

where  $V$  is the weak perturbation. For dilute scatterers

$$T_E = \sum_i t_i(\vec{k}, E), \quad (\text{A8})$$

where  $t_i$  is the  $t(\vec{k}, E)$  for the isolated scatterer at the  $i$ th site.

When  $|\vec{r} - \vec{r}'|$  is very large, the integral in (A5), by use of (A2) or (A4), can easily be shown to be of the order of  $e^{-|\vec{r} - \vec{r}'|/l(E)}$ , and thus (A1) or (3) fol-

lows.

For systems where the scatterers are neither weak nor dilute it is more difficult to prove mathematically that (A1) holds. However, physically, the exponential decay in  $G_E$  is expected to still be true. The decay occurs because Bloch states are scattered, and in a system with concentrated and strong scatterers, the decay should be even more rapid.

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<sup>1</sup>J. Friedel, *Advan. Phys.* **3**, 446 (1953).

<sup>2</sup>J. Friedel, *Proc. Phys. Soc. (London)* **B65**, 769 (1952).

<sup>3</sup>C. Herring and M. H. Nichols, *Rev. Mod. Phys.* **21**,

185 (1949).

<sup>4</sup>N. D. Lang and W. Kohn, *Phys. Rev. B* **3**, 1215 (1971).

<sup>5</sup>G. Rickayzen, *Theory of Superconductivity* (Interscience, New York, 1965), Appendix 4.

<sup>6</sup>J. S. Langer, *Phys. Rev.* **120**, 714 (1960); E. A. Stern, *Phys. Rev. B* **4**, 342 (1971).

<sup>7</sup>B. Velický, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.* **175**, 747 (1968).

## Theory of the Melting of Simple Metals: Application to Na<sup>†</sup>

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The melting curves of the simple metals may be calculated by a method which involves no adjustable parameters whatsoever if the electron-ion pseudopotential is known. This simplicity is made possible by the use of variational principles to determine the free energies of the solid and liquid states. The approach yields a volume- and temperature-dependent effective Debye temperature for the solid, and an effective volume- and temperature-dependent hard-sphere packing fraction for the liquid. As applied to Na, the method gives a melting curve in good agreement with experiment up to at least 40 kbar. The long-wavelength limit of the pseudopotential, which is not well known for most metals, is eliminated via the correct equilibrium density at 0 °K. (The melting curve is not, however, sensitive to the choice of this parameter.) Additional thermodynamic quantities are computed for both phases and along the melting curves in good agreement with available experiment. Lindemann's law is fairly well obeyed in the solid phase, although not perfectly, and its analog (i.e., constant hard-sphere packing fraction along the melting curve) holds in the liquid. The Lindemann ratio varies between 0.013 and 0.015 along the melting curve; the packing fraction is about 0.42. Above certain temperatures, there exist no Debye temperatures for which the free energy of the solid phase is stationary; following previous workers we interpret such temperatures as forming a line of mechanical instability which, however, lies far above the actual melting curve.

### I. INTRODUCTION

This paper is the second in a group of three on the subject of structural phase transformations in metals and alloys. The first paper,<sup>1</sup> dealing with concentration-dependent changes of structure in binary alloys, showed that the well-known Hume-Rothery rules for the relative stability of alloy phases resulted from the divergent slope of the conduction-electron dielectric function at  $2k_F$ . In the transitions considered, temperature was generally an unimportant parameter, and for that reason the essentially zero-temperature theory applied there

yielded rather good agreement with finite-temperature observations. But in many structural transformations temperature is manifestly a dominant parameter. In the present work, therefore, we extend the approach used in I to finite temperatures, and apply the resulting theory to the most familiar and ubiquitous of structural phase transitions in metals and alloys, namely, their melting.

The principal requirement of a theory of melting is to calculate the Gibbs free energies  $G_s$  and  $G_l$  of the solid and liquid phase as functions of pressure and temperature. The melting curve is then determined in the  $P$ - $T$  plane by the conditions

$$G_s(P, T) = G_l(P, T). \quad (1)$$

Elsewhere in the plane the phase with the lower Gibbs free energy is more stable. Since melting is a first-order phase transition, thermodynamic quantities such as internal energy are discontinuous across the melting curve, and it is therefore usually convenient to consider the calculation of  $G_s$  and  $G_l$  as two separate problems. We shall do so here. One may also examine the properties of just one phase to see if some kind of instability, such as an imaginary vibrational frequency, develops beyond a certain temperature. Such an approach is incomplete and will only yield an upper or lower bound to the melting curve. We consider this possible instability (in the phases of metals decreed to be solid), but find that for the particular metals studied the resulting upper bound lies so far above the melting curve as to suggest that the instability is irrelevant to the actual phenomenon of melting.

Theoretical investigations of melting date back at least to the time of Lindemann.<sup>2</sup> Because of the great complexity of the correlations between particles, especially in the liquid state, the statistical aspects of the problem have received the greatest share of attention.<sup>3</sup> Modern computing techniques<sup>4,5</sup> have made it possible to compare various approximate schemes with one another and with actual and computer experiments. The nature of the interatomic forces in real materials has received far less attention, probably because such forces are usually difficult to calculate from first principles. Most studies have instead been based on inverse power law,<sup>6-8</sup> hard-core,<sup>9-11</sup> or other relatively idealized and short-range forces, such as the Lennard-Jones force field.<sup>12</sup>

In the nearly free-electron metals, the interionic forces can easily be computed from a knowledge of the electron-ion pseudopotential.<sup>13,14</sup> From the point of view of melting theory these forces are of particular interest because, unlike the interactions usually assumed to prevail in molecular solids, they are explicitly density dependent.<sup>14</sup> Conversely, the calculation of the melting curve of a metal is a stringent test of any theory of metals because it requires knowledge of free-energy differences of the order of one part in  $10^4$  of the free energy of either pure phase.

Recently there have been indications that the calculation of the equilibrium thermodynamic properties of both the liquid and the solid phases of simple metals, and hence of their melting curves, may be within the reach of existing theory. We may mention, for example, the work of Ascarelli and Harrison,<sup>15</sup> based on a hard-sphere model for liquid metals, and that of Price,<sup>16</sup> which makes use of the structure factor obtained by Rahman<sup>17</sup> from molecular dynamics experiments. In the solid phase,

thermodynamic properties depend heavily on the phonon spectra, which have by now been computed for a number of simple metals.<sup>18</sup> Very recently, Hartmann<sup>19</sup> synthesized much of this previous work, by a method somewhat similar to our own, to compute the heats of fusion of a number of metals.

In this paper, we present a melting curve for the free-electron metal Na which agrees well with experiment in spite of the fact that it has been calculated with no adjustable parameters save one which is related to the long-wavelength limit of the electron-ion interaction. The computed melting curve, moreover, is insensitive to the choice of this parameter. Such a calculation is made possible by the use of a variational principle to determine the free energies of the solid and liquid phases of the metal. The variational principle allows one to determine an effective volume- and temperature-dependent Debye temperature for the solid phase, and an effective hard-sphere packing fraction for the liquid. From these quantities we find that in the solid phase the rms atomic displacement from equilibrium is very nearly a constant fraction of the nearest-neighbor separation all along the melting curve, and that in the liquid phase the melting curve almost coincides with a line of constant packing fraction. Thus our calculations represent an approximate "experimental" verification of Lindemann's law for the solid phase of Na and its analog<sup>20</sup> for the liquid phase.

Before proceeding to the body of the paper it will perhaps be useful to give a summary of the approach to be used. We consider the free energy of the solid phase of the metal to be composed of (i) the internal energy of the static lattice, plus (ii) the additional free energy associated with the excitation of phonons at finite temperatures. Part (i), which is essentially the binding energy of the solid, has been calculated many times for Na and other nearly free-electron metals; we adopt the approach of Ashcroft and Langreth.<sup>21</sup> Thus the internal energy is considered to be the sum of (a) the kinetic, exchange, and correlation energies of the electron gas, (b) the Madelung energy arising from the Coulomb interaction between the ions, and (c) an additional reduction in energy arising from the redistribution of the electron gas in the presence of the attractive electron-ion interaction.

