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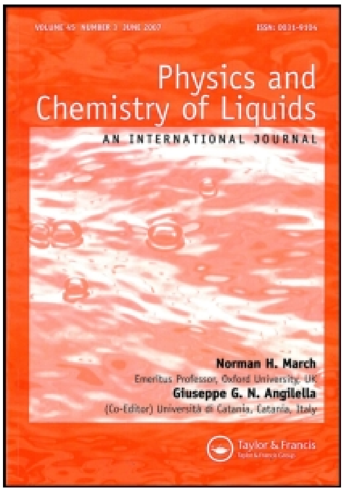

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# Virtual Crystal Model of Melting and the Structure Factor of Liquid Alloys

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In this paper, we extend the theory of melting entropy of metals, of Omini[1], based on the Percus-Yevick[2] collective coordinate theory of liquids, to binary liquid alloys. We reformalate Omini's use of the Percus-Yevick theory to include binary liquid alloys and calculate the long wavelength limit of the binary liquid alloy structure factor as a function of solute concentration for the systems: Li-Na, K-Rb, Rb-Cs, Al-Zn, Zn-Ga and Al-Ga which are the most nearly equi-valent and equi-volume atom pairs Omini worked with.

## 1. THEORY OF THE MELTING ENTROPY OF PURE LIQUID METALS

Omini has recently applied the Percus-Yevick collective coordinate theory of simple liquids to calculate the melting entropy of metals. We review his formulation in depth so that we can build upon it when the problem of alloy melting is presented in Section[2].

Omini relates the melting entropy to the long wavelength limit of the liquid structure factor, S(0). As in the Percus-Yevick theory of simple liquids, the potential energy.

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

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is approximated by

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

where the coefficients $\nu_k$ are chosen to optimize the problem, Collective coordinates are defined

$$q_{\underline{k}} = \sum_i e^{i\underline{k} \cdot \underline{x}_i} \tag{3}$$

so that

$$V^{PY} = (1/2) \sum_{\{k\}} \nu_k \, (q_k \, q_{-k} - N) \tag{4}$$

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

$$\omega_{\underline{k}}^{PY\,2} = k^2 \, (k_B T/m) \, (1+\nu_{\underline{k}} \, / \, k_B T) \tag{5}$$

where m is the atomatic mass. Ascarelli, Harrison and Paskin[3] have shown that the long wavelength limit of the liquid structure factor is

$$S(0) = \lim_{\underline{k} \to 0} S(\underline{k}) = k_B T/(k_B T + \nu_{\underline{k}}) \tag{6}$$

so that the Percus-Yevick dispersion relation for the liquid phonons is

$$\omega_{\underline{k}}^{PY\,2} = k^2 \, k_B T/mS(0) \tag{7}$$

We must choose the set $\{\underline{k}\}$ by physical insight unless we adopt the Ascarelli-Harrison-Paskin relation. Omini's basic assumption is that melting is related to the long wavelength low frequency part of the Percus-Yevick liquid phonon spectrum. He bases this assumption on the findings of March[4] and Mukherjee[5] that the melting temperature and vacancy formation energy of metals are related, and the Debye temperature of the solid is proportional to the square root of the vacancy formation energy, U. Following Enderby and March[6]

$$k_B T_M = \alpha \, m \, v_s^2 \tag{8}$$

where $v_s$ is the sound velocity in the liquid metal and $\alpha$ is a constant. $v_s$ is determined by the long wavelength, low frequency property of the solid so that $T_M$, the melting temperature, is determined by the long wavelength properties in this approximation.

The Percus-Yevick spectrum has a high frequency cut-off at the maximum wavevector

$$Q=(18\pi^2\ \rho/m)^{1/3} = 3^{1/3}\ k_{Debye} \tag{9}$$

By ignoring higher frequency and wavevector components, $k > Q$, we assume a short wavelength cut-off radius in configuration space, $a \sim 2\ \pi/Q$ such that the pair potential is unimportant for $r > a$. $Q\sigma \sim 5.3$ for many liquid metals, where $\sigma$ is the hard core diameter, so that $a=1.18\sigma$, a reasonable value. The entropy of the 3N harmonic oscillators is given by

$$S_{Liq} = \sum_{\{\underline{k}\}} \Big\{ (\hbar\,\omega_{\underline{k}}^{PY}/T)\,((1/2) + (e^{(\hbar\omega_{\underline{k}}^{PY}/k_BT)} - 1)^{-1}) - k_B \ln(2 \sin h\, (\hbar\omega_{\underline{k}}^{PY}/k_BT)) \Big\} \tag{10}$$

where the frequencies $\omega_{\underline{k}}^{PY}$ are given by (5) or (6). By replacing the summation with a continuous integration for small $\underline{k}$ at the melting temperature

$$S_{Liq} = (L/2\pi)^3\ 4\pi \int_0^Q k^2\ dk \Big\{ (\hbar\omega^{PY}(k)/T_M)\,((1/2) + (e^{h\omega^{PY}(k)/k_BT_M} - 1)^{-1}) - k_B\ \ln(2 \sin h\, (\hbar\omega^{PY}(k)/k_BT)) \tag{11}$$

