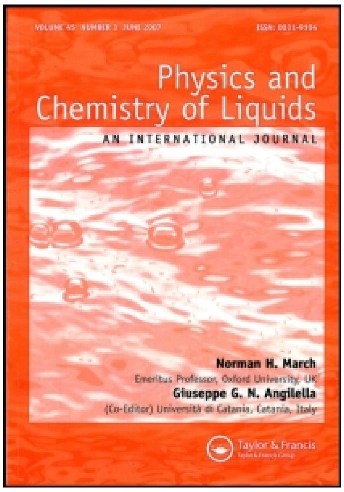

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Equivalence of the Percus-Yevick Collective Coordinate Theory of Liquids with the Self Consistent Field Theory of Melting

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In this paper we compare the recent description of melting via the self consistent field scheme of Johannsson[1] with the Percus-Yevick[2] collective coordinate approach to the theory of liquids, as applied to the melting phenomenon and the liquid structure factor of liquid metals by Omini.[3] We show that the formalism used to extract a self consistent order parameter naturally leads to the concept of a liquid phonon, analogous to a paramagnon in the theory of ferromagnetic-paramagnetic or antiferromagnetic-paramagnetic phase transitions, which can readily be identified with the Percus-Yevick[2] technique of describing the liquid in terms of 3N collective coordinates. This description has been used very successfully by Omini[3] to relate the entropy of melting to the long wavelength limit of the liquid structure factor for a variety of simple metals, so that a relation can be demonstrated between the self consistent field parameter and melting via another route, the Percus-Yevick[2] theory. Lastly, we relate both the self consistent field (order) parameter and the energy of formation of a vacancy-interstitial pair, via the Percus-Yevick dispersion relation, to the Lindemann melting criterion parameter, the root mean square lattice displacement of the atoms critical to melting.

1. SELF CONSISTENT FIELD THEORY OF MELTING

Johannsson[1], continuing in the vein of Brout[4], has recently described melting in an analogous way to the Matsubara-Yokota[5] theory of the antiferromag-

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netic-paramagnetic phase transition via a self consistent energy gap in a Fermion system. The phonons of his system are in the form of a coherent superposition of virtual vacancy-interstitial pairs (Frenkel defects). If the phonon dispersion relation of the solid contains a high enough wavevector, k_c, so that the phonon frequency maximum, ω_c, is equal to the vacancy-interstitial pair production activation energy, U, the phonon will spontaneously become unstable with respect to the pair production, and the lattice will melt. This resembles formally the electron-hole pair production decay of plasmons in an electron gas, and the Stoner excitation (paramagnon) decay of the magnons of an itinerant ferromagnet or antiferromagnet as the Curie or Neel temperature is exceeded. This view of the phonons is equivalent to viewing each phonon as a superposition of Einstein phonons (with equal frequencies), each one of which is actually a vacancy-interstitial pair, with frequency $\omega_0 = U$ (in atomic units, where $\hbar = 1$). The classical theory of Lennard-Jones and Devonshire[6] is identical to the above description and is a classical, molecular field theory.

Johannsson[1] describes the crystal lattice in second quantized notation as follows. The crystal consists of an equal number of two spinless Fermions, A and A′, of the same mass. The system Hamilton is taken as

$$H = \Sigma\, \epsilon_{\underline{k}}\, a_{\underline{k}}^{+} a_{\underline{k}} + \Sigma\, \epsilon_{\underline{k}}\, a_{\underline{k}}'^{+} a_{\underline{k}}' + V/\Omega \sum_{\substack{\underline{k},\underline{m},\\ \underline{l},\underline{n}}} a_{\underline{k}}^{+} a_{\underline{l}}\, a_{\underline{m}}'^{+} a_{\underline{n}}'\, \delta_{\underline{k}+\underline{m}-\underline{l}-\underline{n}} \qquad (1)$$

where an attractive delta function potential, V, exists between particles of the two types, and where $\epsilon_k = k^2/2m$ is the particle kinetic energy and $a_k^{+}(a_k'^{+})$ creates an A (A′) particle in plane wave state $1/\Omega\; e^{ik\cdot r}$. Linear combination creation operators are now constructed