Part (ii) of the free energy is the sum of the thermal contribution of the potential energy (i.e., the deviation of the potential energy from its value in the static lattice), the phonon kinetic energy, and the free energy associated with the phonon entropy. The thermal potential energy may be added to the free energy simply by including in the expressions for (b) and (c) an additional exponential factor of the Debye-Waller type. Adding this potential energy

to the other terms in the free energy, we then determine the phonon frequencies by requiring that the free energy be stationary with respect to each frequency. This variational principle, as is well known, is equivalent<sup>22</sup> to the so-called self-consistent phonon approximation,<sup>23</sup> according to which the phonon frequencies are determined by the assumption that each ion moves in the time-averaged force field of its moving neighbors. The self-consistent approximation has previously been applied many times to solid rare gases,<sup>24</sup> but evidently not to metals at high temperatures. Rather than calculate the full phonon spectrum in this way, however, we approximate it by a Debye spectrum. We thus incorporate all effects associated with lattice motion at a given volume and temperature in a single parameter, namely, the Debye temperature, which includes not only information about the phonon spectrum but also, because of the self-consistent way in which it is calculated, some of the effects of anharmonicity.

For any given density of the metal (or equivalently, any given applied hydrostatic pressure), we find that above a certain temperature there no longer exist any frequencies which satisfy the variational condition. We interpret this temperature as an instability temperature, above which the solid phase would be mechanically unstable if it had not already melted. Such an instability has been previously noted, for example, by Choquard.<sup>25</sup>

In the liquid phase, the internal energy once again involves the sum of the terms (a)–(c) of the solid phase. But (b) and (c) involve sums over the positions of the ions, and thus cannot be calculated for a liquid without knowledge of the liquid pair correlation function  $g(\vec{r})$  or its Fourier transform, the structure factor  $S(\vec{k})$ . Following Ashcroft and Lekner,<sup>20</sup> we take  $S(\vec{k})$  to be the structure factor of an equivalent gas of hard spheres, and calculate the hard-sphere structure factor in the Percus-Yevick approximation,<sup>26</sup> which can be solved analytically in  $\vec{k}$  space for this special case.<sup>20</sup> [The  $S(\vec{k})$  determined in this way is generally a good fit to experiment.] The liquid free energy is thus (i) the electron gas terms, as in the solid, plus (ii) the potential-energy terms, calculated using the hard sphere  $S(\vec{k})$ , plus (iii) the kinetic energy of the ions, plus (iv) the entropy term, taken as the entropy of the hard-sphere gas in the Percus-Yevick approximation.

The only unknown parameter in this approach is the hard-sphere packing fraction. This we determine variationally, requiring that the resulting free energy [i. e., the sum of terms (i)–(iv)] be minimized. The minimized free energy so obtained is probably an excellent approximation to the liquid free energy, and would, in fact, be a rigorous upper bound for it if the Percus-Yevick approach were

exact.

We now proceed to the main part of the paper. Section II gives the formalism for the solid state, and Sec. III that appropriate to the liquid. Section IV presents the calculated melting curve for Na, as well as a number of other thermodynamic properties of the liquid and solid state.

## II. SOLID STATE

We wish to determine the Gibbs free energy per ion for the solid state. This is given by

$$G = E - Ts + PV, \quad (2)$$

where  $E$ ,  $S$ , and  $V$  are, respectively, the internal energy, entropy, and volume per ion in the solid phase. It is convenient, however, to compute the Helmholtz free energy per ion

$$F = E - Ts \quad (3)$$

and obtain the  $PV$  term separately as the volume derivative

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, N}. \quad (4)$$

We shall consider in turn the energy of the static lattice, followed by the temperature-dependent terms.

The static internal energy of a nearly free-electron metal<sup>27</sup> is the sum of the electron gas terms, the Madelung energy, and the electron-ion interaction energy. The first of these is the sum of the kinetic, exchange, and correlation energies of the free-electron gas and is given approximately by

$$E_{eg} = (2.21/r_s^2 - 0.916/r_s - 0.115 + 0.031 \ln r_s) Z, \quad (5)$$

where  $r_s$  is defined in terms of the density of ions  $N$  and the valence  $Z$  of the metal by  $\frac{4}{3}\pi r_s^3 = (NZ)^{-1}$ . The Madelung or ion-ion interaction energy is

$$E_M = \frac{1}{2} \sum_{\vec{k} \neq 0} \frac{8\pi Z^2}{k^2} [S(\vec{k}) - 1], \quad (6)$$

where  $S(\vec{k})$  is defined for any system by

$$S(\vec{k}) = N^{-1} \langle \sum_i \sum_{i'} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_{i'})} \rangle, \quad (7)$$

$\langle \rangle$  denoting an ensemble average over the ionic positions  $\vec{r}_i$  and  $\vec{r}_{i'}$ . In the static monatomic lattice,  $S(\vec{k}) = N \sum_{\vec{K}} \delta_{\vec{k}, \vec{K}}$ ,  $\vec{K}$  being a reciprocal-lattice vector. In this case the average is trivial, since only the one static configuration need be considered. The generalization to lattices with more than one atom per unit cell is straightforward, but will not be required in the present work.

Finally, the electron-ion or band-structure energy is given by

$$E_{BS} = (2N)^{-1} \sum_{\vec{k} \neq 0} \langle \rho_{\vec{k}}^{\text{ion}} V_{\vec{k}} \rho_{-\vec{k}}^{\text{ind}} \rangle, \quad (8)$$

where  $\rho_{\mathbf{k}}^{\text{ion}}$  and  $\rho_{\mathbf{k}}^{\text{el}}$  are Fourier components of the ionic charge density and of the electronic charge density induced by the unscreened electron-ion interaction  $V_{\mathbf{k}}$  (assumed local and energy independent). The metal is taken to have unit volume. From Poisson's equation and the definition of a dielectric function,

$$\rho_{\mathbf{k}}^{\text{el}} = (k^2/8\pi)(1/\epsilon_k - 1)V_{\mathbf{k}}\rho_{\mathbf{k}}^{\text{ion}}. \quad (9)$$

Substituting (9) into (8), and using  $\rho_{\mathbf{k}}^{\text{ion}} = \sum_l e^{i\mathbf{k}\cdot\mathbf{r}_l}$ , we obtain

$$E_{\text{BS}} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{k^2}{8\pi} |V_{\mathbf{k}}|^2 S(\vec{k}) \left( \frac{1}{\epsilon_k} - 1 \right), \quad (10)$$

or, for a static crystalline lattice,

$$E_{\text{BS}} = \frac{1}{2} \sum_{\mathbf{k} \neq 0} \frac{k^2}{8\pi} |V_{\mathbf{k}}|^2 \left( \frac{1}{\epsilon_k} - 1 \right) N. \quad (11)$$

We have omitted the zeroth Fourier components of (6) and (10) because they are infinite and must be balanced against the infinite zeroth Fourier component of the electron-electron interaction, not included in (5). The sum of the three zeroth components is

$$E_0 = NZ \lim_{\vec{k} \rightarrow 0} (8\pi Z/k^2 + V_{\mathbf{k}}) \text{ as } \vec{k} \rightarrow 0. \quad (12)$$

$E_0$  is a substantial term which must be included in the internal energies of both the solid and the liquid phases. At finite temperatures, the expressions for  $E_M$  and  $E_{\text{BS}}$  must be modified from their static forms to take account of the temperature dependence

of  $S(\vec{k})$ . (The corresponding modification of  $E_{\text{eg}}$  is much smaller and will be neglected here.) To compute the change in  $E_{\text{BS}}$  and  $E_M$  we write

$$\vec{r}_l = \vec{R}_l + \vec{u}_l,$$

where  $\vec{u}_l$  is the displacement of the  $l$ th ion from its equilibrium position  $\vec{R}_l$ . Thus

$$\begin{aligned} S(\vec{k}) &= N^{-1} \sum_{l, l'} e^{i\mathbf{k}\cdot(\vec{R}_l - \vec{R}_{l'})} \langle (e^{i\mathbf{k}\cdot\vec{u}_l}) (e^{-i\mathbf{k}\cdot\vec{u}_{l'}}) \rangle \\ &= N^{-1} \sum_{l, l'} e^{i\mathbf{k}\cdot(\vec{R}_l - \vec{R}_{l'})} e^{-k^2 \rho_{l-l'}^2}, \end{aligned} \quad (13)$$

where<sup>28</sup>

$$\rho_l^2 = (2NM)^{-1} \sum_{\vec{q}} \frac{\hbar}{\omega_{\vec{q}}} (2n_{\vec{q}} + 1) (1 - \cos \vec{q} \cdot \vec{R}_l) \quad (14)$$