Omini rewrites this as

$$S_{Liq} = 9\,n\,k_B\ ((I_0/2) + I_1 + I_2) \tag{12}$$

where

$$I_0 = \int_0^1 y^2\ (\hbar\omega^{PY}(y)/k_BT_M)\ dy \tag{13}$$

$$I_1 = \int_0^1 y^2\ (\hbar\omega^{PY}(y)/k_BT_M)\,(e^{h\omega^{PY}(y)/k_BT_M} - 1)^{-1}\ dy \tag{14}$$

$$I_2 = -\int_0^1 y^2 \ln(2 \sin h\, (\hbar\omega^{PY}(y)/k_BT_M))\, dy \tag{15}$$

so that the molar entropy change upon melting is

$$\Delta S/R = 9\ ((I_0/2) + I_1 + I_2) - (S_{Solid}/R) \tag{16}$$

where R is the gas constant and $S_{Solid}$ is the molar entropy of the solid at the melting temperature, $S_{Solid}$ is taken from the Debye theory by Omini.

## 2. LIQUID ALLOYS AND MELTING

We reformulate Omini's theory for a binary alloy, AB, and ternary alloy, ABC. The potential energy of the liquid alloy is, according to an alloy analogy of the Percus-Yevick theory.

$$V^{PY}_{AB} = (1/2) \sum_{i \neq j} (V(\underline{x}_i{}^A - \underline{x}_j{}^A) + V(\underline{x}_i{}^B - \underline{x}_j{}^B) + 2V(\underline{x}_i{}^A - \underline{x}_j{}^B) \qquad (17)$$

$$V^{PY}_{ABC} = (1/2) \sum_{i \neq j} (V(\underline{x}_i{}^A - \underline{x}_j{}^A) + V(\underline{x}_i{}^B - \underline{x}_j{}^B) + V(\underline{x}_i{}^C - \underline{x}_j{}^C) + $$
$$+ V(\underline{x}_i{}^A - \underline{x}_j{}^B) + V(\underline{x}_i{}^A - \underline{x}_j{}^C) + V(\underline{x}_i{}^B - \underline{x}_j{}^C)) \qquad (18)$$

In the Percus-Yevick theory, we approximate these by

$$V^{PY}_{AB} = (1/2) \sum_{i \neq j} \sum_{\{k\}} (\nu_{\underline{k}}{}^A e^{i\underline{k} \cdot (\underline{x}_i{}^A - \underline{x}_j{}^A)}$$
$$+ \nu_{\underline{k}}{}^B e^{i\underline{k} \cdot (\underline{x}_i{}^B - \underline{x}_j{}^B)} + 2\nu_{\underline{k}}{}^{AB} e^{i\underline{k} \cdot (\underline{x}_i{}^A - \underline{x}_j{}^B)} \qquad (19)$$

$$V^{PY}_{ABC} = (1/2) \sum_{i \neq j} \sum_{\{\underline{k}\}} (\nu_{\underline{k}}{}^A \; e^{i\underline{k} \cdot (\underline{x}_i{}^A - \underline{x}_j{}^A)} + \nu_{\underline{k}}{}^B e^{i\underline{k} \cdot (\underline{x}_j{}^B - \underline{x}_j{}^B)} +$$
$$+ \nu_{\underline{k}}{}^C e^{i\underline{k} \cdot (\underline{x}_i{}^C - \underline{x}_j{}^C)} + 2\nu_{\underline{k}}{}^{AB} e^{i\underline{k} \cdot (\underline{x}_i{}^A - \underline{x}_j{}^B)} + 2\nu_{\underline{k}}{}^{BC} e^{i\underline{k} \cdot (\underline{x}_i{}^B - \underline{x}_j{}^C)}$$
$$+ 2\nu_{\underline{k}}{}^{AC} e^{i\underline{k} \cdot (\underline{x}_i{}^A - \underline{x}_j{}^C)}) \qquad (20)$$

The collective coordinates are two types in the binary alloy and of three types in the ternary alloy

$$q_{\underline{k}}{}^A = \sum_i e^{i\underline{k} \cdot \underline{x}_i{}^A} \qquad (21)$$

$$q_{\underline{k}}{}^B = \sum_i e^{i\underline{k} \cdot \underline{x}_i{}^B} \qquad (22)$$

$$q_{\underline{k}}{}^C = \sum_i e^{i\underline{k} \cdot \underline{x}_i{}^C} \qquad (23)$$

and the Percus-Yevick potential energy becomes

$$V^{PY}_{AB} = (1/2) (\sum_{\{\underline{k}\}}) \; [\nu_{\underline{k}}{}^A (q_{\underline{k}}{}^A q_{-\underline{k}}{}^A - N^A) + \nu_{\underline{k}}{}^B (q_{\underline{k}}{}^B q_{-\underline{k}}{}^B - N^B) +$$
$$2\nu_{\underline{k}}{}^{AB} (q_{\underline{k}}{}^A q_{-\underline{k}}{}^B - N^{AB}) \,] \qquad (24)$$

