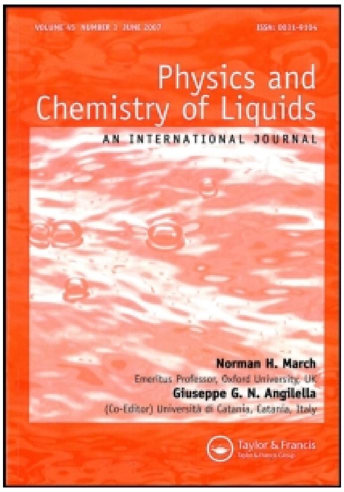

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Edward Siegel[a]
[a] General Motors Technical Center, Warren, MI

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Further Justification for the Concept of a Percus-Yevick Temperature in Liquid Metals

EDWARD SIEGEL†

General Motors Technical Center Warren, MI. 48090

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In this short letter we further justify the concept of an effective Percus-Yevick temperature in liquid metals, in analogy with the well known effective Debye temperature in solids, which describes many of the properties of the phonons of the solid in one parameter.

Siegel[1] has used the concept of a Percus-Yevick temperature to analyze the electron-liquid phonon collision frequency, optical conductivity and optical reflectivity of non-transition and transition liquid metals in the Drude theory of infra-red optical properties of metals. Here we comment on the relation of the concept of a Percus-Yevick temperature to Mott's[4] theory of liquid metals.

Omini[2] has succinctly described the collective coordinate theory of liquid metals, as first proposed for any simple metal by Percus and Yevick.[3] Omini's application was to a calculation of the melting entropy of simple, non-transition metals. The theory consists of the following steps. The potential energy is approximated by a sum of terms

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

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† Present address: 68 Stratford Road, Brooklyn, New York 11218, U.S.A.

where the set of coefficients ν_k are determined to optimize the calculation. Introducing 3N collective coordinates

$$q_{\underline{k}} = \sum_i e^{i\,\underline{k}\cdot\underline{x}_i} \tag{2}$$

the potential energy sum becomes

$$V = 1/2 \sum_{\{\underline{k}\}} \nu_{\underline{k}} \left(q_{\underline{k}}\, q_{-\underline{k}} - N\right) \tag{3}$$

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

$$\omega_{\underline{k}} = \underline{k}\left[(k_B T/m)\left(1 + \nu_{\underline{k}}/k_B T\right)\right]^{1/2} \tag{4}$$

Ascarelli, Harrison and Paskin[5], showed that the long wavelength limit of the liquid structure factor is related to the undetermined coefficients ν_k by

$$S(0) = k_B T / k_B T + \nu_{\underline{k}} \tag{5}$$

where S(0) is the long wavelength limit of the liquid structure factor, k_B is the Boltzmann constant and T is the temperature. The liquid phonon dispersion relation becomes

$$\omega_{\underline{k}} = \underline{k}\left[k_B T / m\, S(0)\right]^{1/2} \tag{6}$$

where m is the ion mass, up to a maximum cut-off frequency

$$\omega^{P.Y.} = (\omega_{\underline{k}})_{MAX} = (18\pi^2 \rho/m)^{1/3} \left(k_B T / m\, S(0)\right)^{1/2} \tag{7}$$

determined by the maximum liquid phonon wavenumber

$$Q = \underline{k}_{MAX} = (18\pi^2 \rho / m)^{1/3} \tag{8}$$

A comparison of the Debye phonon dispersion relation of the solid metal with the Percus-Yevick liquid phonon dispersion relation of the liquid metal reveals that both start out at $\omega=0$, $k=0$ and are linear, with different slopes, up to two different wavenumbers, k_{Debye} and Q, corresponding to two different frequencies, ω_{Debye} and $\omega^{P.Y.}$ respectively, where a sharp cut-off in the frequency spectra exists.

Mott[4] suggested that the ratio of liquid to solid metal resistivities, ρ^L/ρ^S, could be correlated with the latent heat of melting of the metal. In the liquid metal, each ion would vibrate with a greater amplitude than it would in the solid metal. Mott[4] supposed that this would mean that the vibrational frequencies in the liquid would be lower, but this need not be so, since that is only true if the two dispersion relations are identical, while we have seen that while they may be of the same functional form, k_{Debye} and Q, and ω_{Debye} and $\omega^{P.Y.}$, can be quite different, and only an evaluation using (7) and (8) can resolve this question. Since the d.c. electrical resistivity is approximately equal to the mean square vibrational amplitude of the ions ($\sim \omega^{-2}$), he predicted

$$\rho^L/\rho^S \cong (\nu^L/\nu^S)^2 = (\omega^L/\omega^S)^2 = e^{2L/3RT_M} \quad (9)$$

where T_M is the melting temperature and the last expression contains the latent heat of melting, L.

Since the Debye temperature is defined by

$$\hbar\,\omega^S = h\,\omega_{Debye} = k_B\,\theta_D \quad (10)$$

Siegel[1] made the obvious analogy in the liquid state

$$\hbar\,\omega^L = \hbar\,\omega^{P.Y.} = k_B\,\theta_{P.Y.} \quad (11)$$

and thus (9) can be rewritten in terms of this Percus-Yevick temperature and the Debye temperature as

$$\rho^L/\rho^S = (\theta_{P.Y.}/\theta_D)^2 \quad (12)$$

characterizing the shift in d.c. electrical resistivity upon melting with a characteristic shift of the phonon characterization parameters θ as the solid metal melts to form the liquid metal.