for a system with inversion symmetry. Here  $M$  is the ionic mass, and  $\omega_{\vec{q}}$  and  $n_{\vec{q}}$  are the frequency and occupation number of a phonon of wave number  $\vec{q}$  and polarization parallel to  $\vec{k}$ . The sum on  $\vec{q}$  is over the first Brillouin zone. Consistent with the Debye approximation to be made later, we assume  $\omega_{\vec{q}}$  to be independent of polarization, so that  $\rho_l^2$  is independent of  $\vec{k}$ . Substituting (13) into (6) and (10), we obtain

$$\begin{aligned} E_M + E_{\text{BS}} &= \frac{1}{2N} \sum_{l \neq l'} U(\vec{R}_l - \vec{R}_{l'}) \\ &\quad + \text{structure-independent terms}, \end{aligned} \quad (15)$$

where

$$\begin{aligned} U(\vec{R}_l - \vec{R}_{l'}) &= \sum_{\mathbf{k} \neq 0} e^{i\mathbf{k}\cdot(\vec{R}_l - \vec{R}_{l'})} e^{-k^2 \rho_{l-l'}^2} \left[ \frac{8\pi Z^2}{k^2} + \frac{k^2}{8\pi} |V_{\mathbf{k}}|^2 \left( \frac{1}{\epsilon_k} - 1 \right) \right] \\ &= \frac{2Z^2}{|\vec{R}_l - \vec{R}_{l'}|} \text{erf} \left( \frac{|\vec{R}_l - \vec{R}_{l'}|}{2\rho_{l-l'}} \right) \\ &\quad + \frac{1}{2\pi^2} \int_0^\infty \frac{k^4}{8\pi} |V_{\mathbf{k}}|^2 \left( \frac{1}{\epsilon_k} - 1 \right) \frac{\sin k|\vec{R}_l - \vec{R}_{l'}|}{k|\vec{R}_l - \vec{R}_{l'}|} e^{-k^2 \rho_{l-l'}^2} dk. \end{aligned} \quad (16)$$

The function  $U(\vec{R}_l - \vec{R}_{l'})$  behaves like a *temperature-dependent* ion-ion interaction<sup>29</sup> acting between ions at their *static* positions. For the purpose of calculating the free energy of the solid, the use of this pseudointeraction is formally equivalent to the use of the *true* ion-ion potential

$$\begin{aligned} U_{\text{static}}(\vec{R}_l) &= \sum_{\mathbf{k} \neq 0} e^{i\mathbf{k}\cdot\vec{R}_l} \left[ \frac{8\pi Z^2}{k^2} + \frac{k^2}{8\pi} |V_{\mathbf{k}}|^2 \left( \frac{1}{\epsilon_k} - 1 \right) \right] \\ &= \sum_{\mathbf{k} \neq 0} e^{i\mathbf{k}\cdot\vec{R}_l} U_{\mathbf{k}} \end{aligned} \quad (15')$$

acting between the *moving* ions.

The remaining temperature-dependent terms in the free energy are the kinetic energy of the ions,

given by

$$E_{\text{kin}} = (3/2N) \sum_{\vec{q}} \hbar \omega_{\vec{q}} (n_{\vec{q}} + \frac{1}{2}), \quad (17)$$

and the phonon entropy term

$$-T S_{\text{ph}} = \frac{3}{N} \sum_{\vec{q}} [k_B T \ln(1 - e^{-\beta \hbar \omega_{\vec{q}}}) - \hbar \omega_{\vec{q}} n_{\vec{q}}], \quad (18)$$

where  $\beta = 1/k_B T$ . As previously we have assumed  $\omega_{\vec{q}}$  independent of polarization.

It remains to specify the phonon frequencies. These are determined variationally, by requiring that the free energy be stationary with respect to each frequency, i.e.,

$$\frac{\partial F}{\partial \omega_{\vec{q}}} = 0. \quad (19)$$

Substituting for  $F$  the sum of terms (5), (6), (10), (17), and (18), and using Eq. (13) for  $S(\vec{k})$ , we obtain

$$3M\omega_{\vec{q}}^2 = \sum_{\vec{l} \neq 0} \left( - \sum_{\vec{k} \neq 0} k^2 e^{i\vec{k} \cdot \vec{R}_l} e^{-k^2 \rho_l^2} U_{\vec{k}} (1 - \cos \vec{q} \cdot \vec{R}_l) \right) \\ = \sum_{\vec{l} \neq 0} D_l(\vec{q}, \rho_l). \quad (20)$$

$D_l(\vec{q}, \rho_l)$  represents the Laplacian of the effective temperature-dependent ion-ion interaction evaluated at a separation  $\vec{R}_l$ , or, equivalently, the Laplacian of the static interaction averaged over the positions of moving ions with equilibrium separation  $\vec{R}_l$ . Thus the right-hand side of (20) is simply the trace of the dynamical matrix, averaged over ionic positions. Equation (20) is therefore identical to the self-consistent phonon approximation in the special case where phonon frequencies are independent of polarization.

Equation (20) implicitly includes some of the effects of phonon-phonon interaction by means of temperature-dependent shifts of phonon frequencies. But it includes no effects associated with finite phonon lifetime. In actuality, the lifetime of phonons in the alkalis near melting is as little as 10 periods.<sup>30</sup> But for calculating an integral property like the free energy, such lifetime effects, unlike frequency shifts, should be of little importance unless the phonons are no longer good quasiparticles, which, at least in some alkalis, they appear to be even near melting.<sup>30</sup>

The preceding formalism can be substantially simplified for a Debye phonon spectrum in which the first Brillouin zone is approximated by a sphere of the same volume and radius  $q_D$ , and

$$\omega_{\vec{q}} = cq. \quad (21)$$

Equations (17), (18), and (14) then become

$$E_{\text{kin}} = \frac{9}{16} k_B \Theta_D + \frac{3}{2} k_B T I(\Theta_D/T), \quad (22)$$

$$-T S_{\text{ph}} = k_B T [3 \ln(1 - e^{-\Theta_D/T}) - I(\Theta_D/T)], \quad (23)$$

$$\rho_l^2 = \frac{3}{2} (\hbar^2/M) (T/k_B \Theta_D^2) J(\Theta_D/T; R_l), \quad (24)$$

where  $k_B \Theta_D = \hbar c q_D$  is the Debye temperature and

$$I(x) = \frac{3}{x^3} \int_0^x \frac{t^3 dt}{e^t - 1},$$

$$J(x; R_l) = \frac{1}{x} \int_0^x t \coth \frac{1}{2} t \left( 1 - \frac{\sin t \mu_l}{t \mu_l} \right) dt, \quad (25)$$

$$\mu_l = q_D R_l / x.$$

The new self-consistency condition on  $\Theta_D$  is determined by summing the left- and right-hand sides of (20) over all  $q$  in the first Brillouin zone, and using (21). This yields

$$\frac{9}{5} M (k_B \Theta_D)^2 = \sum_{\vec{l} \neq 0} \bar{D}_l(\rho_l), \quad (26)$$

where

$$\bar{D}_l(\rho_l) = - \sum_{\vec{k} \neq 0} k^2 e^{i\vec{k} \cdot \vec{R}_l} e^{-k^2 \rho_l^2} U_{\vec{k}}, \quad (27)$$

with  $\rho_l^2$  given by (24).

The solution to Eq. (26) has a curious temperature dependence which can be understood qualitatively by considering the left- and right-hand sides of the equation as functions of  $\Theta_D^2$  at various temperatures (see Fig. 1). The factor  $\frac{9}{5} M (k_B \Theta_D)^2$  is of course linear in  $\Theta_D^2$  for all temperatures. The behavior of  $\sum \bar{D}_l(\rho_l)$  depends on that of  $\rho_l^2$ . For large  $\Theta_D$  ( $\Theta_D \gg T$ )  $\rho_l^2 \rightarrow 0$ , and the sum approaches a constant value independent of  $\Theta_D$ . For  $\Theta_D \ll T$ ,  $\rho_l^2 \propto T/\Theta_D^2$ , and the sum becomes exponentially small. If the sum varies smoothly in the intermediate region, then for some moderate temperature the possible solution to (26) will be given by the two intersections of the two solid curves in Fig. 1 (plus the unphysical solution  $\Theta_D = 0$ ). As  $T$  increases, the curve for  $\sum \bar{D}_l(\rho_l)$  will decrease as illustrated in Fig. 1(a), and the two solutions to (26) will move closer together. Eventually, for some  $T = T_c$ , the two solutions will merge, and for  $T > T_c$  there will be no solution except  $\Theta_D = 0$ . Following Choquard, we interpret  $T_c$  as an instability temperature, above which the solid phase is mechanically unstable.

