pb	10.59	0.036	1.48	600	104	15.7	10.49

<sup>a</sup> For all elements  $m^*/m = 1$ . The  $c/a$  ratios for Mg, Zn, and Cd are assumed unchanged from their room-temperature values 1.624, 1.856, and 1.886, respectively.

<sup>b</sup> From W. Hartmann.<sup>93</sup>

calculated dependence of various properties on the choice of model used in the liquid state for determining the liquid state free energy. Table IV shows the variations expected when Eqs. (11.10)–(11.12) are used for the hard-sphere entropy. Table III also indicates the sensitivity of the latent heat of melting [ $L = -U_{\text{solid}} + U_{\text{liquid}} + p(V_{\text{liquid}} - V_{\text{solid}}) \approx U_{\text{liquid}} - U_{\text{solid}}$ ] to the choice of liquid structure. In Jones's calculation the structure factor for the solid was calculated using independent Einstein oscillators to describe the ionic motion. A similar model was used earlier by Hartmann<sup>93</sup> in a calculation of  $L$  for a series of simple of simple metals. His results are given in Table V and, except for Li, corroborate reasonably well with experiment. As noted by Jones, at least part of the discrepancies may be attributed to the fact that a calculation of  $L$ , a relatively small quantity, requires the difference of two large energies, each with its separate numerical complexities.

## V. Liquid Alloys

Liquid alloys are of interest in a number of respects. From the point of view of the theory of the liquid state, they are also representatives of the class of simple liquids discussed earlier, that is, their structure is usually dominated by two-body central interactions. From a metallurgical standpoint they are very important because many solid binary alloys are formed initially by cooling from a liquid alloy; to understand the energetics of the formation of solid alloys, it may therefore be useful to have some knowledge of the corresponding liquids. An understanding of liquid alloys may also help to clarify questions about the stability of metallic glasses, which are metastable amorphous systems formed by rapidly quenching liquid alloys of favorable composition. Liquid alloys also have geophysical and astrophysical significance: the earth's core is considered to be a molten mixture of iron and nickel; the interiors of the giant planets may be made up in part of a liquid mixture of metallic hydrogen and metallic helium; white dwarfs and neutron stars may have even more exotic, quasi-metallic components.

Perhaps the fundamental question to be answered with regard to mixtures is that of stability: what is it that determines whether or not two metals will mix to form an alloy? This question is tractable for the simple metals by an extension of the formalism described above, particularly in Section III. The relevant extension is described in the succeeding pages, and numerical applications which have appeared in the literature are briefly described. Thereafter we discuss the phenome-

<sup>93</sup> W. M. Hartmann, *Phys. Rev. Lett.* **26**, 1640 (1971).

non of phase separation in liquid alloys. This phase transition represents an important test of our (incomplete) understanding of the stability of liquid alloys, and it is therefore examined from several points of view.

#### 14. FORMALISM FOR THE FREE ENERGY

Like those of a pure metal, the equilibrium thermodynamics of a binary liquid mixture  $A_x B_{1-x}$  are determined (at constant pressure  $p$ ) by the Gibbs free energy per particle (i.e., per ion)  $G(x, p, T)$ . In terms of the Helmholtz free energy  $F$ ,

$$G = F + pv$$

where  $v$  is the specific volume per particle, determined by the equilibrium condition

$$p = -(\partial F / \partial v)_{x, T}.$$

In most alloys at ordinary pressure the  $pv$  term is very small compared to  $F$  so that to a good approximation  $G \sim F$ .

The starting point for finding  $F$  in a two-component liquid alloy is a natural generalization of the picture adopted in Section III, namely, a *three*-component fluid consisting of the bare ions of the two species plus an initially uniform electron gas consisting of all the valence electrons contributed by each ionic species. The Hamiltonian appropriate to this system can be written, under the same assumptions as discussed earlier, in a form analogous to (2.1):

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_l \frac{P_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{Z_l Z_{l'} e^2}{|\mathbf{R}_l - \mathbf{R}_{l'}|} + \sum_{il} V_l^p(\mathbf{r}_i - \mathbf{R}_l) \quad (14.1)$$

where the symbols have the same meanings as in (2.1), except that  $Z_l$  is the valence of the ion at position  $\mathbf{R}_l$ ,  $V_l^p$  the corresponding pseudopotential, and  $\mathbf{P}_l$  is the momentum of the  $l$ th ion.

Again, as in Section 2, the Hamiltonian (14.1) can be rearranged so as to eliminate divergence problems. The resulting Hamiltonian can be written in the form (2.8), with

$$U_M = \frac{1}{2\Omega} \sum_{\alpha\alpha'} \sum_{\mathbf{k} \neq 0} \frac{4\pi Z_\alpha Z_{\alpha'} e^2}{k^2} (\hat{\rho}_\alpha(\mathbf{k}) \hat{\rho}_{\alpha'}(-\mathbf{k}) - N_\alpha \delta_{\alpha\alpha'}); \quad (14.2a)$$

$$H'_{el} = \frac{1}{\Omega} \sum_\alpha \sum_{\mathbf{k} \neq 0} V_\alpha^p(k) \hat{\rho}_\alpha(\mathbf{k}) \hat{\rho}_e(-\mathbf{k}), \quad (14.2b)$$

$$E_0 = \rho_e \sum_\alpha x_\alpha \mu_\alpha \quad (14.2c)$$

and

$$\mu_\alpha = \lim_{k \rightarrow 0} \left[ \frac{4\pi Z_\alpha e^2}{k^2} + V_\alpha^p(k) \right]. \quad (14.2d)$$

Here  $Z_\alpha$  is the valence of an ion of species  $\alpha$ , thus  $\hat{\rho}_\alpha(\mathbf{k})$  is a component of the corresponding number density,  $V_\alpha^p$  is the pseudopotential for an ion of species  $\alpha$ , and  $\hat{\rho}_e(\mathbf{k})$  is a Fourier component of the electron number density. The term  $H_{eg}$  appearing in (2.8) is now the Hamiltonian for a uniform electron gas of density  $\rho_e = N \sum x_\alpha Z_\alpha / \Omega$ .

If the electron-ion interaction is weak, the alloy Hamiltonian can be treated within the framework of second-order perturbation theory, in analogy with the approach described in earlier sections. The resulting expression for the Helmholtz free energy per ion is

$$F = F_{eg} + \frac{3}{2} k_B T + E_M + E_{BS} + E_0 - T \mathcal{S}_{ion}, \quad (14.3)$$

where, as before,  $F_{eg}$  is the Helmholtz free energy of the electron (per ion). The Madelung energy takes the form

$$E_M = \frac{1}{2\Omega} \sum_{k \neq 0} \sum_{\alpha\alpha'} \frac{4\pi Z_\alpha Z_{\alpha'} e^2}{k^2} (x_\alpha x_{\alpha'})^{1/2} [S_{\alpha\alpha'}(k) - \delta_{\alpha\alpha'}] \quad (14.4)$$

where  $S_{\alpha\alpha'}(k)$  is a partial structure factor<sup>94</sup> of the alloy as described in the Appendix. Note that  $E_M$  can be converted to an integral, with the result

$$E_M = \frac{e^2}{\pi} \int_0^\infty dk \sum_{\alpha\alpha'} Z_\alpha Z_{\alpha'} (x_\alpha x_{\alpha'})^{1/2} [S_{\alpha\alpha'}(k) - \delta_{\alpha\alpha'}]. \quad (14.5)$$

In like manner  $E_{BS}$  takes the form

$$E_{BS} = \frac{1}{2} \sum_{k \neq 0} \sum_{\alpha\alpha'} \frac{k^2}{4\pi e^2} \left( \frac{1}{\epsilon(k)} - 1 \right) V_\alpha^p(k) V_{\alpha'}^p(-k) (x_\alpha x_{\alpha'})^{1/2} S_{\alpha\alpha'}(k) \quad (14.6)$$

$$= \frac{1}{4\pi^2} \int_0^\infty dk k^2 \sum_{\alpha\alpha'} \frac{k^2}{4\pi e^2} \left( \frac{1}{\epsilon(k)} - 1 \right) V_\alpha^p(k) V_{\alpha'}^p(-k) (x_\alpha x_{\alpha'})^{1/2} S_{\alpha\alpha'}(k). \quad (14.7)$$

Finally,  $\mathcal{S}_{ion}$  represents the ionic configurational entropy of the alloy (per ion), including now the classical entropy of mixing.

Again as in pure liquid metals, the internal energy can be divided into terms which depend on ionic arrangement and those which depend only on alloy specific volume and density but *not* on structure. The structure-dependent terms can be written (within second-order perturbation the-

<sup>94</sup> A binary alloy is more properly regarded as a 3-component system. The  $S_{\alpha\alpha'}$  referred to here is one of the three partial structure factors resulting when the electron degrees of freedom are eliminated by a procedure identical to that discussed in the case of one-component liquid metals.

ory) as a sum of pairwise interactions. Thus the internal energy is

$$E = U_0 + \frac{1}{2} \sum_{l \neq l'} \Phi_{ll'}(|\mathbf{R}_l - \mathbf{R}_{l'}|)$$

where  $U_0$  is structure independent and

$$\Phi_{\alpha\alpha'}(R) = \frac{1}{2\pi^2} \int_0^\infty \frac{\sin kR}{kR} \Phi_{\alpha\alpha'}(k) k^2 dk \quad (14.8a)$$

$$\Phi_{\alpha\alpha'}(k) = \frac{4\pi Z_\alpha Z_{\alpha'} e^2}{k^2} \left[ 1 + \left( \frac{1}{\epsilon(k)} - 1 \right) \frac{V_\alpha^v(k) V_{\alpha'}^v(k)}{V_\alpha^c(k) V_{\alpha'}^c(k)} \right] \quad (14.8b)$$

where  $V_\alpha^c(k) = -4\pi Z_\alpha e^2/k^2$  is the Fourier transform of the electron-ion interaction, were that ion regarded as a point ion. The pair potentials  $\Phi_{\alpha\alpha'}(R)$  depend on electron density through  $\epsilon$  and hence indirectly on alloy concentration.