$$A_{\underline{k}}^{+} = u_{\underline{k}}\; a_{\underline{k}}^{+} + v_{\underline{k}}\; a_{\underline{k}+Q_{\underline{k}}}^{+} \qquad (2)$$

$$B_{\underline{k}}^{+} = -\, v_{\underline{k}}\; a_{\underline{k}}^{+} = u_{\underline{k}}\; a_{\underline{k}+Q_{\underline{k}}}^{+} \qquad (3)$$

$$A_{\underline{k}}'^{+} = u_{\underline{k}}\; a_{\underline{k}}'^{+} + v_{\underline{k}}\; a_{\underline{k}+Q_{\underline{k}}}'^{+} \qquad (4)$$

$$B_{\underline{k}}'^{+} = -\, v_{\underline{k}}\; a_{\underline{k}}'^{+} + u_{\underline{k}}\; a_{\underline{k}+Q_{\underline{k}}}'^{+} \qquad (5)$$

where the u_k and v_k are constants, and the A^{+} (A'^{+}) create particles at lattice sites in a two sublattice system, the B^{+} (B'^{+}) creating particles in the interstitial positions. Q_k is the reciprocal lattice vector of the particular crystal lattice being studied.

The one particle orbitals that $A^+, A, A'^+, A', B^+, B, B'^+$ and B' operate on are

$$\varphi_{\underline{k}}^{A}(\underline{r}) = u_{\underline{k}}\ e^{i\underline{k}\cdot\underline{r}} + v_{\underline{k}}\ e^{i(\underline{k}+\underline{Q_k})\cdot\underline{r}} \tag{6}$$

$$\varphi_{\underline{k}}^{B}(\underline{r}) = -\ v_{\underline{k}}\ e^{i\underline{k}\cdot\underline{r}} + u_{\underline{k}}\ e^{i(\underline{k}+\underline{Q_k})\cdot\underline{r}} \tag{7}$$

with associated densities

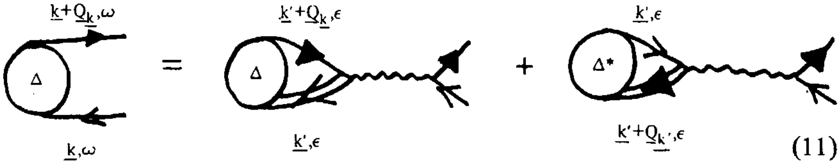
$$|\varphi_{\underline{k}}^{A}(\underline{r})|^2 = 1 + 2\,u_{\underline{k}}\,v_{\underline{k}}\ \cos(\underline{Q_k}\cdot\underline{r}) \tag{8}$$

$$|\varphi_{\underline{k}}^{B}(\underline{r})|^2 = 1 - 2\,u_{\underline{k}}\,v_{\underline{k}}\ \cos(\underline{Q_k}\cdot\underline{r}) \tag{9}$$

The particle-hole creation amplitude, $\Delta_k(\omega)$, is defined by solving a self consistent field equation

$$1 = V/\Omega \sum_{\underline{k}'} (1/4\,(\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{Q_k}})^2 + \Delta^2)^{-1/2} \tag{10}$$

which, in diagram form, is



(11)

This equation is identical with the Matsubara-Yokota[5] equation for the self consistent energy gap in the paramagnetic-antiferromagnetic transition, and that for the superconducting energy gap in the B.C.S. theory of the normal metal-superconducting metal transition. The u_k and v_k parameters are given by

$$u_{\underline{k}}^2 = 1/2 \left\{ 1 + (\epsilon_{\underline{k}+\underline{Q_k}} - \epsilon_{\underline{k}})\,((\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{Q_k}})^2 + 4\Delta^2)^{-1/2} \right\} \tag{12}$$

$$v_{\underline{k}}^2 = 1/2 \left\{ 1 - (\epsilon_{\underline{k}+\underline{Q_k}} - \epsilon_{\underline{k}})\,((\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{Q_k}})^2 + 4\Delta^2)^{-1/2} \right\}$$