The solutions  $\Theta_D(T)$  to Eq. (26) are shown schematically in Fig. 1(b). Of the two branches of solutions, the lower one goes to zero at  $T = 0$  and is therefore unphysical. Near  $T = T_c$ ,  $\Theta_D(T) \sim \Theta_c + \text{const} \times (T_c - T)^{1/2}$ , the behavior expected from a self-consistent or mean-field theory.

The instability just described is not an artifact of the Debye approximation but exists at least for any phonon spectrum in which frequencies do not depend on polarization. To see this divide equation (20) by  $M\omega_{\vec{q}}^2$  and sum over  $\vec{q}$ . For high temperatures

$$\rho_l^2 \sim (MN)^{-1} \sum_{\vec{q}} \frac{kT}{\omega_{\vec{q}}^2} (1 - \cos \vec{q} \cdot \vec{R}_l),$$

so that Eq. (20) becomes

$$3k_B T = \sum_{\vec{l} \neq 0} \left( - \rho_l^2 \sum_{\vec{k} \neq 0} k^2 e^{i\vec{k} \cdot \vec{R}_l} e^{-k^2 \rho_l^2} U_{\vec{k}} \right). \quad (26')$$

Since the right-hand side of this equation is bounded, there must exist a temperature  $T_c$  above which there is not a set of  $\rho_l^2$ 's for which the equation can be solved, so that an instability exists just as for the simple Debye spectrum.

### III. LIQUID STATE

Many of the terms in the free energy of a liquid metal can be transposed directly from the solid. In particular expressions (5), (6), (10), and (12) for the various terms in the internal energy are valid also for the liquid. It remains, however, to find ways of computing the liquid structure factor  $S(\vec{k})$  and the entropy of the liquid. By analogy with our

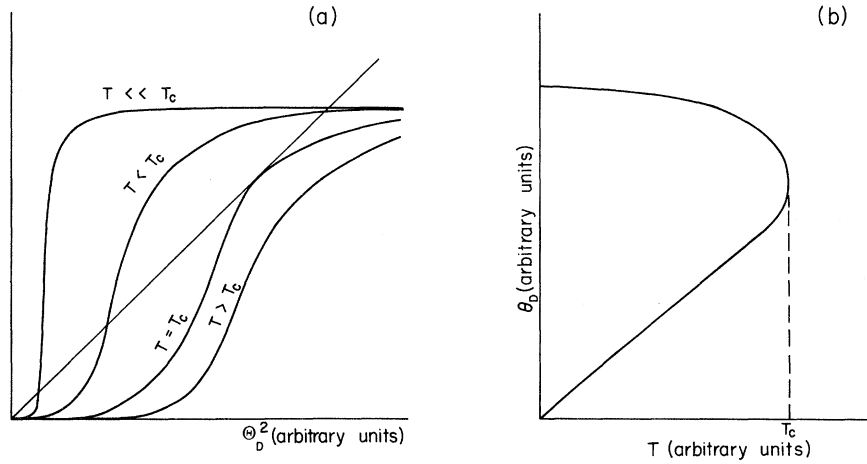


FIG. 1. Schematic illustrating calculation of  $\Theta_D$  from Eq. (26). (a) Left-hand side of Eq. (26) (straight line) and right-hand side (curved lines) at several temperatures. Intersections are allowed values of  $\Theta_D$ . (b) Schematic of  $\Theta_D(T)$  corresponding to (a). Upper branch of curve is the physical branch. The unphysical solution  $\Theta_D(T)=0$  is not indicated.

treatment of the solid state, we would also like to find a variational principle to determine any unknown parameters on which the free energy may depend.

All of these goals can be accomplished with the help of a well-known inequality for the free energy derived from thermodynamic perturbation theory,<sup>31</sup> which we write

$$F \leq F_{hc} + \frac{1}{2} \sum_{\vec{k}} U(\vec{k}) (S_{hc}(\vec{k}) - 1). \quad (28)$$

Here  $F_{hc}$  is the free energy of a gas of hard spheres of the same number density as the metal, plus all structure-independent terms in the free energy.  $S_{hc}(\vec{k})$  is the corresponding hard-sphere structure factor. The second term on the right-hand side is thus the pair interaction energy of metallic ions arranged according to a hard-sphere structure factor. Since (28) is valid for any hard-sphere packing fraction we minimize the right-hand side with respect to this single parameter and simply take the resulting upper bound to be the approximate  $F$ . In a metal such as Na, where the hard-sphere structure factor fits experiment very well, this upper bound is likely to be very close to the true free energy; in other materials, perhaps not so close.

To calculate  $S_{hc}(\vec{k})$  we have a choice of several approximations, of which we have chosen that of Percus and Yevick, which is conveniently solvable analytically in  $\vec{k}$  space where  $U(\vec{k})$  is itself known explicitly.

For completeness, we now write out the various terms in our approximate liquid free energy. We have

$$F \sim E_{eg} + E_M + E_{BS} + E_0 + E_{kin} - T S_{hc}. \quad (29)$$

$E_{eg}$  and  $E_0$  are given by (5) and (12), respectively. Expressions (6) and (10) for  $E_M$  and  $E_{BS}$  reduce to

$$E_M = \frac{2Z^2}{\pi} \int_0^\infty [S(\vec{k}) - 1] dk \quad (30)$$

and

$$E_{BS} = \frac{2Z^2}{\pi} \int_0^\infty \left| \frac{V_{\vec{k}}}{V_{\vec{k}}^c} \right|^2 S(\vec{k}) \left( \frac{1}{\epsilon_{\vec{k}}} - 1 \right) dk, \quad (31)$$

$$V_{\vec{k}}^c = 8\pi Z/k^2.$$

The kinetic energy  $E_{kin}$  per ion is just

$$E_{kin} = \frac{3}{2} k_B T. \quad (32)$$

Finally, the entropy term is given in the Percus-Yevick approximation by<sup>32</sup>

$$\frac{S_{hc}}{k_B} = \frac{S_{gas}}{k_B} + \frac{3}{2} \ln(1 - \eta) - \frac{6\eta}{1 - \eta} - \frac{9}{2} \frac{\eta^2}{(1 - \eta)^2} + \frac{1 - \eta^3}{(1 - \eta)^3}, \quad (33)$$

where

$$\frac{S_{gas}}{k_B} = \frac{3}{2} + \ln \left[ \frac{e}{N} \left( \frac{M k_B T}{2\pi \hbar^2} \right)^{3/2} \right],$$

where the hard-sphere packing fraction  $\eta$  is defined in terms of the hard-sphere diameter  $d$  and ionic volume  $V_i$  by

$$\eta = (\frac{1}{6} \pi d^3) / V_i \quad (34)$$

and  $e$  is the natural base. An expression for the structure factor, on which (30) and (31) depend, is given by Ashcroft and Lekner.<sup>20</sup>

#### IV. APPLICATION TO Na

The formalism of the preceding pages may be applied directly to Na once the electron-ion pseudopotential  $V_{\vec{k}}$  and the dielectric function  $\epsilon_{\vec{k}}$  are specified. For  $V_{\vec{k}}$  we choose the Ashcroft empty-core pseudopotential<sup>33</sup>

$$V_{\vec{k}} = -(8\pi Z/k^2) \cos kr_c, \quad (35)$$

which is determined entirely by the single parameter  $r_c$ . The modification of the formulas of Secs. II and III