$$\begin{aligned}V^{PY}_{ABC} = (1/2)\,(\sum_{\{\underline{k}\}})\,[&\nu_{\underline{k}}{}^{A}(q_{\underline{k}}{}^{A}q_{-\underline{k}}{}^{A}-N^{A}) + \nu_{\underline{k}}{}^{B}(q_{\underline{k}}{}^{B}q_{-\underline{k}}{}^{B}-N^{B}) + \\ &+ \nu_{\underline{k}}{}^{C}(q_{\underline{k}}{}^{C}q_{-\underline{k}}{}^{C}-N^{C}) + 2\nu_{\underline{k}}{}^{AB}(q_{\underline{k}}{}^{A}q_{-\underline{k}}{}^{B}-N^{AB}) + \\ &+ 2\nu_{\underline{k}}{}^{AC}(q_{\underline{k}}{}^{A}q_{-\underline{k}}{}^{C}-N^{AC}) + 2\nu_{\underline{k}}{}^{BC}(q_{\underline{k}}{}^{B}q_{-\underline{k}}{}^{C}-N^{BC})]\end{aligned} \tag{25}$$

such that N in the pure metal is the sum of $N^A$ and $N^B$ in the binary liquid alloy and $N^A$, $N^B$ and $N^C$ in the ternary liquid alloy. Each pure phonon term now has an interaction part, connected with the joint particle coefficients $\nu_{\underline{k}}{}^{AB}$ etc. and the joint particle numbers, $N^{AB}$ etc., which express solute density, such that

$$N = N^A + N^B + N^{AB}, \text{ binary alloy} \tag{26}$$

and

$$N = N^A + N^B + N^C + N^{AB} + N^{AC} + N^{BC}, \text{ ternally alloy} \tag{27}$$

Thus, the Percus-Yevick 3N harmonic phonon system has become a system of 3N anharmonic phonons, but with an anharmonicity not due to temperature. In a liquid metal the 3N liquid phonons have uncoupled equations of motion, while in the liquid alloy the 3N liquid phonons have coupled equations of motion. Modes that, in the monatomic liquid metal were harmonic and undamped, become anharmonic and damped in the binary of ternary liquid alloy. The damping is caused by the new solute-solvent interaction, which is no longer transformed away, as was the solvent-solvent interaction in the monatomic liquid metal when the collective coordinate "liquid phonons" were defined. New modes, presumably exist in the liquid alloy, composed of collective vibrations of solute and solvent particles, "liquid alloy phonons". For example, in the binary alloy, we have number factor $N^{AB}$, where in the pure solvent or pure solute we would have had $N^A$ or $N^B$ only. Similarly, in the ternary liquid alloy, we have number factors $N^{AB}$, $N^{AC}$ and $N^{BC}$, not found in the pure solvent nor solute liquid metals. For a binary alloy $A_xB_{1-x}$ the interaction potential is

$$\begin{aligned}V^{PY}_{A_xB_{1-x}} = (1/2)\sum_{\{\underline{k}\}}[&\nu_{\underline{k}}{}^{x}(q_{\underline{k}}{}^{x}q_{-\underline{k}}{}^{x}-x) + \nu_{\underline{k}}{}^{1-x}(q_{\underline{k}}{}^{1-x}q_{-\underline{k}}{}^{1-x}q-(1-x)) + \\ &+ \nu_{\underline{k}}{}^{x,1-x}\,(q_{\underline{k}}{}^{x}q_{-\underline{k}}{}^{1-x}-x\,(1-x))]\end{aligned} \tag{28}$$

and for a ternary liquid alloy $A_xB_yC_{1-x-y}$,

$$V^{PY}_{A_xB_yC_{1-x-y}} = (1/2) \sum_{\{\underline{k}\}} [\nu_{\underline{k}}{}^{x}(q_{\underline{k}}{}^{x}q_{-\underline{k}}{}^{x}-x) +$$

$$+ \nu_{\underline{k}}{}^{y}(q_{\underline{k}}{}^{y}q_{-\underline{k}}{}^{y}-y) + \nu_{\underline{k}}{}^{1-x-y}(q_{\underline{k}}{}^{1-x-y}\, q_{-\underline{k}}{}^{1-x-y}-(1-x-y)) +$$

$$+ 2\nu_{\underline{k}}{}^{xy}(q_{\underline{k}}{}^{x}q_{-\underline{k}}{}^{y}-xy) + 2\nu_{\underline{k}}{}^{x(1-x-y)}(q_{\underline{k}}{}^{x}q_{-\underline{k}}{}^{1-x-y}-x(1-x-y)) +$$

$$+ 2\nu_{\underline{k}}{}^{y(1-x-y)}\,(q_{\underline{k}}{}^{y}q_{-\underline{k}}{}^{1-x-y}-y(1-x-y))\,] \tag{29}$$

One way out of this anharmonic liquid phonon regime is to transform the collective coordinates so as to decouple the solute-solvent interaction but clearly, since we are going to have coupled solute-solvent phonons as well as pure solute and solvent phonons in the liquid alloy, we should use (28) and (29) as is. Actually, most liquid phonons in the liquid alloy will be composed of both solute and solvent atom vibrations, so the $\nu_k{}^{AB}$ set of coefficients should dominate the $\nu_k{}^{A}$ and $\nu_k{}^{B}$ set in a liquid binary alloy, and the same should hold true in the liquid ternary alloy.