The two energy poles of the Green's function are

$$E_{\underline{k}}^{A} = 1/2\,(\epsilon_{\underline{k}} + \epsilon_{\underline{k}+\underline{Q_k}}) - 1/2\,((\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{Q_k}})^2 + 4\Delta^2)^{-1/2} \tag{13}$$

$$E_{\underline{k}}^{B} = 1/2\,(\epsilon_{\underline{k}} + \epsilon_{\underline{k}+\underline{Q_k}}) + 1/2\,((\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{Q_k}})^2 + 4\Delta^2)^{-1/2}$$

where $E_k{}^A$ and $E_k{}^B$ are the orbital energies for the one particle states $\varphi_k{}^A(r)$ and $\varphi_k{}^B(r)$ and ρ is the particle density. An energy gap of magnitude $2\,\Delta$ has opened up in the quasi-particle spectrum; excitation across the gap corresponds to particle-hole pair production. Thus, vacancy-interstitial pairs are formed with an energy $U = 2\,\Delta$. This conclusion of the formal self consistent theory agrees with that of Mukherjee[7] and March[8], who pointed out that the melting temperature is related to the vacancy formation energy in metals by $\theta_D = \delta\, U^{1/2}/V_o{}^{1/3} m^{1/2}$ where θ_D is the Debye temperature, which is related to the melting temperature, V_o is the volume and m is the particle mass, δ being a constant. The vacancy formation energy is a harmonic property since it is related to the sound velocity, v_s or the Debye temperature θ_D. Enderby and March[9] showed that U and T_M, the melting temperature, are related, so

$$k\,T_M = a\,m\,v_s{}^2 \qquad (14)$$

where a is a constant.

Johannsson[1] further finds that

$$m\,V\,k_F\,/\,\pi^2 = 8.17 \qquad (15)$$

the critical Fermi wavevector, k_F being that for the solid-liquid transition in a metal. If we consider the Fourier expansion of the density

$$\rho(\underline{r}) = \sum_{\underline{k}} \rho_{\underline{k}}\, e^{i\underline{k}\cdot\underline{r}} \qquad (16)$$

with k being the reciprocal lattice wavevector. The Fourier coefficients are the long range order parameters, given by

$$\rho_{\underline{k}} = \sum_{\underline{k}} <\psi \mid a^{+}_{\underline{k}+\underline{K}}\;\; a_{\underline{k}} \mid \psi> \; + \; \sum_{\underline{k}} <\psi \mid a'^{+}_{\underline{k}+\underline{K}}\;\; a'_{\underline{k}} \mid \psi> \qquad (17)$$

When only the first set of reciprocal lattice vectors of a cubic lattice is retained, we find

$$\rho_{Q_{\underline{k}}} = \Delta\,/\,V \qquad (18)$$

Thus, Δ or ρ_{Q_k} are equivalent long range order parameters to lowest order.

A finite temperatures, $\Delta = \Delta\,(T)$, and (10) becomes

$$\Delta(T) = V\,/\,\Omega \;\; \sum_{\underline{k}}{}' (n^A_{\underline{k}} - n^B_{\underline{k}}) \;\; \Delta \;\; (T) \;/\; (1/4\,(\epsilon_{\underline{k}+Q_{\underline{k}}} - \epsilon_{\underline{k}})^2 + \Delta^2(T))^{-1/2} \qquad (19)$$

where $n^A{}_k$ and $n^B{}_k$ are Fermi factors, indicating the occupation probabilities for the states $\varphi^A_k(r)$ and $\varphi^B_k(r)$.

$$n^A_{\underline{k}} = (1 + \exp(E^A_{\underline{k}} - \mu)/k_B T)^{-1} \qquad (20)$$

$$n^B_{\underline{k}} = (1 + \exp(E^B_{\underline{k}} - \mu)/k_B T)^{-1} \qquad (21)$$

and the Fermi level μ is determined by the conservation of particle number, $2\sum_{\underline{k}}(n^A_{\underline{k}} + n^B_{\underline{k}}) = N$, so that U and Δ are determined by (19) and (21) simultaneously. At zero temperature $n^A_{\underline{k}} = 1$, $n^B_{\underline{k}} = 0$. Johannsson[1] shows that (19) should be simplified to

$$\Delta(T) = \Delta(0) \left\{ n^A(T) - n^B(T) \right\} = \Delta(0) \tanh \Delta(T)/2\, k_B T$$