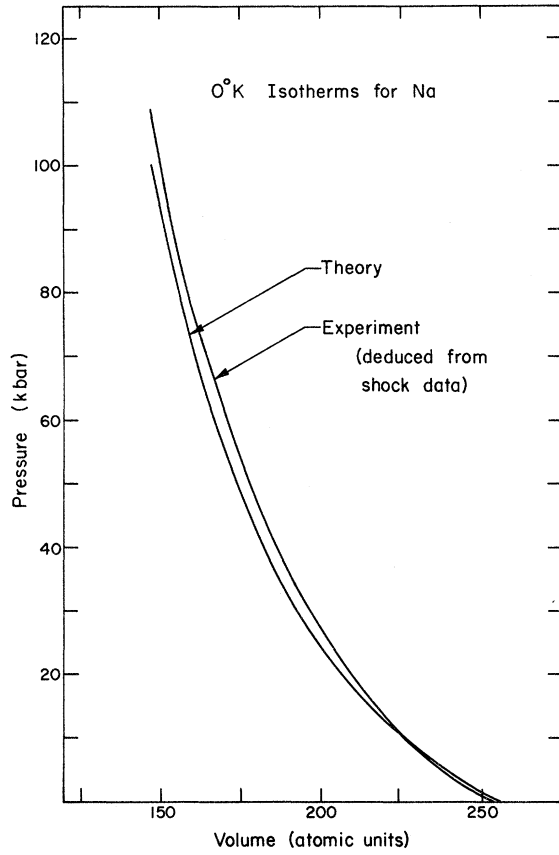


FIG. 2. 0°K pressure isotherms for solid bcc Na. Theoretical curve includes zero-point motion. Experimental curve is extrapolated from shock data of Rice, quoted in Ref. 35.

is immediate; in particular,  $E_0$  [Eq. (12)] becomes  $E_0 = \alpha NZ$ , where  $\alpha = 4\pi r_c^2$ . Rather than determining  $\alpha$  by this equation, however, we have instead chosen it to yield the correct zero-pressure volume at 0°K, setting  $dE/dr_s = 0$  at the observed  $r_s$  at 0°K,  $E$  being the internal energy of the metal at absolute zero (including zero-point energy).

For the dielectric function we have used the modified Hubbard<sup>34</sup> interpolation form, as used by Ashcroft and Langreth<sup>14</sup>:

$$\begin{aligned} \epsilon_k &= 1 + (\lambda^2/y^2) F(y), \\ F(y) &= \frac{f(y)}{1 - \lambda^2 f(y)/(2y^2 + g)}, \\ f(y) &= \frac{1}{2} + \frac{1}{4y} (1 - y^2) \ln \left| \frac{1+y}{1-y} \right|, \\ g &= (1 + 0.158\lambda^2)^{-1}, \\ \lambda^2 &= (\pi k_F)^{-1}, \\ y &= k/2k_F. \end{aligned} \quad (36)$$

Justification of the form (36) is given by Ashcroft

and Langreth.

Figure 2 shows the calculated 0°K pressure isotherm for Na. The experimental isotherm is an extrapolation of the shock data of Rice, as quoted by Neece *et al.*<sup>35</sup> Both theory and experiment are based on the bcc structure, rather than the low-temperature hcp modification. As is evident, the theoretical pressures never deviate by more than 10% from experiment, even at 100 kbar.

The finite-temperature properties of the solid phase depend on  $\Theta(V, T)$ . We have calculated this function from Eq. (26) with the help of a "zero-phonon" approximation<sup>28</sup> and a high-temperature approximation. The first of these is just

$$\bar{D}_i(\rho_i) \sim \bar{D}_i(\rho_{nn}), \quad (37)$$

where  $\bar{D}_i(\rho_i)$  is defined by Eq. (27), and  $\rho_{nn}$  denotes  $\rho_i$  evaluated at  $\bar{R}_i$  equal to a nearest-neighbor separation. Equation (37) will be a satisfactory approximation if the sum in (27) is dominated by contributions from  $\bar{R}_i$ 's almost equal to the nearest-neighbor separation. In Na, where the long-range Friedel oscillations in the ion-ion potential are very small, this condition is reasonably well satisfied. The effect of (37) is probably to underestimate somewhat the temperature variation of terms in (26) arising from distant sites, resulting in an error in the calculated Debye temperature which should, however, be much less significant than the deviation of the Debye spectrum itself from reality. Note also that the structure factor (13) calculated in this zero-phonon approximation still satisfies the sum rule  $\sum_{\vec{k}} [S(\vec{k}) - 1] = 0$  to within terms of order  $e^{-R_{nn}^2/4\rho_{nn}^2}$  which are completely negligible below melting. The high-temperature approximation  $T \gg \Theta_D$  yields

$$\rho_{nn}^2 \sim \frac{3\hbar^2}{M} \frac{k_B T}{(k_B \Theta_D)^2} \left( 1 - \frac{\text{Si}(q_D R_{nn})}{q_D R_{nn}} \right). \quad (38)$$

Equation (38), which is accurately satisfied near melting, makes it possible to obtain  $\Theta_D(T)$  from (26) with a minimum of calculational effort.

Figure 3 shows  $\Theta_D(V, T)$  for Na, as calculated from Eqs. (26), (27), (37), and (38). The instability shown schematically in Fig. 1 is clearly visible for each volume plotted; it occurs, however, at temperatures nearly an order of magnitude above the actual melting curve of Na.

Knowledge of  $\Theta_{Na}(V, T)$  determines an effective volume- and temperature-dependent ion-ion potential, given by Eq. (16). Figure 4 shows this effective potential for Na at three different temperatures and at  $r_s = 3.95$ . The graph is based on the approximate Eqs. (37) and (38), as are all remaining calculations in this paper. The principal effects of increasing temperature are to move the extrema of the potential to larger ionic separation, and to reduce their magnitude, as would be intuitively ex-

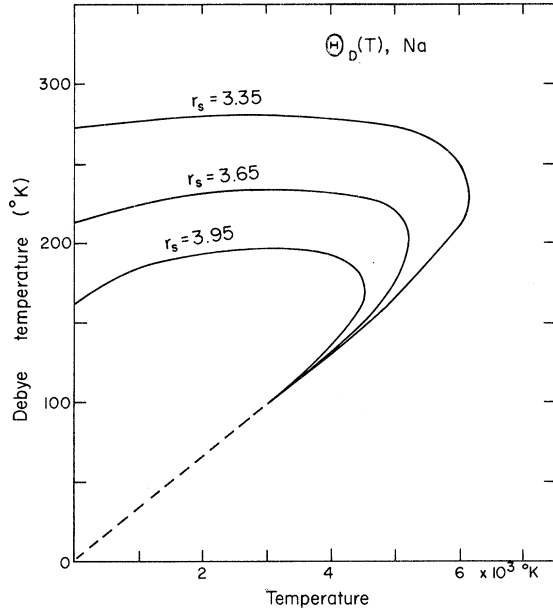


FIG. 3. Debye temperature of Na vs temperature for three different densities. Note that instability (maximum temperature for which a solution exists) occurs far above melting temperature.

pected. For sufficiently large  $r$ , it can be shown from Eq. (16) that the Friedel oscillations are uniformly reduced from their static form by a factor  $e^{-(2k_F r_{nn})^2}$ .

Figure 4 does not take account of the temperature dependence of  $\epsilon_k$  itself. The variation of the electronic Fermi factors with temperature leads to an  $\epsilon_k$  whose slope approaches  $\epsilon_F/k_B T$  at  $k = 2k_F$  ( $\epsilon_F$  is the Fermi energy) instead of diverging logarithmically as at  $T = 0$ . In consequence the Friedel oscillations in the pair interaction must be multiplied by an exponential damping factor  $e^{-k''r}$ , where  $k'' \sim (k_B T/2k_F)$  a.u. is of the order of the effective "thickness" of the Fermi surface due to temperature broadening. Even at  $T = 820^\circ \text{K}$  and  $r = 30$  a.u., however, this exponential factor still equals 0.86. It is even closer to unity for smaller values of  $T$  and  $r$ . Thus the principal temperature dependence of the ion-ion interaction is indeed included in the curves of Fig. 4.

The relative weakness of the temperature dependence of  $\Theta_{Na}$  suggests that the free energy of the solid phase of the metal may be adequately described by a pseudoharmonic approximation in which, however, frequencies still depend on volume and temperature. To test this hypothesis, we have compared the thermal part of the lattice potential energy [that is, the deviation of (15) from its static value] with the phonon potential energy at the same volume and temperature. The latter is obtained by multiplying Eq. (20) by  $\hbar(n_{\vec{q}} + \frac{1}{2})/2M\omega_{\vec{q}}$  and summing

over  $\vec{q}$ , yielding

$$E_{\text{pot}} = \frac{1}{2} E_{\text{ph}} = -\frac{1}{2} \sum_{\vec{l} \neq 0} \rho_l^2 \sum_{\vec{k} \neq 0} k^2 e^{i\vec{k} \cdot \vec{R}_l} e^{-k^2 \rho_l^2} U_{\vec{k}} \\ \approx - \sum_{\vec{l} \neq 0} \rho_{nn}^2 \sum_{\vec{k} \neq 0} k^2 e^{i\vec{k} \cdot \vec{R}_l} e^{-k^2 \rho_{nn}^2} U_{\vec{k}} \quad (39)$$

on using Eq. (14) and (37). We find the two are equal to within better than 0.2 mRy/ion except for temperatures far above melting. We have therefore evaluated the thermal potential energy in this pseudoharmonic approximation, using a Debye approximation for the phonons with  $\Theta_D(V, T)$  as described in the preceding paragraph. Although this procedure nominally introduces an error of 0.1–0.2 mRy/ion in the free energy, we note that the error involved in finding the temperature corresponding to (15) for a given value of  $\rho_{nn}$  is potentially many times greater. We note, furthermore, that we are still including some of the effects of anharmonicity via the volume and temperature dependence of  $\Theta_D$ . Both dependences must be included for reasonable quantitative agreement with the experimental melting curve.