To illustrate the behavior of pairwise interactions in liquid alloys, we show in Fig. 14 the pair potentials appropriate to  $\text{Na}_x\text{K}_{1-x}$ , as calculated by Ashcroft and Langreth.<sup>19</sup>

We note features characteristic of pair potentials in pure metals, in particular, (1) the steeply repulsive core, (2) a minimum in the vicinity of the nearest neighbor separation, and (3) Friedel oscillations at larger separations (these are not shown in the particular case illustrated).

A difficulty that might arise in the application of (14.3) to real alloys is

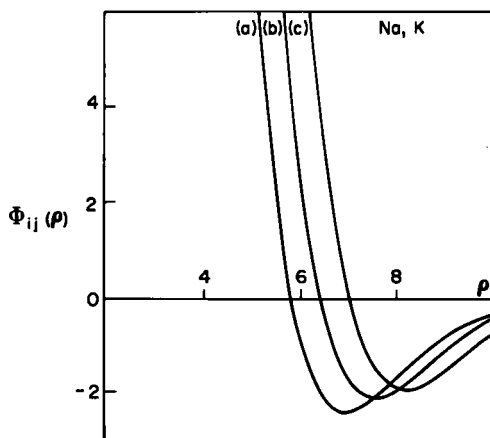


FIG. 14. The calculated interaction  $\Phi_{ij}(r)$  between (a) two Na ions, (b) a Na ion and a K ion, and (c) two K ions immersed in an electron gas of density appropriate to pure liquid Na at 100°C. From Ashcroft and Langreth.<sup>98</sup>  $\Phi$  is measured in units of two-thirds the free-electron Fermi energy.  $\rho = 2k_F r$  is a dimensionless measure of ion-ion separation:



the possibility that the bare pseudopotentials themselves may be concentration dependent. Usually such concentration dependence is simply ignored in practical calculations. This is in principle a reasonable approximation since the  $V_\alpha^P$ 's are presumed to be atomic properties and should not depend on the particular metallic environment in which they may find themselves. On the other hand, pseudopotentials are generally fitted to some experimental datum, usually at the normal density of the pure metal. Since alloying normally involves a significant change of atomic volume or electron density, such an empirically determined pseudopotential may not be accurate in the alloy. For example, corrections due to nonlocality may become important if the atomic volume is so altered that the Fermi energy approaches the energy of a virtual bound d-level, as may be the case, for example, with some of the heavier alkalis under sufficient compression.<sup>95</sup> The proper inclusion of concentration dependence in the bare pseudopotentials, however, is a very complicated task. Some calculations of this nature have been carried out by Hafner.<sup>96</sup>

The various liquid-state approximations, discussed earlier in Section III, may be extended to alloys. For example, the Percus-Yevick integral equation (9.12) is readily generalized to mixtures. The analog of (9.12) is

$$c_{\alpha\beta}(r) = g_{\alpha\beta}(r)\{1 - \exp [\beta\Phi_{\alpha\beta}(r)]\}$$

for a system described by pairwise interactions  $\Phi_{\alpha\beta}(r)$ . The functions  $c_{\alpha\beta}(r)$  are direct correlation functions, defined by the relation<sup>97</sup>

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma} \rho_{\gamma} \int d\mathbf{r}' h_{\alpha\gamma}(\mathbf{r} - \mathbf{r}') c_{\gamma\beta}(r') \quad (14.10)$$

where  $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ . More conveniently, in Fourier transform,

$$\tilde{S}_{\alpha\beta}(k) = (\rho_{\alpha}\rho_{\beta})^{1/2}c_{\alpha\beta}(k) + \sum_{\gamma} (\rho_{\gamma}\rho_{\beta})^{1/2}\tilde{S}_{\alpha\gamma}(k)c_{\gamma\beta}(k) \quad (14.11)$$

where  $\tilde{S}_{\alpha\beta}(k) = S_{\alpha\beta}(k) - \delta_{\alpha\beta}$ . Just as the one-component PY equation is soluble analytically for hard spheres, Eq. (14.10) can be solved in closed form for a *mixture* of hard spheres of different diameters. The interactions in this case take the form

$$\tilde{\Phi}_{\alpha\beta}(r) = \begin{cases} \infty, & r < \sigma_{\alpha\beta} \\ 0, & r > \sigma_{\alpha\beta} \end{cases} \quad (14.12)$$

<sup>95</sup> See, for example, J. M. Dickey, A. Meyer, and W. H. Young, *Proc. Phys. Soc.* **92**, 460 (1967).

<sup>96</sup> J. Hafner, *Proc. Third Int. Conf. Liquid Met.* 1976, p. 102.

<sup>97</sup> J. L. Lebowitz, *Phys. Rev.* **133**, A895 (1964).

with  $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})$  (the so-called "additivity requirement" on hard-sphere diameters). The direct correlation functions  $c_{\alpha\beta}^{\text{HS}}(r)$  for this case were first obtained by Lebowitz;<sup>97</sup> the corresponding structure factors can also be computed in closed form and were found by Ashcroft and Langreth,<sup>98</sup> and Enderby and North.<sup>99</sup> Analytic expressions for the hard-sphere free energy,  $F_{\text{HS}}$ , are also available within the PY approximation;<sup>97</sup> they may be computed from integration of either the compressibility or the virial equation of state. As in the one-component liquid, however, a more accurate procedure is to use an empirical expression for  $F_{\text{HS}}$  fit to Monte Carlo calculations. Such a form has been developed by Mansoori *et al.*<sup>100</sup> In Fig. 15 is plotted, by way of illustration, the excess free energy  $\Delta F_{\text{HS}} = F_{\text{HS}} - F_{\text{ig}}$  ( $F_{\text{ig}}$  being the free energy of an ideal gas mixture, including the ideal gas entropy of mixing) as calculated from this expression for various values of the parameters describing the mixture; the value  $\eta = 0.45$  corresponds, as noted previously, to that of most metals (and alloys) near freezing.

Because of the availability of analytic PY solutions, the variational principle described in Section III is readily generalized to alloys, using

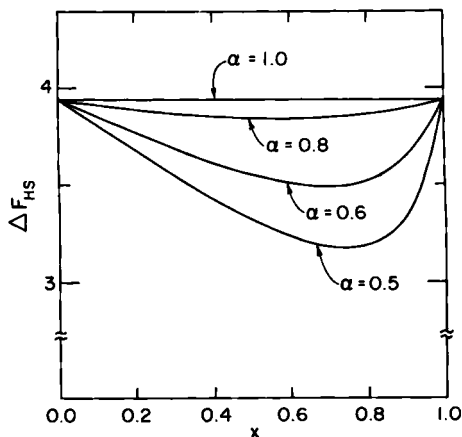


FIG. 15. Excess free energy per ion for a mixture of hard spheres of different diameters, as calculated from the empirical expression of Mansoori *et al.*<sup>100</sup> The ratio of hard sphere diameters is denoted  $\alpha$ ,  $x$  is the concentration of smaller spheres. The volume fraction  $\eta$  occupied by the hard sphere is taken as 0.45 over all concentrations, and  $k_B = 1$ .

<sup>98</sup> N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **156**, 685 (1967).

<sup>99</sup> J. Enderby and D. M. North, *Phys. Chem. Liq.* **1**, 1 (1968).

<sup>100</sup> G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**, 1523 (1971).

as a reference system a mixture of hard spheres of different diameters. Such a reference system would be expected to be particularly appropriate to a mixture such as  $\text{Na}_x\text{K}_{1-x}$ . In that system, as is clear from inspection of Fig. 14, the "hard-sphere diameter" characterizing the Na-K interaction is roughly the arithmetic mean of those describing the Na-Na and K-K interactions, that is, the additivity requirement appears to be satisfied.

The appropriate form of the Gibbs-Bogolyubov inequality is now

$$F \leq F_{\text{eg}} + E_M^{(\text{HS})} + E_{\text{BS}}^{(\text{HS})} + E_o + F_{\text{HS}} \quad (14.13)$$

where  $E_M^{(\text{HS})}$  and  $E_{\text{BS}}^{(\text{HS})}$  are the Madelung and electron-ion energies evaluated with hard-sphere structure factors, and  $F_{\text{HS}} = \frac{3}{2}k_B T - T\mathcal{S}_{\text{HS}}$  is the Helmholtz free energy of the reference system ( $\mathcal{S}_{\text{HS}}$  being the configurational entropy of the reference hard-sphere mixture). The Madelung term  $E_M^{(\text{HS})}$  can be obtained in closed form within the PY approximation, using Laplace transform techniques, as was shown by Ross and Seale;<sup>62</sup> the corresponding effective Madelung constant  $\gamma_{\text{eff}} = -r_s E_M / [xZ_A + (1-x)Z_B]^{5/3}$  is shown in Fig. 16 for various choices of parameters. On the other hand  $E_{\text{BS}}^{(\text{HS})}$  must be evaluated numerically using PY structure factors, but the integration is only one-dimensional and easily done.