the Lennard-Jones-Devonshire[6] result. There is always one solution, $\Delta(T) = 0$, and below a certain critical temperature, T_c, another nonzero solution exists

$$k_B T_c = \Delta(0)/2 = U/4 \qquad (23)$$

corresponding to the crystalline state. Thus

$$T_c / T_M = 2\,a\,m\,v_s^2 / \Delta(0) = 4\,a\,m\,v_s^2/U \qquad (24)$$

To consider the collective phonon description of the system, either in the random phase approximation (R.P.A.)[1] where the R.P.A. equation for the particle-hole channel of the two particle Green's function is studied, or in the equation of motion method[1], we concentrate on the density oscillation operator

$$\begin{aligned} p^+_{\underline{q}} = {} & \sum_{\underline{k}} \left\{ s_{\underline{k}} B^+_{\underline{k}+\underline{q}} A_{\underline{k}} + t_{\underline{k}} A^+_{\underline{k}} B_{\underline{k}+\underline{q}} \right\} + \\ & + \sum_{\underline{k}} \left\{ s_{\underline{k}} B'^+_{\underline{k}+\underline{q}} A'_{\underline{k}} + t_{\underline{k}} A'^+_{k} B'_{\underline{k}+\underline{q}} \right\} \end{aligned} \qquad (25)$$

for acoustic phonons (where density oscillations for the A particles are in phase with those for the A′ particles) or

$$\begin{aligned} O^+_{\underline{q}} = {} & \sum_{\underline{k}} \left\{ s_{\underline{k}} B^+_{\underline{k}+\underline{q}} A_{\underline{k}} + t_{\underline{k}} A^+_{\underline{k}} B_{\underline{k}+\underline{q}} \right\} - \\ & - \sum_{\underline{k}} \left\{ s_{\underline{k}} B'^+_{\underline{k}+\underline{q}} A'_{\underline{k}} + t_{\underline{k}} A'^+_{\underline{k}} B'_{\underline{k}+\underline{q}} \right\} \end{aligned} \qquad (26)$$

for optic modes (where density oscillations for the A particles are out of phase with those for the A′ particles), and where $s_{\underline{k}}$ and $t_{\underline{k}}$ are free parameters. The acoustic dispersion relation is

$$A_{\underline{q}}(\omega) - 1 = 0 \qquad (27)$$

and the optic dispersion relation is

$$A_{\underline{q}}(\omega) + 1 = 0 \qquad (28)$$

which are obtained by solving the Heisenberg equations of motion

$$[\,H, P^{+}_{\underline{q}}\,] = \omega^{A}_{\underline{q}}\, P^{+}_{\underline{q}} \tag{29}$$

and

$$[\,H, O^{+}_{\underline{q}}\,] = \omega^{B}_{\underline{q}}\, O^{+}_{\underline{q}} \tag{30}$$

where Johannsson[1] has calculated the $A_q\,(\omega)_A$ values using a diagram method. We seek the energy eigenvalues, $\omega_{\underline{q}}$ or $\omega^{B}_{\underline{q}}$.

In analogy with the paramagnetic-ferromagnetic phase transition, where paramagnons exist in the paramagnetic phase at temperatures above the Curie temperature, in the liquid-solid transition we have liquid phonons, density fluctuations of wavelength $\lambda \approx 2\pi/K_1$, the precursors of Umklapp phonons in the crystalline state, with a Brillouin zone of length 2 K_1. Usually $\lambda > 2\pi/K_1$ for $T > T_M$ and in general there will be a whole set of wavelengths, but presumably that generated by the first Brillouin zone boundary dimension, K_1, will dominate. In Figure 1 we illustrate the change of phonon dispersion relation upon melting as envisioned by Johannsson.[1]