Isothermal data for the solid phase of Na is presented in Table I.

Compared to the solid, the calculation of the free energy of liquid Na according to the methods of Sec. III presents no serious numerical difficulties. The resulting isothermal data is given in Table II. Unfortunately, however, there appear to exist no experiments with which to compare these data directly.

It is revealing to compare individual terms in the energies of the solid and liquid phases. The Madelung energies are  $E_M = -1.792Z^{5/3}/r_s$  for the solid,

TABLE I. Isothermal data for the solid phase of Na.

Temp. (°K)	Solid			
	$V$ (a. u./ion)	$P$ (kbar)	$S/k_B$	$F$ (Ry/ion)
200	264	0.0	4.8	-0.46756
	240	6.5	4.4	-0.46704
	200	26.0	3.8	-0.46221
	160	72.1	3.1	-0.45051
300	270	0.0	6.1	-0.47106
	240	8.0	5.6	-0.47023
	200	27.5	4.9	-0.46572
	160	73.7	4.3	-0.45287
400	275	0.0	7.0	-0.47517
	240	9.5	6.4	-0.47404
	200	29.0	5.8	-0.46912
	160	75.3	5.1	-0.45584
600	280	1.4	8.3	-0.48491
	240	12.5	7.6	-0.48299
	200	32.1	7.0	-0.47725
	160	78.6	6.3	-0.46310



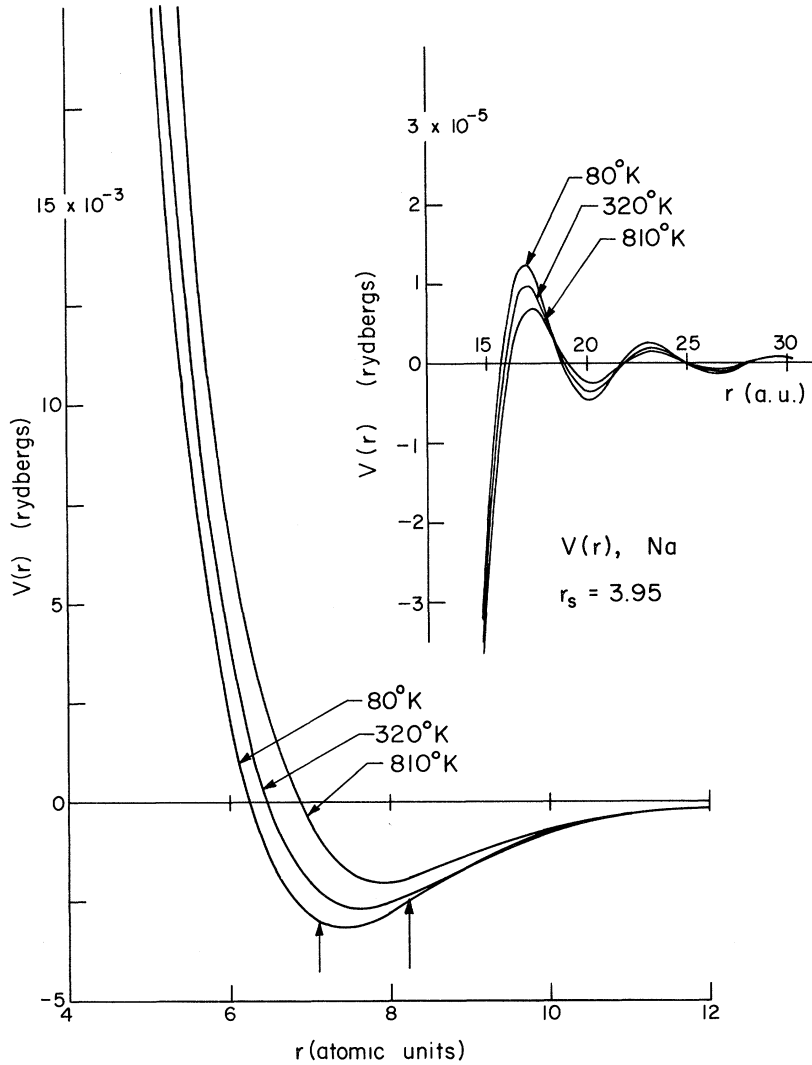


FIG. 4. Effective ion-ion interaction for Na at three different temperatures and  $r_s = 3.95$ . Note change of scale in inset.

and  $E_M = [-1.705 + 1.0(\eta - 0.41)]Z^{5/3}/r_s$  for the liquid. The band-structure energies  $E_{BS}$  cannot be so simply expressed; in Fig. 5, they are plotted versus volume for the solid and liquid phases, the latter at several values of  $\eta$ . Evidently  $E_{BS}^{solid}$  is substantially larger (i.e., less negative) than  $E_{BS}^{liq}$  for all volumes considered. The excess of  $E_{BS}^{solid}$  over  $E_{BS}^{liq}$  arises, as does the excess of  $E_M^{liq}$  over  $E_M^{solid}$ , from the fact that the liquid structure factor, being nonvanishing at a continuum of points in  $k$  space rather than at a discrete set of reciprocal-lattice vectors, extends closer to  $\vec{k} = 0$  than  $S(\vec{k})$  for the solid [cf. Eqs. (6) and (10)]. The sum  $E_M + E_{BS}$  is, however, nearly equal for the two phases.

Additional properties of solid and liquid Na are listed in Table III, and compared to bracketed experimental values.  $\alpha$  denotes the coefficient of linear thermal expansion;  $K/K_0$  is the ratio of the compressibility  $K$  to its free-electron value  $K_0 = 1.7r_s^5$ . Agreement with experiment is quite satis-

fying.

The calculated and experimental<sup>36</sup> melting curves for Na are shown in Fig. 6. The heavy dots represent calculated melting points; the short lines through these dots indicate the theoretical slopes, obtained from the Clausius-Clapeyron equation

TABLE II. Isothermal data for the liquid phase of Na.

Temp. (°K)	Liquid				
	$V$ (a.u. ion)	$P$ (kbar)	$\frac{S}{k_B}$	$\left(\frac{F}{Ry}\right)$ (ion)	$\eta$
400	280	2.3	8.0	-0.475 21	0.41
	240	12.1	7.2	-0.473 47	0.45
	200	31.4	7.4	-0.467 52	0.43
600	240	14.7	8.5	-0.483 57	0.41
	200	32.3	8.0	-0.477 24	0.43