With this input, the variational principle consists of minimizing the right-hand side of Eq. (14.13) (at each concentration and temperature) with respect to the two hard-sphere diameters, taking the resulting minimum upper bound as an approximation to  $F$ . This procedure yields

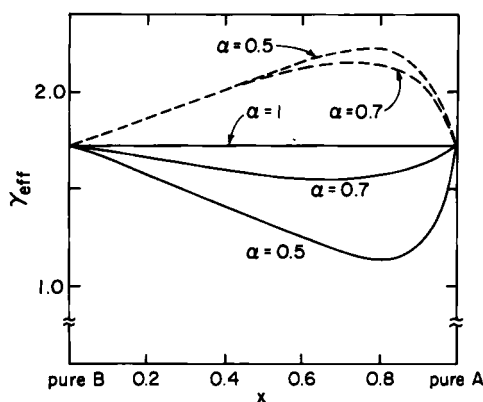


FIG. 16. Effective Madelung constant  $\gamma_{\text{eff}} = -r_s E_M / [xZ_A + (1-x)Z_B]^{5/3}$  for an alloy  $\text{A}_x\text{B}_{1-x}$  as calculated within the Percus-Yevick approximation.  $\eta = 0.45$  in all cases. Solid lines,  $Z_A = Z_B$ ; dashed lines,  $Z_B = 4Z_A$ .  $\alpha = \sigma_A/\sigma_B$  is the ratio of hard-sphere diameters. The solid and dashed lines coincide for  $\alpha = 1$ .

not only  $F(x, T)$ , but also effective concentration- and temperature-dependent hard-sphere diameters. The variational approach is not necessarily limited to the hard-sphere reference system described above. For some materials, a reference system of *nonadditive* hard spheres (in which  $\sigma_{AB} \neq \frac{1}{2}\sigma_{AA} + \frac{1}{2}\sigma_{BB}$ ) could well be more appropriate. Such a reference system might be useful, for example, in alloys such as  $\text{Au}_x\text{Ge}_{1-x}$  where diffraction experiments<sup>101</sup> indicate some breakdown in the additivity hypothesis.

Relatively few calculations<sup>63,64</sup> exist in the literature which make full use of the formalism outlined above. Some of these involve phase separation and are discussed later. Tamaki<sup>102</sup> has calculated the heat of mixing of liquid Na-Li on the basis of a pseudopotential formulation. Umar *et al.*<sup>103</sup> have computed the entropies of mixing  $\Delta S = xS_A + (1 - x)S_B - S_{\text{alloy}}$  for a number of equal mixture alloys near melting. They did not use the complete theory just described, but instead assumed the diameters of each constituent hard sphere remained unchanged on alloying. The pure metal diameters were then found by requiring the corresponding hard-sphere entropies to agree with experiment. The results are shown in Fig. 17 and provide rather good evidence in favor of the hard-sphere approximation. A recent extensive series of calculations based on the full formalism described above in conjunction with a first-principles, nonlocal, concentration-dependent pseudopotential has been carried out by Hafner.<sup>104</sup> Because of the nonlocal nature of the pseudopotential used, the volume-dependent, structure-independent terms in the energy take a somewhat different form than those described above. A full variational calculation was, however, carried through. The resulting hard-sphere diameters and volume, enthalpy, and entropy of formation are shown in Tables VI and VII. In view of the first-principles nature of the calculations, the resulting agreement with experiment is evidently quite good.

## 15. PHASE SEPARATION: FREE ENERGY APPROACH

A property of particular interest in liquid mixtures is the mutual solubility of the two constituents, A and B. This can be determined at pressure  $p$  and temperature  $T$  from a graph of  $G(x, p, T)$  as a function of

<sup>101</sup> See, for example, R. M. Waghorne, V. G. Rivin, and G. I. Williams, *J. Phys. F* **6**, 147 (1976).

<sup>102</sup> S. Tamaki, *Phys. Lett. A* **40**, 17 (1972).

<sup>103</sup> I. H. Umar, I. Yokoyama, and W. H. Young, *Phil. Mag.* **34**, 535 (1976). See also I. H. Umar, M. Watabe, and W. H. Young, *Phil. Mag.* **30**, 957 (1976); I. Yokoyama, M. J. Stott, I. H. Umar, and W. H. Young, *Proc. Third Int. Conf. Liquid Met.* 1976, p. 95.

<sup>104</sup> J. Hafner, *Phys. Rev. A* **16**, 351 (1977).

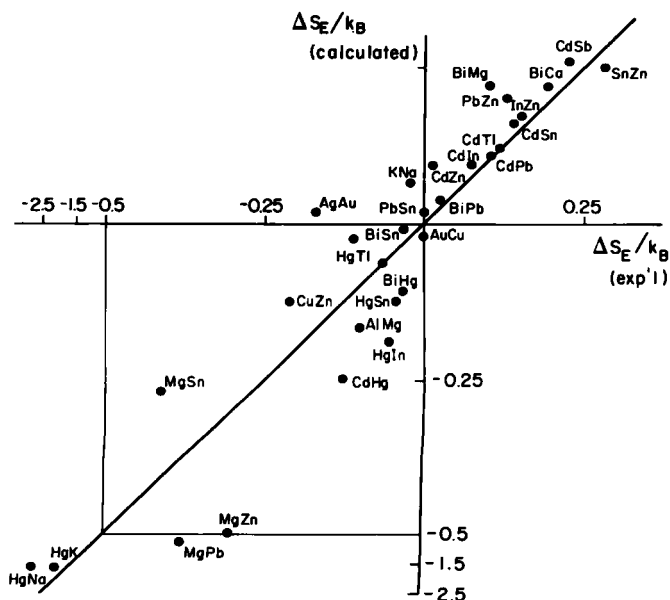


FIG. 17. Calculated and measured excess entropies for a number of equiatomic binary liquid alloys, as calculated by Umar *et al.*<sup>108</sup>

$x$ . If A and B are not completely miscible at  $p$  and  $T$ , the isotherm will resemble the upper curve of Fig. 18. The solubility limits<sup>105</sup> are found by constructing a common tangent to two points on the isotherm as shown. In the region between the two points of tangency the alloy is unstable because it can lower its Gibbs free energy by separating into an A-rich phase of concentration  $x_A$  and a B-rich liquid of composition  $x_B$ . On the other hand, if A and B are completely miscible at the given temperature and pressure, the isotherm will look like the lower curve of Fig. 18. This curve is concave up at all concentrations, that is,

$$(\partial^2 G / \partial x^2)_{p,T} > 0 \quad (15.1)$$

at all  $x$ . A common tangent construction is therefore impossible and the alloy is stable against phase separation.

The variational formalism described above can easily be used to calculate the phase boundary separating the one-phase region from the two-phase region in mixtures of liquid metals. Such a calculation was carried out by Stroud<sup>63</sup> for the alloy  $\text{Li}_x\text{Na}_{1-x}$ . An empty core pseudopo-

<sup>105</sup> There will always be a small activated limiting solubility of one component in another, even in conventionally "insoluble" systems.

TABLE VI. EFFECTIVE HARD-SPHERE DIAMETER  $\sigma_A$ ,  $\sigma_B$  AND PACKING FRACTIONS  $\eta$  FOR A-B ALLOYS<sup>a,b,c</sup>

A	B	T(°C)		$\eta$	$\Delta\eta$	$\sigma_A$	$\sigma_B$	$\alpha = \sigma_A/\sigma_B$
Li	Na	200	C	0.404	-0.006	5.12	5.99	0.856
			CS	0.411	-0.006	5.14	6.00	0.856
Na	K	100	C	0.431	0.015	6.06	7.57	0.800
			CS	0.435	0.017	6.04	7.62	0.792
Na	Cs	100	C	0.456	0.043	5.96	9.08	0.656
			CS	0.466	0.048	5.95	9.12	0.652
K	Rb	65	C	0.422	0.003	7.43	8.06	0.922
			CS	0.427	0.005	7.49	8.12	0.922
K	Cs	65	C	0.430	0.011	7.35	9.01	0.816
			CS	0.434	0.013	7.30	9.09	0.812
Rb	Cs	35	C	0.434	0.002	7.90	8.97	0.881
			CS	0.441	0.004	7.94	9.05	0.878
Li	Mg	700	C	0.440	0.063	4.27	5.50	0.776
			CS	0.450	0.064	4.28	5.50	0.778
Li	Al	700	C	0.481	0.088	3.68	4.97	0.740
			CS	0.503	0.103	3.70	5.01	0.740
Al	Mg	665	C	0.464	0.003	5.06	5.18	0.976
			CS	0.469	0.003	5.03	5.14	0.976

<sup>a</sup>  $\Delta\eta = \eta - (\eta_A/\Omega_A + \eta_B/\Omega_B)/(1/\Omega_A + 1/\Omega_B)$  is the increase in the packing fraction on alloying. C and CS denote calculations involving the compressibility and Carnahan-Starling equations of state.

<sup>b</sup> Values given in atomic units.

<sup>c</sup> As calculated by Hafner.<sup>104</sup>

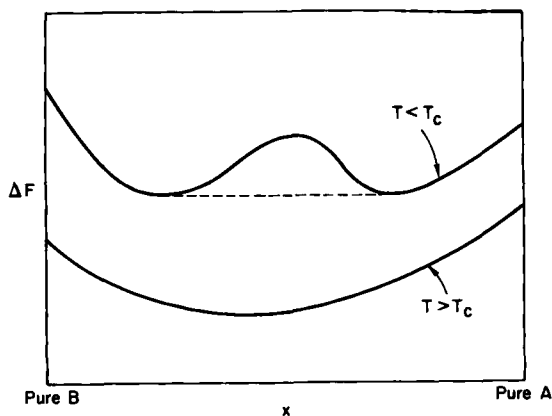


FIG. 18. Schematic illustrating the behavior of the Gibbs free energy of an alloy, above and below the critical temperature for phase separation.