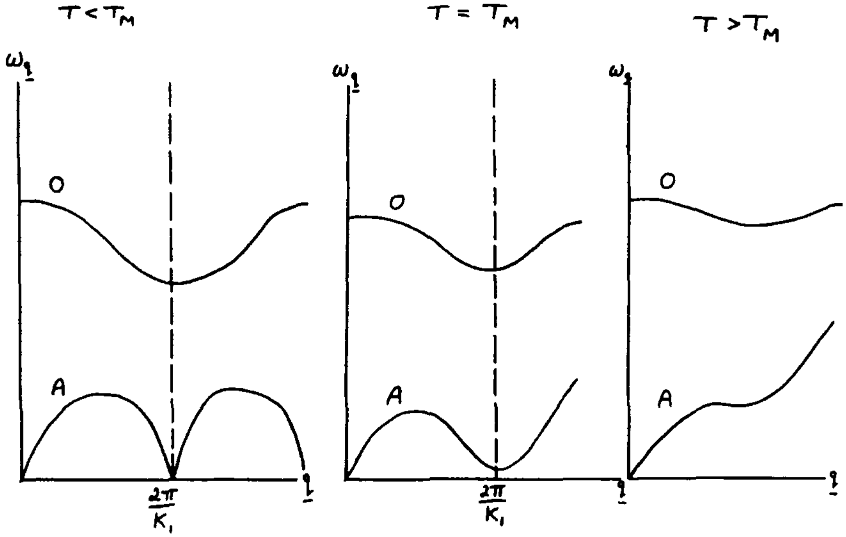


FIGURE 1 Percus-Yevick dispersion relations for solid and liquid, acoustic and optic phonons as temperature passes through the melting point.

2. PERCUS-YEVICK THEORY OF MELTING

Omini[3] has utilized the collective coordinate approach of Percus and Yevick[2] to relate the entropy change upon melting of metals to the long wavelength part of the liquid structure factor. March[11] and Egelstaff[12] have nicely summarized the Percus-Yevick[2] collective coordinate approach to the many body problem in liquid dynamics. We shall here follow Omini's application to the melting phenomenon. Mott[10] originally described a liquid as an ensemble of 3N Einstein oscillators, each harmonic and with a frequency ω_E about 1.4-2 times smaller than that in an Einstein crystal. Percus and Yevick[2] approximated the pair potential by a sum over an arbitrary, finite set $\{k\}$ of 3N vectors in reciprocal space, whose components are multiples of K_1. The actual potential energy

$$V = 1/2 \sum_{i \neq j} V(\underline{x}_i - \underline{x}_j) = 1/2 \sum_{i \neq j} (1/8\pi^3) \int d^3k\, e^{i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)}\, \tilde{V}(\underline{k}) \qquad (30)$$

is approximated by an oscillator sum

$$V^{PY} = 1/2 \sum_{i \neq j} \sum_{\{\underline{k}\}} \nu_{\underline{k}}\, e^{i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)} \qquad (31)$$

where the coefficients ν_k are chosen to optimize the problem. They define collective coordinates

$$q_{\underline{k}}^{PY} = \sum_i e^{i\underline{k}\cdot\underline{x}_i} \qquad (32)$$

so that the potential energy becomes

$$V^{PY} = 1/2 \sum_{\{\underline{k}\}} \nu_{\underline{k}} (q_{\underline{k}}\, q_{-\underline{k}} - N) \qquad (33)$$

the potential energy of an assembly of 3N harmonic oscillators, with angular frequencies

$$(\omega_{\underline{k}}^{PY})^2 = k^2\, k_B\, T\, (1 + \nu_{\underline{k}}/k_B T)/m \qquad (34)$$

The liquid structure factor is defined as the time independent Van-Hove particle-particle correlation function

$$S(\underline{k}) = 1/2\pi \int d\omega\, S(\underline{k},\omega) \qquad (35)$$

Its long wavelength limit was derived by Ascarelli, Harrison and Paskin[13] to be

$$S(0) = \lim_{\underline{k}\to 0} S(k) = k_B T/(k_B T + \nu_{\underline{k}}) \qquad (36)$$

so that the Percus-Yevick[2] frequencies become

$$(\omega_{\underline{k}}^{PY})^2 = k^2 k_B T/m\ S(0) = k^2\ 2\pi\ k_B T/m \int S(\underline{k},\omega)\, d\omega \tag{37}$$