In Table I we tabulate ρ^L/ρ^S values as listed by Faber[4], $\theta_{P.Y.}$ values as calculated by Siegel[1] and the resulting $(\theta_D/\theta_{P.Y.})^2$ values calculated if we assume with Faber[4] that $\rho \sim \omega^{-2}$, rather than $\rho \sim \omega^2$, as one would expect. There is no agreement whatsoever, since $\theta_{P.Y.}(T_M) > \theta_{Debye}$ for all metals examined. If we compare, though, ρ^L/ρ^S with $(\theta_{P.Y.}/\theta_D)$ values, we see a marked agreement for all non-transition and transition metals except for Cu, Zn, Cd, Al and Sn. Thus, for most metals we find

$$\rho^L/\rho^S = \theta_{P.Y.}/\theta_D \quad (13)$$

while for Cu, Zn, Cd, Al and Sn

$$\rho^L/\rho^S = (\theta_{P.Y.}/\theta_D)^n, \quad n>2 \quad (14)$$

The explanation is that ω_D and therefore θ_D correspond to phonons with frequencies at the Debye frequency, and $\omega_{P.Y.}$ and therefore $\theta_{P.Y.}$ correspond to liquid phonons with frequencies at the liquid phonon cut-off frequency. Since the Debye and Percus-Yevick theories are approximations

TABLE I

Metal	a/b	ρ^L/ρ^S	θ_D(°K.)	θP.Y.(°K.)	$(\theta_D/\theta_{P.Y.})^2$	$\theta_{P.Y.}/\theta_D$	$\theta_{P.Y.}/\theta_D)^2$
Li	0.68	1.59	335	625	0.287	1.87	3.48
Na	0.79	1.45	156	254	0.377	1.63	2.34
K	0.76	1.58	91	150	0.368	1.64	2.72
Rb	0.77	1.60	56	92	0.371	1.64	2.70
Cs	0.76	1.67	40	68	0.346	1.70	2.89
Cu	1.13	2.1	343	439	0.610	1.28	1.64
Au	0.63	2.3	162	388	0.174	2.40	5.74
Ag	0.84	2.1	226	389	0.338	1.72	2.96
Mg	0.83	1.8	290	468	0.620	1.61	2.60
Zn	1.28	2.2	250	289	0.748	1.16	1.35
Cd	1.24	2.0	209	183	0.767	1.14	1.30
Al	1.27	2.2	428	500	0.733	1.17	1.36
Ga	-	0.45-3.1	125	188	0.335	1.50	2.26
In	0.60	2.2	111	273	0.165	2.50	6.04
Tl	0.54	2.1	79	212	0.139	2.68	7.20
Sn	1.03	2.1	199	281	0.502	1.41	1.99
Pb	0.74	1.9	88	163	0.291	1.85	3.43
Fe	0.77	1.01	420	549	0.585	1.31	1.71
Co	0.70	1.09	385	574	0.500	1.49	2.22
Ni	0.82	1.33	375	527	0.506	1.41	1.97

to the true phonon dispersion relations in the solid and liquid phases, ω_D is only an approximation to the true ω^S, and $\omega_{P.Y.}$ is only an approximation to the true ω^L, so θ_D and $\theta_{P.Y.}$, the single parameters chosen to represent the whole solid or liquid phonon frequency spectrum, are only approximately accurate in representing the solid and liquid states, respectively. In general we should write

$$\rho^L/\rho^S = (\omega^L/\omega^S)^2 \approx (\theta_{P.Y.}/\theta_D)^n \qquad (15)$$

where n is determined by how well an effective temperature represents the true frequency spectrum of the solid or liquid. There is also no a priori reason to assume that the accuracy of effective temperature approximations to the frequency spectra in the solid or liquid phase will be the same for all metals, or even that it will be as good in the liquid phase of any particular metal as in the solid phase. The effective temperature concept must then be viewed with caution as a first step in any calculation, although the hope in the liquid phase, and past experience in the solid phase, indicated that effective temperatures are adequate representations of true phonon spectra.

In conclusion, the use of a Percus-Yevick effective temperature to characterize the liquid phonon frequency spectrum in the liquid metals is certainly a valid approach. It gives fair agreement with Mott's theory of liquid and solid metal resistivity ratios at the melting temperatures of many metals. We can also re-express (15) as

$$\rho^L/\rho^S = (a\,\omega^L/b\omega^S)^2 = (a\theta_{P.Y.}/b\theta_D)2 \qquad (16)$$

where a and b are constants characterizing the liquid and solid states of any particular metal, thus satisfying Faber's[4] n = 2 exponent in the resistivity ratio at melting, but there is no a priori reason why n = 2 in such an approximate theory as Mott's.[4] Our findings are that for many non-transition and transition metals (Li, Na, K, Rb, Cs, Au, Ag, Mg, In, Tl, Pb, Fe, Co, Ni) $0.54 \leq a/b \leq 0{,}84$, while for some (Cu, Zn, Cd, Al, Sn) $a/b \geq 1.0$.

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