TABLE VII. VOLUME, ENTHALPY AND ENTROPY OF FORMATION FOR EQUIATOMIC AB ALLOYS<sup>a</sup>

AB	T(°C)		$\Delta\Omega(\%)$		$\Delta H$ (cal/g atom)		$\Delta S$ (cal/g atom K)	
			theor.	exp.	theor.	exp.	theor.	exp.
LiNa	200	C	0.25		1220		1.57	
		CS	0.40		1240		1.50	
NaK	100	C	-1.8	-1.4	470	174	1.03	1.35
		CS	-1.9		380		0.98	
NaCs	100	C	-7.1	-5.4	1870	218	0.33	1.20
		CS	-8.4		1640		0.30	
KRb	100	C	-0.16	-0.19	120	30	1.29	
		CS	-0.19		160		1.22	
KCs	100	C	-0.67		213	28	1.10	
		CS	-0.87		200		1.08	
RbCs	100	C	-1.3		-60	-32	1.13	
		CS	-1.2		-39		1.12	
LiMg	700	C	-20.3		-3410	-2477	-0.50	1.20 $\pm$ 0.6
		CS	-20.5		-3870		-0.54	
LiAl	700	C	-40.8		2450		-2.6	
		CS	-41.1		3320		-2.8	
AlMg	665	C	-4.3	-3.0	-1980	-806	1.19	1.18 $\pm$ 0.2
		CS	-4.4		-2170		1.20	

<sup>a</sup> As calculated by Hafner.<sup>104</sup>

tential was used for both Na and Li, the core radius for Na being chosen to fit the resistivity of liquid Na at melting and that for Li so that the resulting variationally determined packing fraction of pure liquid Li should agree with that which fit the experimental structure factor. The parameters [cf., Eq. (14.2d)]  $\mu_{\text{Na}}$  and  $\mu_{\text{Li}}$  were determined by the requirement that the pressure should vanish at the equilibrium densities of liquid Na and Li. The resulting phase boundary is compared to experiment in Fig. 19. Unlike the regular solution model,<sup>106</sup> this calculation predicts an asymmetric phase boundary, in agreement with experiment. The calculated critical temperature is about a third higher than experiment, but this was not considered a serious discrepancy in view of the fact that phase boundary, as with the melting curve discussed earlier, depends on small differences between large numbers. In contrast to the situation found in the description of the melting transition, no particular terms in the free energy are found to be of dominant importance in bringing about phase separation. This is illustrated in

<sup>106</sup> See, for example, O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," pp. 274-281. Freeman, San Francisco, 1967.

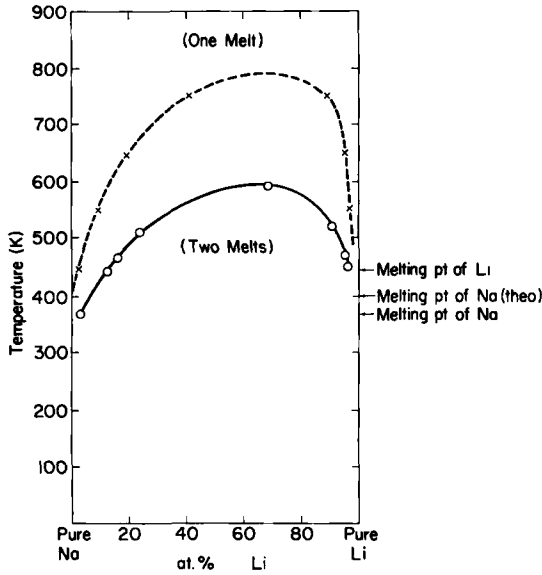


FIG. 19. (---) Calculated and (—) measured phase boundaries of liquid  $\text{Li}_x\text{Na}_{1-x}$  as given by Stroud.<sup>63</sup>

Table VIII, where are listed the contributions of the various terms in  $F$  to the free energy mixing  $\Delta F = F(x, T) - xF_{\text{Na}}(T) - (1 - x)F_{\text{Li}}(T)$  at a temperature of 850 K.

The analytic behavior of the phase boundary near  $T_c$  is of particular interest in the theory of phase transitions. In the calculations just described, the shape of the phase boundary near  $T_c$  is readily found to be

$$|x_A(T) - x_B(T)| \propto (T_c - T)^{1/2}$$

where  $x_A$  and  $x_B$  are the limits of mutual solubility at temperature  $T$ . The exponent  $\frac{1}{2}$  is characteristic of mean field theories. Experiment<sup>107</sup> gives  $|x_A - x_B| \propto (T_c - T)^{0.3-0.35}$ , the discrepancy is due to a neglect of fluctuations and is remedied in more sophisticated statistical mechanical treatments of phase transitions.

Recently Stevenson<sup>74</sup> has calculated the phase separation curve for a mixture of metallic hydrogen and metallic helium at various pressures. (As noted earlier, this system may have astrophysical significance.<sup>108</sup>) Because the interactions between electrons and the hydrogen and helium

<sup>107</sup> H. K. Schürmann and R. D. Parks, *Phys. Rev. Lett.* **26**, 367 (1971).

<sup>108</sup> W. B. Hubbard and R. Smoluchowski, *Space Sci. Rev.* **14**, 599 (1973).



TABLE VIII. CONTRIBUTIONS TO THE FREE ENERGY OF MIXING  $\Delta F = \frac{1}{2}(F_{\text{Li}} + F_{\text{Na}}) - F_{\text{Li}_{0.5}\text{Na}_{0.5}}$  OF A LIQUID EQUIATOMIC Li-Na ALLOY AT 850<sup>a,b</sup>

Free-energy term	Contribution to $\Delta F$ (mRy/ion)
$E_{\text{kin}}^{\text{elec}}$	+8.3
$E_{\text{xc}}^{\text{elec}}$	-5.5
$E_0$	+1.3
$-T\mathcal{S}$	+4.7
$E_{\text{M}}$	-12.7
$E_{\text{BS}}$	+4.8
Total	+0.9

<sup>a</sup> Row by row, the contributions are due to the electronic kinetic energy  $E_{\text{kin}}^{\text{elec}}$ , the electronic exchange-correlation energy  $E_{\text{xc}}^{\text{elec}}$ , the Hartree energy  $E_0$ , the entropy term  $-T\mathcal{S}$ , the Madelung energy  $E_{\text{M}}$ , and the band-structure energy  $E_{\text{BS}}$ . The ionic kinetic energy makes no contribution.

<sup>b</sup> From Stroud.<sup>63</sup>

nuclei are strong (being Coulombic), Stevenson included terms of third order in the electron-ion potential, using a modified superposition approximation to express the resulting contribution to the free energy in terms of the structure factors. He then evaluated the free energy by means of Anderson-Chandler-Weeks perturbation theory. The resulting phase diagram is shown in Fig. 20 for various pressures typical of those expected in the interior of the planet Jupiter, where it is thought that such a mixture may exist. A similar system (consisting of ions of valence 1 and valence 2 interacting via a *screened* Coulomb potential) has been treated by Firey and Ashcroft<sup>109</sup> using the variational hard-sphere approach described above. Phase separation also occurs in mixtures of purely Coulombic systems, as has been discussed by Hansen and Vieillefosse.<sup>110</sup>

In view of the complexity of these calculations, it is perhaps of use to develop a simplified model which contains some of the features of the full theory, yet can easily be analyzed. Let us return, therefore, to the picture of an alloy as a *three*-component fluid of interacting ions in a *uniform* background of negative electrons. The internal energy per ion of

<sup>109</sup> B. Firey and N. W. Ashcroft, *Phys. Rev. A* **15**, 2072 (1977).

<sup>110</sup> J.-P. Hansen and P. Vieillefosse, *Phys. Rev. Lett.* **37**, 391 (1976).

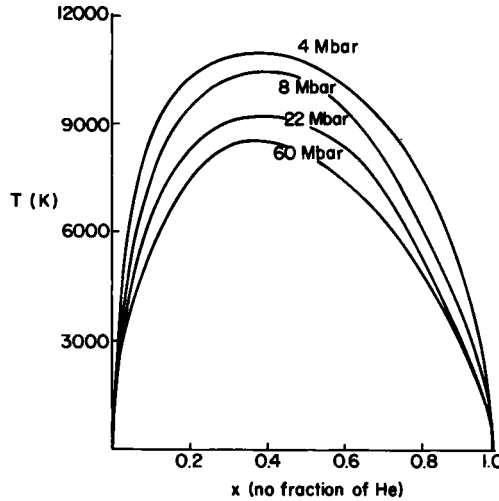


FIG. 20. Phase separation curves for metallic  $H_{1-x}He_x$  at various pressures, as calculated by Stevenson.<sup>74</sup>

this system can be written

$$E = E_{eg} + E_0 + E_{kin} + E_M - T\mathcal{G}_{ion}, \quad (15.2)$$

$E_{BS}$  vanishing for a uniform electron system. The only structure-dependent terms in (15.2) is  $E_M$ . For this we may assume a *highly correlated* liquid in which each ion is surrounded by a uniform sphere of neutralizing charge, the diameter of which is chosen so that the enclosed charge just balances the positive ionic charge. If the overlap of these *uniform spheres* can be neglected, we obtain

$$E_M = -1.8Z^{*5/3}/r_s \text{ Ry} \quad Z^* = xZ_A + (1-x)Z_B \quad (15.3)$$

where  $r_s$  is the conventional parameter defining the average electron density, and is given by

$$\frac{4}{3}\pi r_s^3 = NZ^*/\Omega.$$

The electron gas energy takes the standard form

$$E_{eg} = Z^* \left( \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + E_{corr}(r_s) \right) \quad (15.4)$$

where the first two terms are the kinetic and exchange energy of the uniform electron gas, and  $E_{corr}(r_s)$  is the correlation energy.<sup>111</sup> We noted earlier that this is a slowly varying function of  $r_s$  at normal electron

<sup>111</sup> See, for example, D. Pines and P. Nozières, "The Theory of Quantum Liquids," Vol. I. Benjamin, New York, 1966.

densities. Finally, for  $E_0$  it is sufficient to use an empty-core pseudopotential of the form shown in Fig. 1. This gives

$$E_0 = 3Z^*/r_s^3 [xr_A^2 + (1-x)r_B^2] \quad (15.5)$$

where  $r_A$  and  $r_B$  are the core radii describing the A and B pseudopotentials.