In the Percus-Yevick[2] theory, as in the Debye theory of solids, an upper cut-off in imposed on the dispersion relation

$$k_{MAX} = (18\pi^2\rho / m)^{1/3} = 3^{1/3}\, k_{MAX}^{Debye} \tag{38}$$

giving a maximum upper frequency of

$$(\omega_{\underline{k}}^{PY})^2_{MAX} = k_B\ T/m\ S(0)\ (18\pi^2 \rho / m)^{2/3} \tag{39}$$

It seems natural to equate this to the vacancy-interstitial pair production activation energy, since if U were less than $(\omega_{\underline{k}}^{PY})_{MAX}$ than the dispersion relation, and the harmonic oscillators in the form they take in the solid, would decay spontaneously and so not exist. This value is then the onset of the liquid phonon regime. The Percus-Yevick[2] dispersion relation, a straight line (with no dispersion), temperature dependent, and of slope $(k_B T/mS(0))^{1/2}$ for small k, ie. in the long wavelength limit. Recalling that $k_B T = a\, m\, v_s^2$, we can eliminate the particle mass to obtain

$$(\omega_{\underline{k}}^{PY})^2 = k^2\ T\ a\ v_s^2 / T_M\ S(0) \tag{40}$$

a relation between the frequency and wavevector of the lowest frequency liquid phonon in terms of the sound velocity, melting temperature and temperature. But $T = T_M$ at the melting temperature, so, in that iso-thermal process

$$(\omega_{\underline{k}}^{PY})^2 = k^2\ a\ v_s^2 / S(0) \tag{41}$$

Now, the dispersion relation is expressed in terms of a temperature, a melting temperature, a sound velocity and the long wavelength limit of the liquid structure factor for temperatures greater than the melting temperature.

3. LINDEMANN MELTING CRITERION

We discuss the Lindemann melting criterion, as reviewed by Pines[14], to give a more intuitive flavor to our discussion. Lindemann defined the critical parameter that determines the melting of a crystal lattice as the iso-thermal, fractional mean square amplitude of vibration of the atoms of the lattice

$$\gamma(T) = <\delta R^2_i (T)> / R^2_0 \tag{42}$$

where

$$\delta\, R^2{}_i\,(T) = (1/mN) \sum_{\substack{\underline{k}'\lambda \\ \underline{k},\lambda'}} q_{\underline{k}\lambda}\; q_{\underline{k}'\lambda'}\; e^{i(\underline{k}-\underline{k}')\cdot R_{io}}\; \epsilon_{\underline{k}\lambda}\epsilon_{\underline{k}'\lambda'} \tag{43}$$

where the ϵ's are the phonon polarization vectors. For terms with $\underline{k} = \underline{k}'$, $\lambda = \lambda'$

$$< \delta\, R^2{}_i\,(T) > \; = \; (1/mN) \sum_{\underline{k}\lambda} < q^+_{\underline{k}\lambda}\;\; q_{\underline{k}\lambda} > \tag{44}$$

which Pines[14] shows is equal to

$$< \delta\, R^2{}_i\,(T) > \; = \; (1/mN) \sum_{\underline{k}\lambda} < E_{\underline{k}\lambda} > /\omega^2{}_{\underline{k}\lambda} =$$

$$= (1/mN) \sum_{\underline{k}\lambda} \;(< n_{\underline{k}\lambda} > + 1/2)/\,\omega_{\underline{k}\lambda} \tag{45}$$

where $< E_{\underline{k}\lambda} >$ is the average energy of phonons with wavevector $\underline{k}$ and $< n_{\underline{k}\lambda} >$ is the average number of phonons with that wavevector. Thus

$$\gamma\,(T) \cong \sum_{\underline{k}\lambda} \;< E_{\underline{k}\lambda} > \;/\; m\; N\; R_o{}^2\;\; \omega^2_{\underline{k}\lambda} \tag{46}$$