We proceed to follow Omini's analysis, concentrating on an application to liquid alloys. The 3N Percus-Yevick harmonic oscillators have a dispersion relation for a binary liquid alloy of form

$$\omega_{\underline{k}}{}^{PY\ AB} = k\,[\,(k_BT/m_A)\,(1+\nu_{\underline{k}}{}^{A}/k_BT) + (k_BT/m_B)\,(1+\nu_{\underline{k}}{}^{B}/k_BT) + \tag{30}$$

$$+ (k_BT/m_{AB})\,(1+\nu_{\underline{k}}{}^{AB}/k_BT)]^{1/2} \sim k\,[(k_BT/m_{AB})\,(1+\nu_{\underline{k}}{}^{AB}/k_BT)]^{1/2}$$

where $m_{AB}{}^{-1} = m_A{}^{-1} + m_B{}^{-1}$ is the reduced mass of the "binary liquid alloy particle." For the ternary liquid alloy

$$\omega_{\underline{k}}{}^{PY\ ABC} = k\,[\,(k_BT/m_A)\,(1+\nu_{\underline{k}}{}^{A}/k_BT) + (k_BT/m_B)\,(1+\nu_{\underline{k}}{}^{B}/k_BT) +$$

$$+ (k_BT/m_C)\,(1+\nu_{\underline{k}}{}^{C}/k_BT) + (k_BT/m_{AB})\,(1+\nu_k{}^{AB}/k_BT) +$$

$$+ (k_BT/m_{AC})\,(1+\nu_{\underline{k}}{}^{AC}/k_BT) + (k_BT/m_{BC})\,(1+\nu_{\underline{k}}{}^{BC}/k_BT) +$$

$$+ (k_BT/m_{ABC})\,(1+\nu_{\underline{k}}{}^{ABC}/k_BT)\,]^{1/2} \sim (k\,[(k_BT/m_{ABC})\,(1+\nu_{\underline{k}}{}^{ABC}/k_BT)\,]^{1/2} \tag{31}$$

where the "ternary liquid alloy particle" has an effective mass $m_{ABC}{}^{-1} = m_A{}^{-1} + m_B{}^{-1} + m_C{}^{-1}$.

Working through the Ascarelli-Harrison-Paskin relation, relating S(O) to the set $\nu_{\underline{k}}$, and assuming it is at all applicable to a liquid alloy, we write

$$S^A(0) = k_B T/(1 + \nu_{\underline{k}}{}^A/k_B T) \tag{32}$$

$$S^B(0) = k_B T/(1 + \nu_{\underline{k}}{}^A/k_B T) \tag{33}$$

$$S^C(0) = k_B T/(1 + \nu_{\underline{k}}{}^C/k_B T) \tag{34}$$

$$S^{AB}(0) = k_B T/(1 + \nu_{\underline{k}}{}^{AB}/k_B T) \tag{35}$$

$$S^{AC}(0) = k_B T/(1 + \nu_{\underline{k}}{}^{AC}/k_B T) \tag{36}$$

$$S^{BC}(0) = k_B T/(1 + \nu_{\underline{k}}{}^{BC}/k_B T) \tag{37}$$

$$S^{ABC}(0) = k_B T/(1 + \nu_{\underline{k}}{}^{ABC}/k_B T) \tag{38}$$

where we expect $S^{ABC}$ (0) to dominate all other liquid structure factor long wavelength limit in the liquid ternary alloy and $S^{AB}(0)$ to dominate $S^A(0)$ and $S^B(0)$ in the liquid binary alloy. The Percus-Yevick dispersion relation for the liquid binary alloy liquid phonons becomes.

$$\omega_{\underline{k}}{}^{PY\ AB} = k\,[\,(k_B T/m_{AB})\,(1/S^{AB}(0))]^{1/2} \tag{39}$$

and the Percus-Yevick dispersion relation for the liquid ternary alloy liquid phonons becomes

$$\omega_{\underline{k}}{}^{PY\ ABC} = k\,[\,(k_B T/m_{ABC})\,(1/S^{ABC}(0))]^{1/2} \tag{40}$$

where we have utilized effective liquid structure factor long wavelength limits

$$S^{AB}(0)^{-1} = S^A(0)^{-1} + S^B(0)^{-1} \tag{41}$$

in the binary alloy and

$$S^{ABC}(0)^{-1} = S^A(0)^{-1} + S^B(0)^{-1} + S^C(0)^{-1} \tag{42}$$

in the liquid ternary alloy. We can now follow Omini's analysis exactly, bearing in mind that these effective liquid alloy structure factors are approximations invented to allow us to do so, and thus develop a first approximation to the true state of affairs in liquid binary and ternary alloys.

The upper cut-off in the dispersion relation for liquid alloy phonons in a liquid binary alloy becomes

$$Q^{AB} = (18\pi^2 \rho^{AB}/m_{AB})^{1/3} \tag{43}$$

and the upper cut-off in the dispersion relation for liquid alloy phonons in a liquid ternary alloy becomes

$$Q^{ABC} = (18\pi^2 \rho^{ABC}/m_{ABC})^{1/3} \tag{44}$$

where $\rho^{AB}$ and $\rho^{ABC}$ are the binary and ternary liquid alloy densities, respectively. These Q values are derived from

$$(L/2\pi)^3 (4\pi Q^{AB\,3}/3 = 3\,(N^A + N^B) \tag{45}$$

in the binary liquid alloy and

$$(L/2\pi)^3 (4\pi Q^{ABC\,3}/3) = 3\,(N^A + N^B + N^C) \tag{46}$$

by analogy with Omini.