Without undue loss of generality we restrict attention to a homovalent, monovalent alloy. From the point of view of phase separation, in the liquid state the important terms in the internal energy, within the uniform sphere approximation, are then

$$E = \frac{\gamma}{r_s^2} - \frac{\beta}{r_s} + \frac{3}{r_s^3} [xr_A^2 + (1-x)r_B^2] \quad (15.6)$$

where  $\gamma = 2.21$  and in the uniform sphere approximation  $\beta = 2.716$ . This form has some simple but instructive consequences. First define quantities

$$\bar{r}_s = -1 + \beta r_s / \gamma \quad \bar{r}_{s\alpha} = -1 + \beta r_{s\alpha} / \gamma \quad (15.7)$$

where the  $r_{s\alpha}$  ( $\alpha = A, B$ ) are the *measured* equilibrium  $r_s$  values of the pure constituents. Then applying the zero pressure condition ( $dE/dr_s = 0$ ), it is easy to show that

$$\bar{r}_s^2 = \sum x_\alpha \bar{r}_{s\alpha}^2 \quad (15.8)$$

which gives the densities of the monovalent alloy in terms of the densities of its constituents. When  $\beta = 2.716$ , this leads to a quite satisfactory interpolation for the densities of miscible alkali metals.<sup>112</sup>

Second, the excess energy is readily calculated using the equilibrium values of  $r_s$  given by (15.8). The result is

$$\begin{aligned} \Delta E &= E(x) - xE(1) - (1-x)E(0) \\ &= \frac{\beta^2}{\gamma} \left\{ \left( \frac{\bar{r}_s}{1 + \bar{r}_s} \right)^2 - x \left( \frac{\bar{r}_{sA}}{1 + \bar{r}_{sA}} \right)^2 - (1-x) \left( \frac{\bar{r}_{sB}}{1 + \bar{r}_{sB}} \right)^2 \right\}. \end{aligned} \quad (15.9)$$

Some properties of  $\Delta E(x)$  are readily derived.<sup>112</sup> It is always positive, generally asymmetric, and its magnitude (typically  $\sim 10^{-2}$  Ry) tends to increase the more disparate are  $r_A$  and  $r_B$ . The quantities  $E(x)$  and  $\bar{E}(x) = xE(1) + (1-x)E(0)$  are plotted in Fig. 21. The curves there make the point that the mixture will be unstable against concentration fluctuations unless the temperature is sufficiently high that the entropy, principally the mixing entropy  $S_m = x \ln x + (1-x) \ln (1-x)$ , stabilizes the system.

<sup>112</sup> N. W. Ashcroft, *Proc. Third Int. Conf. Liquid Met.* 1976, p. 39.

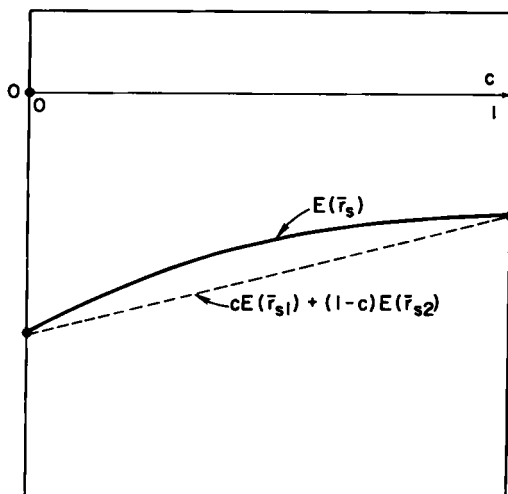


FIG. 21. The quantities  $E(x)$  and  $\bar{E}(x)$  as defined in the text.

The preceding model<sup>112</sup> shows that phase separation can occur even in a quite simple, yet not unphysically based model of a liquid metal. Moreover, the fact that  $\Delta E$  tends to increase with increasing  $\Delta r_c = |r_A - r_B|$  tends to provide a microscopic basis to the phenomenological Hume-Rothery rule of mixing, which states that two metals will mix only if their ionic radii are similar. Here, of course, the ionic radius is to be interpreted as the pseudopotential core radius. The case in which the ions are point-ions has recently been discussed by Stevenson.<sup>113</sup>

## 16. PHASE SEPARATION: FLUCTUATION APPROACH

It is possible to take a different approach to phase separation by considering, instead of the free energy, the concentration fluctuations present in a liquid alloy. In a liquid-metal alloy of critical composition, as in other binary mixtures, the onset of phase separation is signaled by long-wavelength concentration fluctuations that diverge at  $T$  approaches  $T_c$  from above. These fluctuations are defined (for an alloy  $A_xB_{1-x}$ ) by the relation

$$\begin{aligned}
 \langle (\delta x)^2 \rangle &= \langle (\delta N_A / N)^2 \rangle \\
 &= N^{-2} [y^2 \langle \delta N_A^2 \rangle - 2xy \langle \delta N_A \delta N_B \rangle + x^2 \langle \delta N_B^2 \rangle] \\
 &= N^{-1} xy [y S_{AA}(0) - 2\sqrt{xy} S_{AB}(0) + x S_{BB}(0)] \quad (16.1)
 \end{aligned}$$

<sup>113</sup> D. J. Stevenson, *Phys. Lett. A* **58**, 282 (1976).

where  $y = 1 - x$ . They are of interest for the problem of phase separation because of the sum rule <sup>114</sup>

$$N^{-1}\langle(\delta x)^2\rangle = Nk_B T/(\partial^2 G/\partial x^2)_{T,p}. \quad (16.2)$$

A necessary (but not sufficient) condition for stability of a binary alloy is that  $(\partial^2 G/\partial x^2)_{T,p} \geq 0$ . When  $(\partial^2 G/\partial x^2)_{T,p} \rightarrow 0$ ,  $\langle(\delta x)^2\rangle$ , and hence the linear combination of structure factors (16.1), diverges. For every concentration  $x$ , there exists a temperature  $T_s(x)$  at which  $(\partial^2 G/\partial x^2)_{T,p} = 0$ . (These points correspond to the points of inflection in the Gibbs free energy isotherms.) This condition therefore defines a *line* of critical temperatures. Only the highest temperature  $T_c = T_s(x_c)$  is attainable physically. At other concentrations the critical line (known as the spinodal line<sup>115</sup>) is masked by the phase boundary, which lies at temperatures higher than the critical line, except at  $x = x_c$  (see Fig. 18).

The hard-sphere structure factors described earlier always lead to finite concentration fluctuations, at least in the PY approximation.<sup>116</sup> Evidently, the instabilities which result in phase separation, insofar as they can be accounted for in terms of pair potentials, are due to deviations in these potentials from ideal hard-sphere behavior, principally those resulting from the attractive tails in the potentials. This suggests writing the pair potentials in the form

$$\Phi_{\alpha\beta}(r) = \Phi_{\alpha\beta}^0(r) + \delta\Phi_{\alpha\beta}(r) \quad (16.3)$$

where  $\Phi_{\alpha\beta}^0(r)$  is the pair potential of a reference system (e.g., a hard-sphere mixture). The corresponding structure factors are most easily discussed in terms of the density-density response functions appropriate to the two-component mixture. These are defined in the Appendix. The definition (A.24) is compactly written

$$\delta\rho(\mathbf{k}) = \chi(\mathbf{k})\delta V_{\text{ext}}(\mathbf{k}) \quad (16.4)$$

where the components of  $\delta V$  and  $\delta\rho$  are  $\delta V_\alpha$  and  $\delta\rho_\alpha$ , and  $\chi_{\alpha\beta}(\mathbf{k}) = -\beta(\rho_\alpha\rho_\beta)^{1/2}S_{\alpha\beta}(k)$  according to (A.26). It is convenient to write the response functions corresponding to the real and reference system in terms of the *inverse* functions

$$\mathbf{f} = -\chi^{-1} \quad (16.5)$$

$$\mathbf{f}_0 = -\chi_0^{-1}, \quad (16.6)$$

$\chi_0$  being the response matrix corresponding to  $\Phi_0$ . It may be shown that the components of  $\mathbf{f}$  are related to the corresponding Ornstein-Zernike

<sup>114</sup> See, for example, Chap. 4 of Rowlinson.<sup>2</sup>

<sup>115</sup> J. C. Maxwell, "Theory of Heat." Longmans, Green, London, 1904, p. 205.

<sup>116</sup> J. L. Lebowitz and J. S. Rowlinson, *J. Chem. Phys.* **41**, 133 (1964).

correlation functions  $c_{\alpha\beta}$  by

$$f_{\alpha\beta} = (k_B T / \rho_\alpha) \delta_{\alpha\beta} - k_B T c_{\alpha\beta}. \quad (16.7)$$

Introducing

$$\mathbf{f}_1 = \mathbf{f} - \mathbf{f}_0 \quad (16.8)$$

we find

$$\chi = [1 - \chi_0 \mathbf{f}_1]^{-1} \chi_0 \quad (16.9)$$

where  $1$  is the  $2 \times 2$  unit matrix. Equivalently

$$\delta \rho = \chi_0 \delta \mathbf{V}_{\text{eff}} \quad (16.10)$$

where

$$\delta \mathbf{V}_{\text{eff}} = \delta \mathbf{V}_{\text{ext}} + \mathbf{f}_1 \delta \rho \quad (16.11)$$

which states that the response of the *real* fluid to external fields can be formally written in terms of the response of the *reference* fluid to an *effective* field  $\delta \mathbf{V}_{\text{eff}}$ .