The low temperature limit is shown to be

$$\gamma\,(0) \cong 0.4\, k_D\;\; (a\;\; m\;\; /k_B\;\; T_M)^{1/2} = 0.4\; k_B\, \theta_D\; (a/\; m\;\; k_B\;\; T_M)^{1/2} \tag{47}$$

giving the mean square deviation of the lattice atoms for melting in terms of the melting and Debye temperatures of the solid. The high temperature limit, of interest in the melting phenomenon, where

$$\omega_{\underline{k}\lambda} \; = \; v_s\, k \;\text{ and }\; < E_{\underline{k}\lambda} > \; = \; k_B\; T \text{ is}$$

$$\gamma\,(T) \cong 1.6\, k_B\; T \,/\, m\, v_s{}^2 \; = \; 1.6\; k_D{}^2\;\, k_B\;\, T \,/\, m\, \theta^2{}_D \tag{48}$$

so that we can relate T_M to θ_D via

$$\theta_D \; = \; (1.6 \,/\, \gamma_M)^{1/2}\;\; (k_B\;\, T_M\; (2.4 \,/\, R_o)^2)^{1/2} \; = \tag{49}$$

$$\cong 40\; (T_M \,/\, \gamma_M\;\, A\;\;\, R_s{}^2)^{1/2} \;\cong\; (k_B\;\, T_M \,/\, A\;\;\, V_o{}^{2/3})^{1/2}$$

where R_s is the interatomic spacing, A is the atomic weight, $A = 6.023 \times 10^{23}$ m, and V_o is the atomic volume. In the next section we will relate γ (T), Δ (T), U and $(\omega^{PY}_{\underline{k}})^2_{MAX}$ to unite all these theories of melting.

4. RELATION OF S.C.F. AND PERCUS-YEVICK THEORIES

We now relate the self consistent field theory of melting of Johannsson[1] to the collective coordinate, Percus-Yevick[2] theory of melting of Omini[3], and see the relation of both to the classical Lindemann melting criterion.

Johannsson[1] utilized the Fourier components of the density ρ_k as a set of long range order parameters. Each one defines a harmonic oscillator and some upper cut-off determines how many harmonic oscillators are allowed in the theory. The cut-off determines, or its determined by the Brillouin zone boundary (or boundaries) of the solid phase in question, as Figure 1 illustrates. We must notice that this is exactly the Percus-Yevick[2,3] description of a liquid, in that a set of harmonic oscillators, 3N in number, with some highest frequency i.e., some upper cut-off in their dispersion relation, describes the liquid, and according to Omini[3], the entropy of melting of the solid, approached from the liquid side of the phase transformation. Since this is so, the Percus-Yevick[2] dispersion relation (37) can be related to the Johannsson[1] vacancy-interstitial energy gap parameter Δ (T), the Muhkerjee[7] and March[8] vacancy formation energy, and the critical mean square displacement of the Lindemann melting criterion. We know

$$(\omega_k^{PY})_{MAX} = (k_B\, T/m\, s(0))^{1/2}\ (18\pi^2 \rho\, /\, m)^{1/3} \tag{50}$$

and, since $\omega_D = v_s k_D = k_B \theta_D$, we see from (38) that

$$k_{MAX} = 3^{1/3}\ (k_B\ \theta_D\ /\ v_s)_{MAX} = 3^{1/3}\ (k_B \theta_D / v_{s_{MIN}} \tag{51}$$

So the vacancy-interstitial pair creation energy, which should beequal to the maximum in the Percus-Yevick[2] dispersion relation, and equal to twice the energy gap parameter is

$$U = 2\,\Delta\,(T) = (k_B\, T/m\, S(0))^{1/2}\ (18\pi^2 \rho/m)^{1/3} \tag{52}$$

$$= m\ V_o{}^{2/3}\ \theta D^{\,2} / \delta^2$$

So, $\Delta\ (T) \sim T^{1/2}$ and $U \sim T^{1/2}$, or conversely $\Delta\ (T) \sim \theta_D^2$ and $U \sim \theta_D^2$. The temperature dependence of the Johannsson[1] gap parameter thus is deducible from the collective coordinate Percus-Yevick[2] dispersion relation. The gap is determined, iso-thermally, by long range parameters of the liquid, like S(0), and ρ, the only short range parameter (local) entering being the particle mass, m, a constant of both the solid and liquid phases. Since S(0) is an integral over the Van-Hove particle-particle correlation function, all frequency and time dependence has already been removed from the problem, so that Δ, nor U can be time or frequency dependent. Also, the vacancy-interstitial pair production activation energy turns out to be only dependent on long range values, S(0) and ρ, of the liquid.