The entropy of the liquid binary alloy at the melting temperature is

$$S^{AB}_{Liq} = \sum_{\{\underline{k}\}} \Big\{ (\hbar\omega_{\underline{k}}{}^{AB}/T_M)\,((1/2) + \\ + (e^{\hbar\omega_{\underline{k}}{}^{AB}/k_B T_m} - 1)^{-1}) - k_B \ln(2 \sin h\, (\hbar\omega_{\underline{k}}{}^{AB}/2k_B T_M))\Big\} \tag{47}$$

and for the liquid ternary alloy

$$S^{ABC}_{Liq} = \sum_{\{\underline{k}\}} \Big\{ (\hbar\omega_{\underline{k}}{}^{ABC}/T_M)\,((1/2) + \\ + (e^{\hbar\omega_{\underline{k}}{}^{ABC}/k_B T_M} - 1)^{-1} - k_B \ln(2 \sin h\, (\hbar\omega_{\underline{k}}{}^{ABC}/2k_B T_M))\Big\} \tag{48}$$

Converting the sums to low k integrals, as Omini did in the liquid metals,

$$S^{AB}_{Liq} = (L/2\pi)^3\, 4\pi \int_0^{Q^{AB}} k^2\, dk\, \Big\{ (\hbar\omega^{AB}(k)/T_M)\,[\,(1/2) + \\ + (e^{\hbar\omega^{AB}(k)/k_B T_M} - 1)^{-1}\,] - k_B \ln(2 \sin h\, (\hbar\omega^{AB}(k)/k_B T_M))\Big\} \tag{49}$$

and

$$S^{ABC}_{Liq} = (L/2\pi)^3\, 4\pi \int_0^{Q^{ABC}} k^2\, dk\, \Big\{ (\hbar\omega^{ABC}(k)/T_M)\,[(1/2) + \\ + (e^{\hbar\omega^{ABC}(k)/k_B T_M} - 1)^{-1}\,] - k_B \ln(2 \sin h\, (\hbar\omega^{ABC}(k)/k_B T_M))\Big\} \tag{50}$$

As before, these can be rewritten as

$$S^{AB}_{Liq} = 9\,N\,k_B\,((I_o^{AB}/2) + I_1^{AB} + I_2^{AB}) \tag{51}$$

and

$$S^{ABC}_{Liq} = 9\,N\,k_B\,((I_o^{ABC}/2) + I_1^{ABC} + I_2^{ABC}) \tag{52}$$

where the integrals are like those in (13)–(15), but with $\omega^{PY\ AB}(y)$ or $\omega^{PY\ ABC}(y)$ replacing $\omega^{PY}(y)$ there. Thus, the entropy change upon melting for binary and ternary alloys is

$$\Delta\,S^{AB}/R = 9\,((I_o^{AB}/2) + I_1^{AB} + I_2^{AB}) - (S^{AB}_{Sol}/R) \tag{53}$$

and

$$\Delta\,S^{ABC}/R = 9\,((I_o^{ABC}/2 + I2^{ABC} + I_2^{ABC}) - (S^{ABC}_{Sol}/R) \tag{54}$$

Our aim, as Omini stresses, should be to utilize the low wave vector (long wavelength) structure of the liquid system; the liquid structure factors, which are easily measurable, to predict the melting entropy. Perhaps in a few isolated cases we can use these liquid structure factors, if known, to predict the melting temperature dependence upon solute concentration, but far more experimentally is known about the dependence of melting temperature on solute concentration than alloy liquid structure factors, so we prefer to work in the former vein and utilize these relations to understand the calculated liquid alloy structure factor long wavelength limit in terms of the physical structure and dynamics of the liquid alloy.

Omini's technique at this point was to utilize the theoretical structure factors of Ashcroft and Lekner.[7] For light metals (Li, Na, K, Rb, Cs, Mg, Al and Zn) a packing fraction of $\eta = 0.45$ sufficed, while for heavy metals (Ga, Sn, Pb and Tl) a packing fraction of 0.45 would have severely overestimated the melting entropy, so one of $\eta \leq 0.15$ is more suitable. For these heavy metals the neutron scattering results of Egelstaff *et al.*[8] yield S(0) curves, shown in Figure 2 of Omini's paper, with $S^{Pb}(0)=0.009$, $S^{Sn}(0)=S^{Tl}(0)=0.008$. In Table I we reproduce Omini's estimated values for the integrals $I_0$, $I_1$ and $I_2$ in the pure liquid metals from the Percus-Yevick liquid phonon dispersion relations. We note that, for all metals treated except Li, $I_2 > I_1 > I_0$.