As an example of these considerations, consider the simplest model<sup>117</sup> liquid mixture with nonvanishing ion-ion interactions, in which we take for a reference system an ideal gas ( $\Phi_{\alpha\beta} = 0$ ), and for the effective field we take simply the mean (or Hartree) field:

$$\delta \mathbf{V}_{\text{eff}} = \delta \mathbf{V}_{\text{ext}} + \Phi \delta \rho \quad (16.12)$$

from which it follows that

$$\mathbf{f}_1 = \Phi \quad (16.13)$$

and hence that

$$\begin{aligned} S_{11} &= (1 + \rho_2 \beta \Phi_{22}) / D, \\ S_{22} &= (1 + \rho_1 \beta \Phi_{11}) / D, \\ S_{12} &= S_{21} = (\rho_1 \rho_2)^{1/2} \beta \Phi_{12} / D, \end{aligned}$$

and

$$D = (1 + \rho_1 \beta \Phi_{11})(1 + \rho_2 \beta \Phi_{22}) - \rho_1 \rho_2 \beta^2 \Phi_{12}^2. \quad (16.14)$$

This result is just a two-component generalization of the well-known RPA result<sup>118</sup>

$$S(k) = \frac{1}{1 + \beta \rho \Phi(k)} \quad (16.15)$$

<sup>117</sup> D. Stroud, *Phys. Rev. B* **8**, 1308 (1973).

<sup>118</sup> See, e.g., R. Brout, "Phase Transitions." Benjamin, New York, 1965.

for a one-component fluid. If the  $\Phi_{\alpha\beta}$  are Coulombic (16.14) is just the Debye-Hückel result for the correlation functions of molten electrolytes. While (16.14) is too crude to describe realistic mixtures, some qualitative insight can be gained. For instance, the mixture described by (16.14) is unstable whenever  $D(q, \beta, x) = 0$ . Since  $D$  is essentially quadratic in  $\beta$  (or  $T$ ), there are two characteristic instability temperatures for each value of  $q$  and  $x$ . For a given value of  $x$  only the highest of these temperatures is attainable physically, since once it is reached the mixture, of course, becomes unstable. In general, one of these branches corresponds primarily to divergent concentration fluctuations, while on the other there are divergent density fluctuations. In a given liquid mixture, an instability against long-wavelength *concentration* fluctuations (phase separation) presumably competes against a shorter wavelength instability against *density* fluctuations (freezing instability). The latter should occur presumably in the vicinity of the first reciprocal lattice vector of the corresponding solid.

The spinodal line for  $\text{Li}_x\text{Na}_{1-x}$  as calculated from this approach<sup>117</sup> is shown in Fig. 22. While the agreement with experiment is surprisingly good it may be in part fortuitous, in view of the neglect of short-range

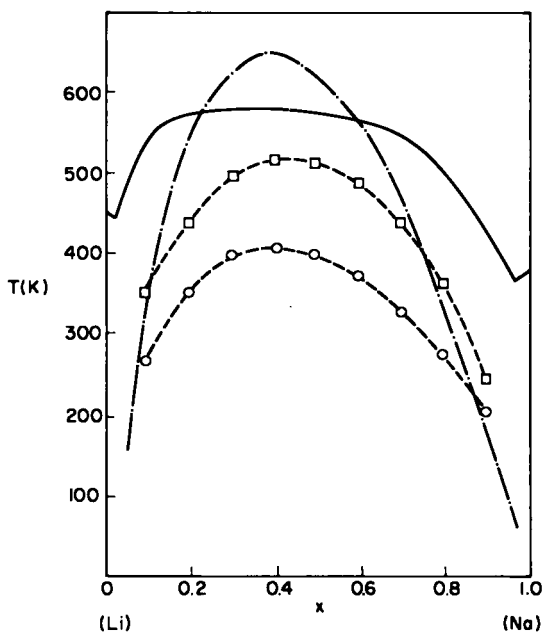


FIG. 22. Calculated spinodal lines for  $\text{Li}_x\text{Na}_{1-x}$ . (· — ·), Hartree approximation.<sup>117</sup> Points (○) (□), mean field, and mean density approximations, respectively.<sup>120</sup> Also shown is the experimental phase (—) boundary.

correlations due to hard-core repulsion. A more accurate approach is to use the hard-sphere mixture as a reference system, and to carry out a perturbation expansion involving the remaining attractive tail. A variety of such thermodynamic perturbation theories may be found in the literature.<sup>119</sup> These are primarily directed towards the single-component classical fluid and relatively few have been addressed to the problem of phase separation. A recent study specifically directed towards phase separation has been carried out by Henderson and Ashcroft.<sup>120</sup> They observe that  $f_1$  appears in an expansion of the free energy of *inhomogeneous* classical mixtures in terms of the corresponding *homogeneous* mixture.<sup>121</sup> This identification aids in finding an expression for  $f_1$  to first order in  $\delta\Phi$  in the long-wavelength limit. The corresponding spinodal line for  $\text{Li}_x\text{Na}_{1-x}$  is shown in Fig. 22.

It is clear from the foregoing discussion that the shape of the phase separation curve can be qualitatively understood purely from accurate knowledge of the effective ion-ion interactions in liquid mixtures. This would appear to be somewhat in contradiction to the implication of the preceding section that volume-dependent, structure-independent terms play a dominant role in determining miscibility in the liquid state. We note, however, that in a fully self-consistent treatment both methods must give rise to the same spinodal line.<sup>122</sup> It is worth remarking, in this context, that the band-structure energy  $E_{\text{BS}}$  seems to play, by and large, a lesser role in phase separation and in freezing than it does in structural phase transitions in solid alloys, where it appears to be of dominant importance.<sup>123</sup>

## VI. Complex Systems

Up to this point we have considered only liquid metals which, to a zeroth approximation, could usefully be regarded as collections of

<sup>119</sup> The subject of perturbation theory as applied to fluids has been reviewed by W. R. Smith in "A Specialist Periodical Report." Statistical Mechanics, Vol. 1, p. 71. The Chemical Society, 1973.

<sup>120</sup> R. L. Henderson and N. W. Ashcroft, *Phys. Rev. A* **13**, 859 (1976).

<sup>121</sup> The expansion is analogous to that of Hohenberg and Kohn [*Phys. Rev.* **136**, B864 (1964)] for the inhomogeneous electron gas. A similar expansion has been used with some success by C. Ebner, W. F. Saam, and D. Stroud [*Phys. Rev. A* **14**, 2264 (1976)] to compute the surface tension and surface profile of classical fluids.

<sup>122</sup> Even if ionic correlations are treated completely, the critical point as calculated from the partial structure factors will not necessarily agree with that obtained from a Maxwell construction unless terms of at least third order in the pseudopotentials are included in effective pairwise interactions. An analogous problem occurs in calculating the compressibility of metals by the method of finite deformations as compared to the long wavelength limit of the phonon spectrum [C. J. Pethick, *Phys. Rev. B* **2**, 1789 (1970)].

<sup>123</sup> D. Stroud and N. W. Ashcroft, *J. Phys. F* **1**, 113 (1971).



simple ions immersed in a neutralizing background of conduction electrons. There are, of course, numerous liquid systems for which this picture is wholly inappropriate, and several classes of such materials will now be discussed briefly, with the aim of pointing out the variety of largely unsolved problems that still remain in liquid metal thermodynamics.

We begin by considering the noble metals Cu, Ag, and Au, and the transition metals of the 3d and 4d series. As noted in the Introduction, these metals are distinguished by electronic levels which are bound strongly enough to the ionic cores that the binding cannot be treated within a perturbation approach, and yet not so strongly that the corresponding electronic degrees of freedom can be neglected in treating the thermodynamics of the metal. Because of this even the zero-temperature binding energies of the corresponding solid metals are relatively difficult to calculate completely from first principles.<sup>124</sup> As yet there have been no such calculations for liquid noble and transition metals. Because of the strong d-electron binding, a structural expansion such as that described in Section II would appear to be impractical. On the other hand, there is abundant experimental evidence that this group of liquid metals<sup>125</sup> does fall into the category of "simple liquids" defined in Section III. (The structure factors, for example, are quite hard-spherelike.<sup>1,126</sup>) Thus one might expect that the thermodynamics of such liquids could be described by an effective potential energy function for the ions, of the form (5.1), consisting of a volume-dependent but structure-independent term plus a sum of pairwise effective ion-ion interactions. No such function has, however, yet been rigorously derived.<sup>127</sup>

In addition to the liquid metals just mentioned, there exists another class of elemental metals which cannot readily be treated within a free electron picture. These are liquids like Te<sup>128</sup> that show evidence of covalent bonding or chainlike structure. Unlike the metals previously discussed, these are *not* simple liquids. Moreover, they are, in comparison, poor conductors, having resistivities often in excess of  $1000 \mu\Omega\cdot\text{cm}$

<sup>124</sup> Such binding energies can be successfully calculated in the context of the renormalized atom approach [cf., L. Hodges, R. E. Watson, and H. Ehrenreich, *Phys. Rev. B* **5**, 3953 (1972)].

<sup>125</sup> Their properties are abundantly described in the review by Busch and Güntherodt.<sup>1</sup>

<sup>126</sup> For a recent review, see Y. Waseda, in *Proc. Third Int. Conf. Properties Liquid Met.* 1976, p. 230.