We now proceed to compare these results to those of the Lindemann melting criterion. We say in (48) that $\gamma\,(T) \sim T$, while in (52) we saw that $U = 2\Delta\,(T) \sim T^{1/2}$ so that we can trivially relate γ, Δ, U, $(\omega_k^{PY})_{MAX}$ and S(0); the Critical mean square displacement for melting in the Lindemann melting criterion, the self consistent energy gap for vacancy-interstitial pair production, the vacancy-interstitial formation energy, the cut-off in the Percus-Yevick theory of liquids via the collective coordinate approach and the long wavelength limit of the liquid structure factor. Using (50), and the high temperature result of the Lindemann theory, we find

$$\gamma\,(T) \cong 1.6\, k_D{}^2\, A^2\, V_o{}^{4/3}\, T \,/\, m\, T_M \tag{53}$$

and since $\theta_D = v_s\, k_D \,/\, k_B$ we rewrite this expression as

$$\gamma\,(T) \cong (1.6\, k_B{}^2 \,/\, m\, v_s{}^2)\, T \tag{54}$$

Eliminating T from this equation and those relating $(\omega_k^{PY})_{MAX}$, U and Δ to T, by inverting (54) to use

$$T \cong (m\ v_s{}^2 /\, 1.6\, k_B{}^2)\gamma = (m\, T_M \,/\, 1.6\, k_D{}^2\, A\, V_o{}^{4/3})\,\gamma \tag{55}$$

we arrive at

$$\begin{aligned} U\,(\gamma) = 2\Delta\,(\gamma) \ &= \ (\omega_k^{PY})_{MAX} \ = \\ &= \ (18\pi^2 \rho/m)^{2/3}\ (v_s{}^2\ \gamma \,/\, 1.6\, k_B\ S(0))^{1/2} \ = \\ &= \ (18\pi^2 \rho/m)^{2/3}\ (T_M\ \gamma \,/\, 1.6\, k_D{}^2\ A\, V_o{}^{4/3}\ \ S(0))^{1/2} \end{aligned} \tag{56}$$

or inversely, using

$$\begin{aligned} T = \ &(\omega_k^{PY})^2_{MAX}\ (m/\ 18\pi^2 \rho)^{4/3}\ m\ \ S(0)/k_B \ = \\ &= \ U^2\ (m/\ 18\pi^2\rho)^{4/3}\ m\ S(0)/k_B = \\ &= \ 4\ \Delta^2\ \ (m/\ 18\pi^2\rho)^{4/3}\ m\ S(0)/k_B \end{aligned} \tag{57}$$

we see

$$\gamma\,(\omega_k{}^{PY}{}_{MAX}) = \ 1.6\, k_B/v_s{}^2\ (m/\ 18\pi^2\rho)^{4/3}\ S(0)\,(\omega_k{}^{PY}{}_{MAX})^2 \tag{58}$$

$$\gamma(U) = 1.6\, k_B/v_s^2\ (m/\ 18\pi^2 \rho)^{4/3}\ S(0)\, U^2 \tag{59}$$

$$\gamma(\Delta) = 1.6 \times 4.0\, k_B/v_s^2\ (m/\ 18\pi^2 \rho)^{4/3}\ S(0)\, \Delta^2 \tag{60}$$

Thus, a self consistent field determination of Δ (T), a kinetic determination of U, a dispersion relation of the maximum in the collective coordinate dispersion relation frequency for a liquid, and the Lindemann melting criterion for the critical mean square atom displacement for melting are all essentially equivalent. Furthermore, since $(\omega_k^{PY})_{MAX}$, U and Δ are all $\sim T^{1/2}$, the vacancy-interstitial pair production activation energy, the self consistent energy gap, and the high frequency limit of the Percus-Yevick collective coordinate theory of liquids are all proportional to the root mean square lattice site displacement of atoms necessary for melting, since each is proportional to $\gamma^{1/2}$.

In conclusion, a determination of any of these parameters in a description of melting should be equivalent to a determination of any other of these parameters, so that, when applied to a particular system, the self consistent field theory, the Percus-Yevick theory, the Lindemann melting criterion and the vacancy-interstitial pair production theory of melting should yield identical predictions. In a future paper, we shall examine this equivalence for various simple metals.

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