When it comes to the evaluation of the melting entropy of liquid alloys, we should use the definitions for these integrals, as in (13)–(15) but with $\omega^{AB}(y)$ replacing $\omega^{PY}(y)$ and with $T_M{}^{AB}$ replacing $T_M$ in the liquid binary alloys and similar replacements in the liquid ternary alloys. The depression of

TABLE I

Omini's compilation of relevant integrals, melting entropies and cut-off wavevectors for the solute and solvent metals in these binary liquid alloys

| Metal | Q | $\theta_D$(°K) | $T_M$ (°K) | $\sigma$ (A°) | $I_0$ | $I_1$ | $I_2$ | $S_{sol}/R$ ($k_B$ units) |
|---|---|---|---|---|---|---|---|---|
| Li | 1.975 | 430. | 452. | 2.70 | 0.175 | 0.254 | 0.218 | 4.20 |
| Na | 1.625 | 160. | 371. | 3.28 | 0.090 | 0.294 | 0.454 | 6.52 |
| K | 1.307 | 100. | 337. | 4.07 | 0.058 | 0.308 | 0.599 | 7.62 |
| Rb | 1.223 | 59. | 312. | 4.30 | 0.039 | 0.317 | 0.728 | 8.95 |
| Cs | 1.138 | 43. | 301. | 4.73 | 0.029 | 0.322 | 0.840 | 9.86 |
| Mg | 1.901 | 342. | 924. | 2.80 | 0.066 | 0.306 | 0.560 | 6.99 |
| Al | 2.108 | 390. | 933. | 2.53 | 0.066 | 0.303 | 0.550 | 6.61 |
| Zn | 2.240 | 235. | 693. | 2.38 | 0.052 | 0.308 | 0.620 | 7.26 |
| Ga | 2.102 | 240. | 303. | 2.54 | 0.071 | 0.297 | 0.509 | 4.75 |
| Pb | 1.754 | 88. | 600. | – | 0.023 | 0.319 | 0.886 | 9.82 |
| Tl | 1.805 | 100. | 576. | – | 0.033 | 0.318 | 0.790 | 9.30 |
| Sn | 1.843 | 180. | 505. | – | 0.049 | 0.309 | 0.655 | 7.11 |

the melting temperature by solute addition in liquid binary alloys is shown, after Hansen[9], in Table II.

For binary liquid alloys, our aim here is not to calculate the melting entropy, as Omini did for pure metals, but to utilize concentration weighed interpolations of $I_0$, $I_1$ and $I_2$, the known solute, solvent and binary alloy melting temperatures and the known solute and solvent Percus-Yevick liquid phonon dispersion relations to predict the unkown liquid alloy phonon dispersion relations, $\omega^{PY\ AB}(y)$. In the binary liquid alloy we assume

$$x\, I_0{}^A + (1-x)\, I_0{}^B = I_0{}^{AB} \tag{55}$$

$$x\, I_1{}^A + (1-x)\, I_1{}^B = I_1{}^{AB}$$

$$x\, I_2{}^A + (1-x)\, I_2{}^B = I_2{}^{AB}$$

and in liquid ternary alloys

$$x\, I_0{}^A + y\, I_0{}^B + (1-x-y)\, I_0{}^C = I_0{}^{ABC} \tag{56}$$

$$x\, I_1{}^A + y\, I_1{}^B + (1-x-y)\, I_1{}^C = I_1{}^{ABC}$$

$$x\, I_2{}^A + y\, I_2{}^B + (1-x-y)\, I_2{}^C = I_2{}^{ABC}$$

Then, we utilize (7) to relate $\omega^{AB}(y)$ to the long wavelength limit of the liquid binary alloy structure factor, $S^{AB}(0)$. For ternary liquid alloys,

TABLE II

Long wavelength limit liquid structure factors at the melting temperatures for the equi-valent, equi-volume liquid binary alloys treated here

| Liquid alloy system | Liquid binary alloy | $I_0^{AB}$ | $I_1^{AB}$ | $I_2^{AB}$ | $T_M^{AB}$(°K.) | $\tilde{m}_{AB}^{-1} \times 10^{23}$ (gm$^{-1}$) | $S_{T_M}^{AB}(0)$ |
|---|---|---|---|---|---|---|---|
| Li-Na | $Li_{100}$ | 0.175 | 0.254 | 0.218 | 479.4 | 0.05424 | 0.043 |
| | $Li_{75}Na_{25}$ | 0.046 | 0.265 | 0.278 | 670. | 0.07061 | 0.014 |
| | $Li_{50}Na_{50}$ | 0.132 | 0.274 | 0.336 | 660. | 0.07061 | 0.022 |
| | $Li_{25}Na_{75}$ | 0.112 | 0.285 | 0.396 | 540. | 0.07061 | 0.040 |
| | $Na_{100}$ | 0.090 | 0.294 | 0.454 | 397.8 | 0.01637 | 0.006 |
| K-Rb | $K_{100}$ | 0.058 | 0.308 | 0.599 | 363. | 0.00963 | 0.010 |
| | $K_{75}Rb_{25}$ | 0.054 | 0.310 | 0.631 | 345. | 0.01403 | 0.017 |
| | $K_{50}Rb_{50}$ | 0.049 | 0.313 | 0.664 | 338. | 0.01403 | 0.021 |
| | $K_{25}Rb_{75}$ | 0.044 | 0.355 | 0.696 | 335. | 0.01403 | 0.027 |
| | $Rb_{100}$ | 0.039 | 0.317 | 0.728 | 338.9 | 0.00440 | 0.015 |
| Rb-Cs | $Rb_{100}$ | 0.039 | 0.317 | 0.728 | 338.9 | 0.00440 | 0.011 |
| | $Rb_{75}Cs_{25}$ | 0.036 | 0.319 | 0.756 | 314. | 0.00723 | 0.543 |
| | $Rb_{50}Cs_{50}$ | 0.035 | 0.320 | 0.784 | 309. | 0.00723 | 0.195 |
| | $Rb_{25}Cs_{75}$ | 0.032 | 0.321 | 0.812 | 318.5 | 0.00723 | 0.341 |
| | $Cs_{100}$ | 0.029 | 0.322 | 0.840 | 328.4 | 0.00283 | 0.013 |
| Al-Zn | $Al_{100}$ | 0.066 | 0.303 | 0.550 | 960. | 0.01395 | 0.004 |
| | $Al_{75}Zn_{25}$ | 0.063 | 0.304 | 0.668 | 880. | 0.01971 | 0.006 |
| | $Al_{50}Zn_{50}$ | 0.059 | 0.306 | 0.585 | 820. | 0.01971 | 0.007 |
| | $Al_{25}Zn_{75}$ | 0.017 | 0.307 | 0.603 | 750. | 0.01971 | 0.008 |
| | $Zn_{100}$ | 0.052 | 0.308 | 0.620 | 719.5 | 0.00576 | 0.003 |
| Zn-Ga | $Zn_{100}$ | 0.052 | 0.308 | 0.620 | 719.5 | 0.00576 | 0.003 |
| | $Zn_{75}Ga_{25}$ | 0.057 | 0.305 | 0.592 | 615. | 0.03433 | 0.020 |
| | $Zn_{50}Ga_{50}$ | 0.062 | 0.303 | 0.765 | 550. | 0.03433 | 0.023 |
| | $Zn_{25}Ga_{75}$ | 0.056 | 0.300 | 0.537 | 450. | 0.03433 | 0.025 |
| | $Ga_{100}$ | 0.071 | 0.297 | 0.509 | 329.8 | 0.00540 | 0.020 |