<sup>127</sup> In this context, a cellular approach such as that developed by Christman for liquid alkali mixtures [J. R. Christman, *Phys. Rev.* **159**, 108 (1967) and references cited therein] might be a useful starting point.

<sup>128</sup> For a theoretical study of the properties of liquid Te, see, e.g., B. Cabane and J. Friedel, *J. Phys. (Paris)* **32**, 73 (1971).

as against typically  $10\text{--}200\ \mu\Omega\cdot\text{cm}$  for the simple metals. Further, their transport properties frequently exhibit an activated temperature dependence rather than the weak temperature variation characteristic of the other liquid metals mentioned.

Even the liquid simple metals themselves do not always behave in a free-electron way. As noted in the Introduction, all metals undergo a metal-insulator transition upon vaporization; the theory of the liquid-gas transition in liquid metals must therefore take into account this transition, especially near the liquid-gas critical point.<sup>129</sup> Furthermore, a theory of the surface tension of liquid metals must presumably take into account the transition across the interface from metallic behavior in the bulk liquids to insulating behavior in the coexisting vapor. Evans and Kumaravadivel<sup>130</sup> have constructed a theory of the transition based on a perturbation approach adapted from the theory of the surface tension of insulating liquids.

Liquid metal mixtures exhibit a wider range of behavior than do elemental liquid metals, and there is a correspondingly greater variety of systems whose behavior cannot easily be understood within a free-electron picture. Among the most intriguing of these are mixtures which exhibit, as functions of composition, singularities in their transport coefficients. A general discussion of these "compound-forming" systems may be found in Faber's book.<sup>3</sup> Among these mixtures are several, such as Mg-Bi, whose constituents are individually fairly good free electron metals in the liquid state, and for this reason one must not rule out the possibility that the thermodynamics properties of the mixtures may not be explicable in terms of the free electron theory. The energetics of compound formation in a few *solid* alloys has been successfully discussed within a pseudopotential formalism by Inglesfield.<sup>131</sup> In general, however, since these liquid systems may exhibit under appropriate conditions metallic, covalent, ionic, or even molecular behavior, the energetics of the liquid would be expected to be more difficult to explain. To date, the thermodynamics of these materials have been studied only in the context of essentially phenomenological theo-

<sup>129</sup> In this context, the effect of ionic arrangement upon electronic structure must certainly be investigated at a level beyond the perturbative one considered in this review. Such studies have been carried out for parameters corresponding to expanded liquid Hg near the critical point by, e.g., Yonezawa and collaborators [cf., F. Yonezawa and F. Martino, *J. Phys. F* **6**, 739 (1976)].

<sup>130</sup> R. Evans and R. Kumaravadivel, *J. Phys. C* **9**, 1891 (1976).

<sup>131</sup> J. E. Inglesfield, *J. Phys. C* **2**, (1969); *J. Phys. C* **2**, 1293 (1969); *Acta Metall.*, **17**, 1395 (1969).

ries<sup>132</sup> which have, however, been quite successful in correlating certain of their properties.

In addition to mixtures of metals with metals, there are several liquid systems involving both metallic and nonmetallic elements which exhibit, under appropriate conditions, metallic behavior. Two examples of such materials are metal-ammonia solutions,<sup>133</sup> and metal-molten salt solutions,<sup>134</sup> both of which may exhibit electronic conductivities in the metallic range under appropriate conditions of concentration and temperature. In the metal-rich region, it is possible that the thermodynamics of these materials can be studied within a free electron picture; calculations of this type have been carried out by Gellings<sup>135</sup> with some success in order to estimate the solubilities of anions such as Cl and O in simple metals. At other concentrations the behavior is complex in both types of materials.

### Appendix: Correlation Functions

The description of liquid metals (as well as other liquids) is most conveniently carried out in terms of correlation functions. In this Appendix we introduce the relevant definitions and also list some of the salient properties of these functions. The expressions given will be seen to be quite general, independent of particle statistics, and hence equally applicable to a classical mixture and to a plasma of charged electrons and ions.

#### a. Definitions

We shall consider a p-component homogeneous, isotropic liquid of volume  $\Omega$ . This volume  $\Omega$  is to be regarded as open, so that the liquid is part of a system of infinite extent. The *density operator* for particles of species  $\alpha$  (the "singlet density") is defined by

$$\hat{\rho}_\alpha(r) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i^{(\alpha)}), \quad (\text{A.1})$$

<sup>132</sup> See, for example, A. B. Bhatia and V. K. Ratti, *J. Phys. F* **6**, 927 (1976) and references cited therein.

<sup>133</sup> See, for example, K. Ichikawa and J. C. Thompson, *J. Chem. Phys.* **59**, 1680 (1973); K. Ichikawa, S. M. Granstaff, and J. C. Thompson, *J. Chem. Phys.* **61**, 4059 (1974), and references cited therein.

<sup>134</sup> A recent review has been given by C. C. Addison in *Proc. Third Int. Conf. Liquid Met.* 1976, p. 537.

<sup>135</sup> M. Dosterbruik, H. P. Van de Braak, and P. J. Gellings, *Proc. Third Int. Conf. Liquid Met.* 1976, p. 547.

the sum running over the position vectors  $\mathbf{R}_i^{(\alpha)}$  of all the particles of species  $\alpha$ . Similarly, the *pair density operator* is defined by

$$\hat{\rho}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{R}_i^{(\alpha)}) \delta(\mathbf{r}_2 - \mathbf{R}_j^{(\beta)}) \quad (\text{A.2})$$

(note the exclusion of  $i = j$ ). Higher order functions may be defined in a like manner.

The observable properties of the liquid depend on averages of various quantities with respect to a grand canonical ensemble (the averages to be denoted  $\langle \quad \rangle$ ). Because the liquid is normally homogeneous and isotropic,

$$\langle \hat{\rho}_{\alpha}(\mathbf{r}) \rangle \equiv \rho_{\alpha}(\mathbf{r}) = N_{\alpha} / \Omega, \quad (\text{A.3})$$

$N_{\alpha}$  being the average number of particles of species  $\alpha$  within  $\Omega$ . Expressed in terms of the number operator  $\hat{N}_{\alpha}$  for particles of species  $\alpha$ , we have  $N_{\alpha} = \langle \hat{N}_{\alpha} \rangle$ . For the same reason  $\langle \hat{\rho}_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_1) \rangle$  can depend only on  $|\mathbf{r}_1 - \mathbf{r}_2|$ , so that we can write

$$\langle \rho_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \rho_{\alpha} \rho_{\beta} g_{\alpha\beta}(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (\text{A.4})$$

Equation (A.4) defines a *pair* or *radial distribution function*  $g_{\alpha\beta}(r)$  which has a simple physical interpretation: it is proportional to the conditional probability for finding a particle of species  $\beta$  a distance  $r$  from the origin, given that there is a particle of species  $\alpha$  at the origin. With the normalization (A.4) all the functions  $g_{\alpha\beta}(r)$  tend to unity in the limit  $r \rightarrow \infty$ , since for such separations the particles are certainly uncorrelated.

The partial structure factors of the liquid are proportional to the Fourier transforms of  $g_{\alpha\beta} - 1$ . They are defined by

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + (\rho_{\alpha}\rho_{\beta})^{1/2} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} [g_{\alpha\beta}(r) - 1]. \quad (\text{A.5})$$

An alternative definition, which can be shown from Eqs. (A.1)–(A.4) to be equivalent, is

$$S_{\alpha\beta}(k) = (N_{\alpha}N_{\beta})^{-1/2} \langle \sum_{ij} \exp[i\mathbf{k}\cdot(\mathbf{R}_i^{(\alpha)} - \mathbf{R}_j^{(\beta)})] \rangle - (N_{\alpha}N_{\beta})^{1/2} \delta_{k,0}. \quad (\text{A.6})$$

These functions are of particular importance in the description of liquids, because they are directly probed by neutron and X-ray diffraction.

It is perhaps worth commenting on the usual assumption that X-ray and neutron diffraction *both* explicitly measure the *ion-ion* correlation function in a liquid metal. Let us assume that the electrons in a metal are divided into two classes: (a) valence electrons and (b) those rigidly attached to the ions (the core electrons). Consider the metal as a two-

component fluid of ions and valence electrons, of which species 1 represents ions. If effects associated with the electronic magnetic moments can be neglected, the neutrons will interact only with the nuclei and hence determine  $S_{11}(k)$  directly. The X-rays, however, scatter from *electrons* (both core and valence) and hence their scattered intensity is proportional to a linear combination of  $S_{11}$ ,  $S_{12}$ , and  $S_{22}$ . Now  $S_{11}$  is usually extracted from X-ray measurements by assuming an *atomic* form factor for the electron density distribution. Clearly this can only be an approximation. If X-ray data are analyzed on the basis of this assumption, the resulting  $S_{11}(k)$  may appear to differ from that determined from neutron measurements, as has been discussed by Egelstaff *et al.*<sup>136</sup> and Straus and Ashcroft.<sup>90</sup>

### b. Compressibility Sum Rule

The structure factors defined by Eq. (A.6) are, in the long-wavelength limit, direct measures of fluctuations in particular number within the fluid. This may be seen by evaluating (A.6) in the limit of small  $k$ , which gives

$$S_{\alpha\beta}(k=0) = (N_\alpha N_\beta)^{-1/2} [\langle \hat{N}_\alpha \hat{N}_\beta \rangle - \langle \hat{N}_\alpha \rangle \langle \hat{N}_\beta \rangle]. \quad (\text{A.7})$$

For a single-component fluid, Eq. (A.7) reduces to

$$S(0) = N^{-1} [\langle \hat{N}^2 \rangle - \langle \hat{N} \rangle^2]$$

or, on using a standard identity,

$$S(0) = \rho k_B T K_T \quad (\text{A.8})$$

where  $K_T = -\Omega^{-1}(\partial\Omega/\partial p)_{T,N}$  is the isothermal compressibility and  $T$  is the absolute temperature. The compressibility sum rule (A.8) may be generalized to a fluid of several components. The result for a two-component system, for example, is<sup>137,138</sup>

$$\rho k_B T K_T = \frac{S_{11}(0)S_{22}(0) - S_{12}^2(0)}{x_2 S_{11}(0) + x_1 S_{22}(0) - 2(x_1 x_2)^{1/2} S_{12}(0)} \quad (\text{A.9})$$

where  $\rho = \rho_1 + \rho_2$ , and  $x_\alpha = \rho_\alpha/\rho$  ( $\alpha = 1, 2$ ) is the concentration of species  $\alpha$ .