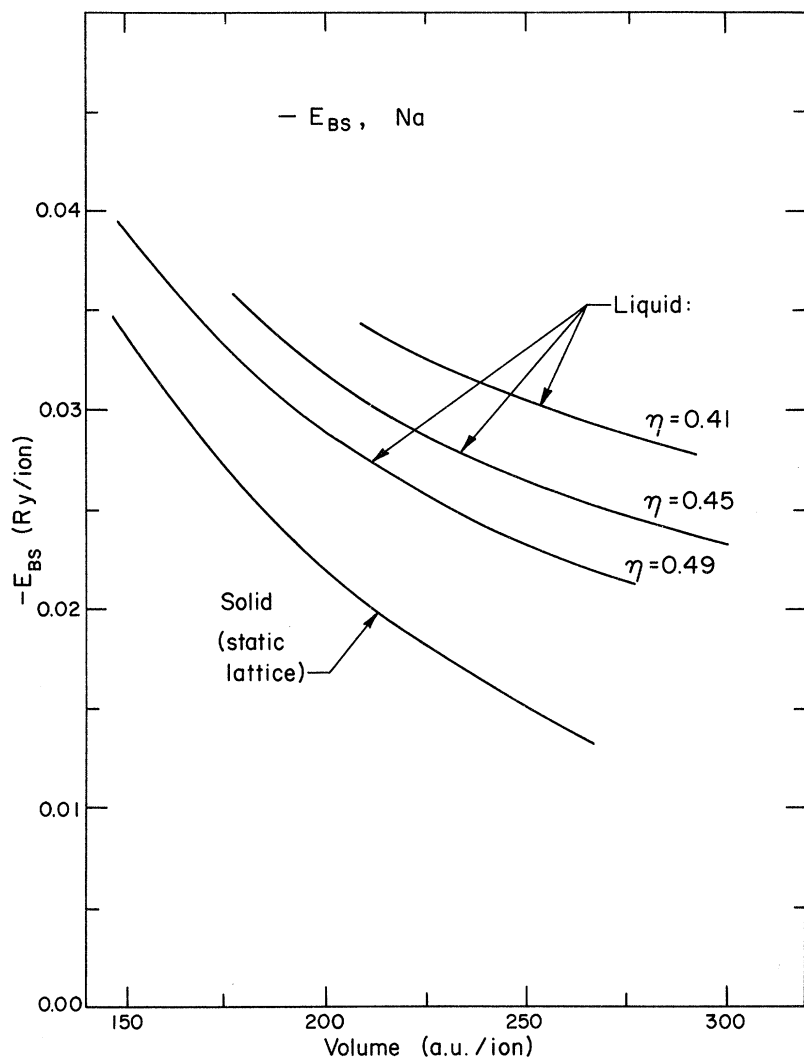


FIG. 5. Band-structure energies for solid and liquid Na. The curve for the solid phase refers to a static lattice. Those for the liquid are given at three different hard-sphere packing fractions.

$$\frac{dP}{dT} = \frac{S_{\text{liq}} - S_{\text{solid}}}{V_{\text{liq}} - V_{\text{solid}}} \quad (40)$$

which holds along the melting curve. The apparent maximum in the melting curve is certainly an artifact, arising from the increasing inaccuracy of our computations for the liquid state above 30 kbar. The agreement with the experimental curve is, however, remarkable, considering the fact that a change of only 0.5 mRy/ion in the free energy of either phase could shift a calculated melting point by as much as 6 kbar. Note also that the slopes of the calculated and experimental melting curves agree fairly well except at low pressures.

Additional properties of the solid and liquid metal along the melting curve are listed in Table IV. Experimental quantities are in brackets. As suggested by the Table as well as by Fig. 6, the calculated change in entropy is somewhat large. From the fact that the solid entropy agrees very well with ex-

periment at room temperature, one would be inclined to attribute most of the discrepancy in  $S_{\text{liq}} - S_{\text{solid}}$  to errors in  $S_{\text{liq}}$ . Even so, it appears that

TABLE III. Additional thermodynamic properties of the solid and liquid phases of Na.  $\alpha$  is the coefficient of linear thermal expansion;  $K/K_0$  is the ratio of the isothermal compressibility to its free-electron value  $1.7r_s^5$ . Experimental results are in brackets.

	Solid	Liquid
$\alpha (\times 10^{-6})$	73 (100–200 °K) 61 (300–400 °K) [71 <sup>a</sup> (0–100 °C)]	60 (200–600 °K) [85 <sup>b</sup> (100 °C)]
$K/K_0$	1.5 [1.5 <sup>c</sup> ]	1.5

<sup>a</sup>Quoted in W. B. Pearson, *Handbook of Lattice Spacings* (Pergamon, New York, 1958).

<sup>b</sup>*Liquid Metals Handbook*, 2nd ed., edited by R. N. Lyon (U. S. GPO., Washington, D. C., 1952).

<sup>c</sup>Quoted in Ref. 16.

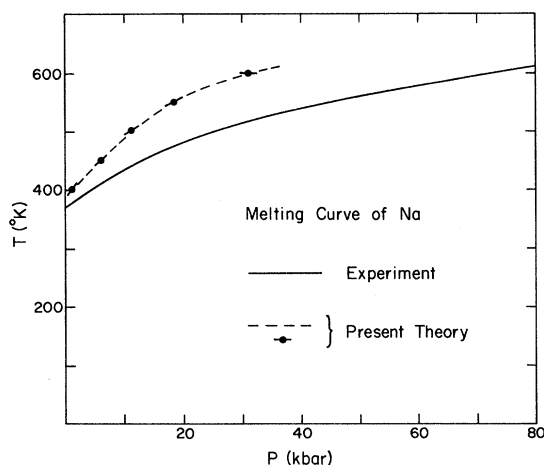


FIG. 6. Melting curve of Na. The experimental curve is taken from Ref. 36. The dashed curve is interpolated through five calculated points. The short line segments passing through the computed points denote the calculated slopes, obtained from the Clausius-Clapeyron relation [Eq. (40)].

$S_{liq}$  as calculated in the present hard-core model and with Percus-Yevick structure factors is still within 4% of experiment.

The last two columns of Table IV give the hard-sphere packing fraction  $\eta$  and Lindemann ratio  $3\rho_0^2/R_{nn}^2$  (i.e., the ratio of the mean-square ionic displacement  $3\rho_0^2$  to nearest-neighbor distance  $R_{nn}^2$ ) along the melting curve. To a fair approximation both of these quantities, especially  $\eta$ , are constant. Thus, apparently for the first time, we have obtained, essentially from first principles, an approximate Lindemann law for both the solid and liquid phases of a real material. The rather small deviation from perfect Lindemann behavior, notable chiefly in the solid, is probably real and not an artifact of the model. It most likely arises from the density dependence of the conduction-electron screening, which makes it impossible to express either the melting curve or the thermodynamic

properties of either phase in any kind of reduced unit.

The extreme sensitivity of the calculated melting curve to small errors in the free energy might appear to suggest that the good agreement with experiment is fortuitous. We note, however, that two large contributions to the free energy are the structure-independent terms  $E_{eg}$  and  $E_0$ . Of these  $E_0$ , which is related to the long-wavelength limit of the electron-ion pseudopotential, is the less accurately established by theory or experiment. But the calculated melting curve proves not to be significantly altered even when the parameter  $\alpha$  (the only adjustable parameter in our theory) is adjusted by as much as 5%. This same change is, however, sufficient to bring the zero-temperature isotherm of the solid into agreement with experiment at high pressures (at the cost of agreement with the observed equilibrium volume).

The structure-dependent terms in the free energy are probably well accounted for by the present variational approach. The computed Debye temperatures (obtained by fitting the exact second moment of the frequency spectrum to the second moment of the Debye spectrum) agree fairly well with those obtained by specific-heat measurements.<sup>37</sup> The hard-core structure factors for the liquid fit well<sup>20</sup> with experiment.<sup>38</sup> Thermodynamic properties such as entropy and thermal expansion coefficient, which are sensitive to individual structure-dependent terms in the free energy, also match experiment.

Although many of the terms in the computed free energy seem to be corroborated by experiment, several other corrections of varying potential importance have not been considered. First, anharmonic effects have been included only in the relatively crude self-consistent phonon approximation.<sup>23</sup> This approximation is known,<sup>39</sup> however, to give much better agreement with experiment than the so-called quasiharmonic approximation, which includes no anharmonic effects other than the volume dependence of the phonon frequencies. Moreover,

TABLE IV. Data for the solid and liquid phases of Na along the melting curve. 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.

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

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

<sup>c</sup>Reference 32.

<sup>b</sup>Luedemann and Kennedy, Ref. 31.

the present approach cannot be improved on simply by perturbation theory, which seems to diverge near melting. The next step is evidently the "higher-order self-consistent approximations,"<sup>19,39</sup> which at this writing, however, are difficult to treat numerically.

Even disregarding the question of anharmonicity, the Debye approximation is itself quite crude. In Na, however, it is probably accurate enough to calculate an integral property such as the melting curve. (In other materials it might be less satisfactory.) In the liquid state, the Percus-Yevick approximation for the structure factors is probably inadequate at high densities, although for the packing fractions appropriate to Na near melting it is probably good enough. A more accurate approach would certainly be to use the true hard-sphere structure factors as obtained from Monte Carlo experiments.<sup>9</sup> These, of course, are not available analytically. For polyvalent metals such as Al, in which the Friedel oscillations play a larger role, it might be appropriate to use a reference system other than hard spheres.