which we do not treat, we would follow the same program, but with $\omega^{AB}(y)$, $\omega^{AC}(y)$ and $\omega^{BC}(y)$ from the binary liquid alloy problem to determine the unknown ternary liquid alloy Percus-Yevick dispersion relation $\omega^{ABC}(y)$. Then, we would utilize (7) to relate $\omega^{ABC}(y)$ to the long wavelength limit of the ternary liquid alloy structure factor, $S^{ABC}(0)$. The versions of (7) we would use are respectively, for the binary and ternary liquid alloy

$$\omega^{AB}(y)^2 = y^2 \; k_BT/m_{AB} \; S^{AB}(0) \tag{57}$$

$$\omega^{ABC}(y)^2 = y^2 \; k_BT/m_{ABC} \; S^{ABC}(0) \tag{58}$$

Our simplified treatment of binary and ternary liquid alloys suffers from one flaw. Following March[10] we note that to completely determine a binary alloy, we need the three liquid structure factors, $S^A(0)$, $S^B(0)$, and $S^{AB}(0)$, and to completely determine the ternary alloy, we need the liquid structure factors: $S^A(0)$, $S^B(0)$, $S^C(0)$, $S^{AB}(0)$, $S^{AC}(0)$, $S^{BC}(0)$ and $S^{ABC}(0)$. We shall follow March's (page 77) artifice of considering only binary alloys and ternary alloys whose solute and solvent atoms have similar atomic volume and atomic valency. Then, for binary alloys

$$S^A(0) = S^B(0) = S^{AB}(0) \tag{59}$$

and for ternary liquid alloys

$$S^A(0) = S^B(0) = S^C(0) = S^{AB}(0) = S^{AC}(0) = S^{BC}(0) = S^{ABC}(0) \tag{60}$$

Out of Omini's table of calculated $I_0$, $I_1$ and $I_2$ integrals, the only equi-volume, equi-valent combinations whose binary liquid alloys we consider are Li-Na, Na-K, K-Rb, Rb-Cs, Al-Zn, Zn-Ga and Al-Ga. Were we considering ternary alloys here explicitly, the most nearly equi-volume, equi-valent ternary alloys are: Li-Na-K, Na-K-Rb, K-Rb-Cs. Less equi-volume, equi-valent binary alloys are: Pb-Sn, Mg-Al, Mg-Zn, Mg-Ga, Pb-Mg, and Mg-Sn, but we are not justified in making the March approximation about the equality of the solute, solvent and alloy liquid structure factors, and so we do not treat this latter group either.

## 3. CALCULATION OF BINARY LIQUID ALLOY STRUCTURE FACTORS AT LONG WAVELENGTHS

The binary combinations of Omini's pure metals we treat are nearly equi-volume and equi-valent. The results are shown in Table II, where we use the virtual crystal approximation (41) to define the binary liquid alloy integral, $I_0{}^{AB}$, $I_1{}^{AB}$ and $I_2{}^{AB}$ as concentration weighed averages of $I_0{}^{A}$ and $I_0{}^{B}$ for the pure solute and solvent, and similarly for $I_1{}^{A}$, $I_1{}^{B}$, $I_2{}^{A}$ and $I_2{}^{B}$. Also listed are $T_M{}^{AB}$ values for the actual binary liquid alloy systems, as taken from Hansen.[9] We utilize $I_0{}^{AB}$ and convert the integral to a finite sum over the eight points given for the pure solvent dispersion relations. The relation we use is reexpressed in terms of the Ascarelli-Harrison-Paskin relation between $\omega^{PY\,2}$ and S(0) for the alloy as

$$I_0{}^{ABx}(x) = (h/k_B 1/2) \sum_{y_i}^{Q} y_i{}^3 \, (m_{AB}\, S^{AB}(0)/T^{AB}{}_M)^{-1/2} \qquad (61)$$