It is of some interest to investigate the result (A.9) in the special case of a *charged* two-component system, such as a liquid metal. In that case

<sup>136</sup> P. A. Egelstaff, N. H. March, and N. C. McGill, *Can. J. Phys.* **52**, 1651 (1974).

<sup>137</sup> F. J. Pearson and G. S. Rushbrooke, *Proc. R. Soc. Edinburgh Sect. A* **64**, 305 (1957).

<sup>138</sup> J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.* **19**, 774 (1951).

the requirement of electroneutrality can be used to reduce (A.9) to an expression involving  $S_{11}$  alone, as has been shown by Watabe.<sup>139</sup>

The argument is this: we suppose species  $\alpha$  to have concentration  $x_\alpha$  and charge  $Z_\alpha |e|$ , so that  $x_1 Z_1 + x_2 Z_2 = 0$ . By charge neutrality we must have<sup>139</sup>

$$\sum_{\beta=1}^2 \int d\mathbf{r} Z_\beta \rho_\beta (g_{\alpha\beta}(r) - 1) = -Z_\alpha, \quad \alpha = 1, 2, \quad (\text{A.10})$$

this condition being a statement that the charge density in the fluid surrounding an ion of species  $\alpha$  shall, on the average, integrate to  $-Z_\alpha |e|$ . Use of the definitions (A.5) leads to the following relations,<sup>140</sup> which are valid at small  $k$ :

$$\begin{aligned} S_{11}(k) &= S_{11}(0) + a_{11}k^2 \\ S_{12}(k) &= (-Z_1/Z_2)^{1/2} S_{11}(0) + a_{12}k^2 \\ S_{22}(k) &= (-Z_1/Z_2) S_{11}(0) + a_{22}k^2. \end{aligned} \quad (\text{A.11})$$

The coefficients  $a_{ij}$  cannot be determined purely from considerations of charge conservation. Substitution of (A.11) into (A.9) and taking the limit  $k \rightarrow 0$  gives, however,

$$\rho_1 k_B T K_T = S_{11}(0) \quad (\text{A.12})$$

where  $\rho_1$  is the ionic number density, but  $K_T$  is the compressibility of the *mixture*. For the particular case of a liquid metal, with the ions viewed as species 1 of a two-component fluid, Eq. (A.12) states that the usual form of the compressibility sum rule continues to be valid even when due allowance is made for the extra electronic degrees of freedom. Note that the derivation of (A.12) depends only on charge neutrality and not on any particular division of electrons into "valence" or "core," nor on the statistics of the particles involved. (The compressibility  $K_T$  in a liquid metal is, however, largely determined by the electrons.)

### c. Connection to Response Functions

Liquids can also be described in terms of functions which describe their linear response to an external perturbation. These functions are readily defined for a one-component fluid. Let us imagine that the fluid is placed in a weak spatially varying and time-dependent external field,

<sup>139</sup> M. Watabe, in *Proc. Second Int. Conf. Properties Liquid Met.* 1975, p. 133.

<sup>140</sup> F. H. Stillinger and R. Lovett, *J. Chem. Phys.* 49, 1991 (1968).

which couples to the particle density. The most general field of this kind is described by the Hamiltonian

$$H' = \frac{1}{\Omega} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} d\omega \delta V^{\text{ext}}(\mathbf{q}, \omega) \hat{\rho}(-\mathbf{q}) e^{-i\omega t} \quad (\text{A.13})$$

where

$$\hat{\rho}(\mathbf{q}) = \int \hat{\rho}(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} = \sum_i e^{i\mathbf{q} \cdot \mathbf{R}_i} \quad (\text{A.14})$$

and we require, in order that  $H'$  be real,

$$\delta V^{\text{ext}}(-\mathbf{q}, -\omega) = \delta V^{\text{ext}}(\mathbf{q}, \omega)^*. \quad (\text{A.15})$$

If the field is switched on very slowly (adiabatically), then causality requires that  $\omega$  have an infinitesimal positive imaginary part, and this will be assumed in what follows. The perturbation (A.13) will induce a density response in the fluid which has the form

$$\langle \delta \hat{\rho}(\mathbf{r}, t) \rangle = \frac{1}{\Omega} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} d\omega \langle \delta \hat{\rho}(\mathbf{q}, \omega) \rangle e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)}. \quad (\text{A.16})$$

If the external field is sufficiently weak, the induced density will be linear in  $H'$ . Moreover, to this order, each Fourier component of  $H'$  will clearly produce a response of the same wave number and frequency. Thus we can write

$$\langle \delta \hat{\rho}(\mathbf{q}, \omega) \rangle = \chi(q, \omega) \delta V^{\text{ext}}(\mathbf{q}, \omega), \quad (\text{A.17})$$

a relation which defines the linear response function  $\chi(q, \omega)$ .

The structure factor is related to the linear response function defined in (A.17) by the fluctuation-dissipation theorem

$$S(q) = -\frac{\hbar}{\rho\pi} \int_0^{\infty} d\omega \coth \frac{1}{2}\beta\hbar\omega \text{Im } \chi(q, \omega) \quad (\text{A.18})$$

where  $\beta = (k_B T)^{-1}$ . Equation (A.18) is valid for particles of any statistics. In the classical limit ( $\hbar \rightarrow 0$ ) use of the Kramers-Kronig relation

$$\text{Re } \chi(q, \omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Im } \chi(q, \omega')}{\omega - \omega'} d\omega' \quad (\text{A.19})$$

and the relation  $\chi(q, -\omega) = \chi^*(q, \omega)$  (which can be derived from the definition of the response function) leads to the result

$$S(q) = -(\beta\rho)^{-1} \chi(q, 0). \quad (\text{A.20})$$

In the quantum limit ( $\beta\hbar\omega \gg 1$ ) we obtain

$$S(q) = -\frac{\hbar}{\rho\pi} \int_0^\infty \text{Im } \chi(q, \omega) d\omega. \quad (\text{A.21})$$

Evidently  $\chi(q, 0)$  satisfies a compressibility sum rule<sup>14</sup> analogous to that obeyed by  $S(q)$ :

$$\lim_{q \rightarrow 0} \chi(q, 0) = -\rho^2 K_T, \quad (\text{A.22})$$

$K_T$  being the isothermal compressibility. For a classical fluid the usual compressibility sum rule (A.8) follows from this and the relation (A.20). For a quantum fluid such as an electron gas, (A.22) leads to sum rules on  $\epsilon(q, 0)$  and on  $G(q)$  (see Section II).

The relations between  $S$  and  $\chi$  are readily generalized to a fluid of more than one component. A weak external perturbation described the Hamiltonian

$$H' = \frac{1}{\Omega} \sum_{\mathbf{q}} \int_{-\infty}^{\infty} \sum_{\alpha} \delta V^{\text{ext}}(\mathbf{q}, \omega) \hat{\rho}_{\alpha}(-\mathbf{q}) e^{-i\omega t} d\omega \quad (\text{A.23})$$

will induce partial densities

$$\langle \delta \hat{\rho}_{\alpha}(\mathbf{q}, \omega) \rangle = \sum_{\beta} \chi_{\alpha\beta}(q, \omega) \delta V_{\beta}^{\text{ext}}(\mathbf{q}, \omega). \quad (\text{A.24})$$

The partial structure factors are related to the response functions defined in (A.24) by the equation

$$S_{\alpha\beta}(q) = -(\rho_{\alpha}\rho_{\beta})^{-1/2} \frac{\hbar}{\pi} \int_0^\infty d\omega \coth \frac{1}{2}\beta\hbar\omega \text{Im } \chi_{\alpha\beta}(q, \omega), \quad (\text{A.25})$$

which becomes, in the classical limit,

$$S_{\alpha\beta}(q) = -(\rho_{\alpha}\rho_{\beta})^{-1/2} k_B T \chi_{\alpha\beta}(q, 0). \quad (\text{A.26})$$

Equation (A.25) applies equally well to a system of electrons and ions as to other binary mixtures. In the former case, however,  $\chi_{22}$  will not represent the response function of a *uniform* electron gas, but must include the effects of electron-ion interactions. Chihara<sup>141</sup> has calculated  $S_{22}$  for a monovalent liquid metal and finds very little modification from that of a uniform electron gas, except at small  $q$ , where Eq. (A.11) requires a substantial deviation. Recently, Trigger<sup>142</sup> has suggested a

<sup>141</sup> J. Chihara, "Properties of Liquid Metals," p. 137. Taylor and Francis, London, 1975.

<sup>142</sup> S. A. Trigger, *Phys. Lett. A* **56**, 325 (1976).



simple approximation expressing  $S_{22}$  in terms of  $S_{11}$  and  $\chi_{ee}$ , the response function of a uniform electron gas; this expression also appears to imply that  $S_{22}$  and  $S_{ee}$  should differ little except at small  $q$ .

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