Another omission is the higher-order terms in the band-structure energy arising from components of the induced electronic charge density proportional to the second and higher powers of the electron-ion interaction. Such terms are known to play a significant role in determining the elastic constants of certain polyvalent metals.<sup>40</sup> For monovalent metals, in which the characteristic wave vectors are larger than  $2k_F$ , they are probably less important. Furthermore, since  $V_K$  varies in sign with  $k$ , the third-order term may well cancel against itself. In any event, it would be hoped that such terms would not differ much from the solid to the liquid phase. At present, however, their calculation in the liquid phase requires knowledge (not presently available) of three-ion and higher correlation functions. Thus, their effect on the melting curve would be hard to predict at this writing.

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

<sup>2</sup>F. A. Lindemann, *Z. Physik* **11**, 609 (1910).

<sup>3</sup>For a recent review, see, for example, W. G. Hoover and M. Ross, *Contemp. Phys.* **12**, 339 (1971).

<sup>4</sup>N. A. Metropolis *et al.*, *J. Chem. Phys.* **21**, 1087 (1953).

<sup>5</sup>B. J. Alder and T. E. Wainwright, *Phys. Rev.* **127**, 359 (1962).

<sup>6</sup>S. G. Brush, H. L. Sahlin, and E. Teller, *J. Chem. Phys.* **45**, 2102 (1966).

<sup>7</sup>J.-P. Hansen, *Phys. Rev. A* **2**, 221 (1970).

<sup>8</sup>W. G. Hoover, S. G. Gray, and K. W. Johnson, *J. Chem. Phys.* (to be published).

<sup>9</sup>B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).

<sup>10</sup>W. W. Wood and T. E. Jacobson, *J. Chem. Phys.* **27**, 1207 (1957).

<sup>11</sup>B. J. Alder, W. J. Hoover, and D. A. Young, *J. Chem. Phys.* **49**, 3688 (1968).

<sup>12</sup>J.-P. Hansen and L. Verlet, *Phys. Rev.* **184**, 151 (1969).

<sup>13</sup>M. H. Cohen, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (Benjamin, New York, 1962).

<sup>14</sup>N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **159**, 500 (1967).

<sup>15</sup>P. Ascarelli and R. J. Harrison, *Phys. Rev. Letters* **22**, 385 (1969); see also H. Jones, *J. Chem. Phys.* **55**, 2640 (1971), who employs a variational approach very similar to our own.

<sup>16</sup>D. L. Price (unpublished).

<sup>17</sup>A. Rahman (unpublished).

<sup>18</sup>For a recent review, see S. K. Joshi and A. K. Rajagopal, *Lattice Dynamics of Metals*, Vol. 22 of *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968).

<sup>19</sup>W. M. Hartmann, *Phys. Rev. Letters* **26**, 1640 (1971).

<sup>20</sup>N. W. Ashcroft and J. Lekner, *Phys. Rev.* **145**, 83 (1966).

<sup>21</sup>N. W. Ashcroft and D. C. Langreth, *Phys. Rev.* **155**, 682 (1967).

<sup>22</sup>T. R. Koehler, *Phys. Rev.* **165**, 943 (1968).

<sup>23</sup>M. Born, in *Festschrift zur Feier des zwei hundert-jährigen Bestehens der Akademie der Wissenschaften in Göttingen* (Springer, Berlin, 1951).

<sup>24</sup>See, for example, V. V. Goldman *et al.*, *J. Phys. C* **3**, L33 (1970), and references cited therein.

<sup>25</sup>P. F. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1967).

<sup>26</sup>J. K. Percus and G. J. Yevick, *Phys. Rev.* **110**, 1 (1958).

<sup>27</sup>We use Rydberg atomic units throughout. The correlation energy is representative of many similar forms.

<sup>28</sup>See, for example, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).

<sup>29</sup> $\rho_i^2$  depends on temperature. The  $T$  dependence of  $\epsilon_k$  is much less important (see below).

<sup>30</sup>W. J. L. Buyers and R. A. Cowley, *Phys. Rev.* **180**, 755 (1969).

<sup>31</sup>See, for example, G. A. Mansoori and F. B. Canfield, *J. Chem. Phys.* **51**, 4958 (1969); J. Rasaiah and G. Stell, *Mol. Phys.* **18**, 249 (1970). A particularly elegant proof is to be found in T. Lukes and R. Jones, *J. Phys. A* **1**, 29 (1968).

<sup>32</sup>For example, see H. L. Frisch and J. L. Lebowitz, *The Equilibrium Theory of Classical Fluids* (Benjamin, New York, 1964), p. II-299ff. The solution is quoted here

for the more general case of mixtures of hard spheres.

<sup>33</sup>N. W. Ashcroft, *Phys. Letters* **23**, 48 (1966).

<sup>34</sup>J. Hubbard, *Proc. Roy. Soc. (London)* **A243**, 336 (1957).

<sup>35</sup>G. A. Neece, F. J. Rogers, and W. G. Hoover (unpublished).

<sup>36</sup>H. D. Luedemann and G. C. Kennedy, *J. Geophys. Res.* **73**, 2795 (1968).

<sup>37</sup>*Handbook of Chemistry and Physics*, 48th ed., edited

by R. C. Weast (Chemical Rubber Co., Cleveland, Ohio, 1967).

<sup>38</sup>N. S. Gingrich and L. Heaton, *J. Chem. Phys.* **34**, 873 (1961).

<sup>39</sup>V. V. Goldman, G. K. Horton, and M. L. Klein, *Phys. Letters* **28A**, 341 (1968).

<sup>40</sup>E. G. Brovman, Yu. Kagan, and A. Kholas, *Zh. Eksperim. i Teor. Fiz.* **57**, 1635 (1969) [*Sov. Phys. JETP* **30**, 883 (1970)].

PHYSICAL REVIEW B

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## Pair Effects in Substitutional Alloys. I. Systematic Analysis of the Coherent-Potential Approximation\*

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A single-band model is used to study the electronic structure of disordered binary alloys. Functional-derivative techniques are used to generate an expansion for the electron self-energy that is free of all "multiple-occupancy" corrections. This analysis reveals that the relevant small parameter for the coherent-potential approximation (CPA) is  $Z^{-1}$ , where  $Z$  is the number of nearest neighbors. In addition to being exact to first order in the concentration  $x$  and third order in the impurity potential  $\delta$ , the CPA retains just those contributions of higher order in  $x$  and  $\delta$  that are independent of  $Z^{-1}$ . Various methods have been suggested to calculate corrections to the CPA due to two-atom clusters. While all of these are exact to order  $x^2$  and  $\delta^5$ , we argue that a proper generalization of the CPA must also be correct to higher orders in  $Z^{-1}$ . The appropriate equations are derived and shown to imply the existence of satellite levels on either side of the impurity subband. A formalism is developed to examine the departure from the usual assumption of complete compositional disorder. To order  $x^2$ , the single-band Hamiltonian is found to imply the existence of short-range order in the alloy. The influence of this short-range order on the density of states is discussed and is shown to modify the clustering effects previously evaluated.

### I. INTRODUCTION

This paper is concerned with the single-particle theory of the electronic structure of disordered binary alloys. The problem is most simply discussed in terms of a nearest-neighbor tight-binding-model Hamiltonian.<sup>1,2</sup> This model has the simplifying feature that the disordered potential is cell localized and may therefore be decomposed into a sum of contributions from each site. In a Wannier basis these contributions are simply the energy levels  $\epsilon^A$  and  $\epsilon^B$  of the two constituents. It is assumed that the distribution of these levels is completely random. A principal advantage of this model lies in the fact that there are available a number of exact results concerning the localization of the energy spectrum and the values of the leading moments of the density of states.<sup>1</sup> These exact results have been used to compare several common theories based on a "single-site" decoupling of the

equations of motion. Following this course several authors<sup>1-8</sup> have concluded that the coherent-potential approximation (CPA) of Soven<sup>3</sup> and others provides the best possible single-site description of the alloy. Within the appropriate limits, the CPA exhibits dilute alloy, virtual crystal, and well-separated-impurity-band behavior.<sup>1</sup>

The coherent-potential (CP) concept has generally been developed within the framework of a multiple-scattering description of disordered systems.<sup>1-3,8-12</sup> In this approach the propagation of the electron is regarded as a succession of elementary atomic scatterings which are then averaged over all configurations of the alloy. The essential feature of the CPA is that the individual scatterers are viewed as being embedded in an effective medium whose choice is open and can be made self-consistently. This physical condition corresponding to this choice is simply that if the part of the medium belonging to a given site is removed and replaced by the true