Instead of proceeding this way, we can directly utilize the virtual crystal-like dispersion relations of the liquid alloy as

$$\omega_{k\,VC}^{PY} = x\,\omega_k{}^{PY\,A} + (1-x)\,\omega_k^{PY\,B} = k\,(k_B\; T_M^{AB}/\,m_{AB}\, S^{AB}(0))^{1/2} \qquad (62)$$

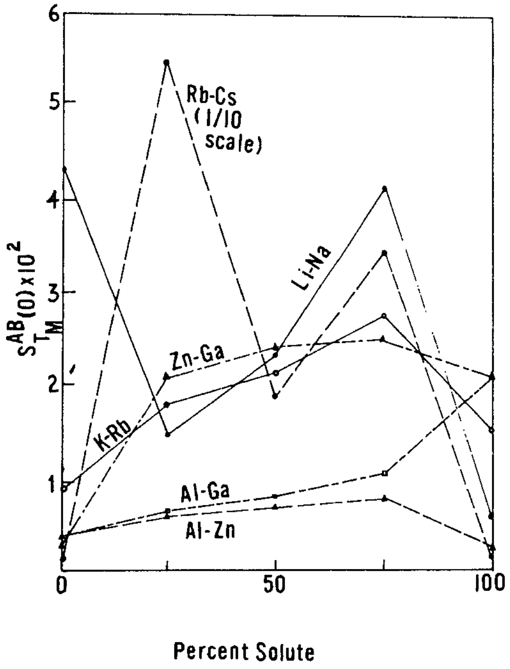

FIGURE 1 Long wavelength limits of the alloy liquid structure factors at their melting temperatures as a function of solute concentration.

so that

$$S^{AB}_{T_M}(0) = (\omega_k{}^{PY}{}_{VC}{}^{2}/k^2)(k_B T^{AB}_M/m_{AB}) =$$

$$= (x\,\omega_k{}^{PY\,A} + (1-x)\,\omega_k{}^{PY\,B})^2/k^2\,(k_B T^{AB}_M/m_{AB}) \qquad (63)$$

taking the lowest ω and y values from Omini's Table I.

The results for $S^{AB}_{T_M}(0)$ are shown in Table II, and plotted in Figure 1 as a function of alloy solute concentration, x. We see that for the most nearly equi-valent and equi-volume binary solute-solvent pairs chosen from those considered by Omini, the long wavelength limit of the liquid structure factor at the melting temperature has no common form as a function of solute concentration in the virtual crystal approximation. For Rb-Cs it exhibits two steep maxima (at $Rb_{75}Cs_{25}$ and $Rb_{25}Cs_{75}$) and a steep minimum (at $Rb_{50}Cs_{50}$). For Li-Na, S(0) exhibits a minimum (at $Li_{75}Na_{25}$), then a maximum (at $Li_{75}Na_{25}$), then drops to the value for pure Rb. For Zn-Ga, S(0) rises monatonically to a maximum (at $Zn_{25}Ga_{75}$), then drops off to the pure Ga value. For K-Rb S(0) is also monatonic to a maximum (at $K_{25}Rb_{75}$) then it falls to the value for pure Rb. For Al-Ga, S(0) rises again monatonically, but very slowly, and then more steeply to a maximum (at pure Ga). For Al-Zn, S(0) rises monatonically very slowly (like Al-Ga) to a maximum (at $Al_{25}Zn_{75}$), then it falls off to a low value (at pure Zn). No two of these trends on binary liquid alloy structure factors as a function of solute concentration are alike in detail, though K-Rb and Zn-Ga are similar, and Al-Ga and Al-Zn are similar out to 75% solute. As mentioned before, we did not attempt to reproduce the above results in ternary alloys for two reasons. Firstly, the use of the virtual crystal concept for a liquid binary alloy itself is not well founded, so that we feel that the errors incurred would be magnified if it were applied to a ternary liquid alloy. Secondly, there is a lack of empirical ternary alloy melting temperatures for equi-volume, equi-valent constituents.

## 4. CONCLUSIONS

We have shown how to describe the long wavelength limit of the liquid structure factor for a group of equi-valent, equi-volume binary liquid alloys, in analogy with the virtual crystal approximation as used in binary solid alloys. We have utilized the integrals of Omini to accomplish this, and have weighed them by the relative solute and solvent concentrations in the spirit of the virtual crystal approximation. The virtual crystal approximation in solid alloys is questionable at high solute concentrations, we so might still more severely question its use in a concentrated liquid alloy, in addition to which the question of whether it can be applied to a liquid alloy of any concentration might invalidate its use immediately. With these cautions, we have still proceeded to calculate $S^{AB}_{T_M}(0)$ at the alloy melting temperature for equi-valent, equi-volume pairs of solutes and solvents. The simplifying equality of alloy liquid structure factor to the solute and solvent pure liquid metal structure factor will not hold for non-equi-valent, non-equi-volume solute-solvent pair alloys, and this calculation then cannot be done so simply. In this case, we would somehow have to calculate $S^{A}_{T_M}(0)$, $S^{B}_{T_M}(0)$ and $S^{AB}_{T_M}(0)$ separately, and it is not clear which $T_M$, m or $\omega_k^{PY}$ values to use to calculate these.

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