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SINGLE-PARTICLE AND COLLECTIVE EFFECTS IN LIQUID METALS NEAR FREEZING AND IN THEIR HOT SOLIDS

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A 'jump' model of single-particle motion in a liquid is first used to calculate the frequency spectrum $g(\omega)$ of a liquid metal near freezing. In this treatment $g(\omega)$ is characterized by shear (η) and bulk viscosities, plus a time τ breaking the coherence of normal mode oscillations within a 'cell' or subvolume. The connection with earlier treatments of the relation between self-diffusion coefficient D and η at the melting temperature T_m of liquid metals is pointed out.

The self motion, characterized by $g(\omega)$, is considered then in relation to the dynamical structure factor $S(q, \omega)$ of a liquid metal such as Rb. In particular, theories of the dispersion relation ω_q of the collective mode in liquid alkali metals and in their hot solids are re-examined, with $-k_B T c(q)$ used as an effective q space form of a pseudo-pair potential, c being the direct correlation function. This leads to a new proposal for the dispersion relation ω_q , which in turn is related to the static structure factor $S(q)$. The close relation of the hot-solid results to the density functional treatment of phonons in K by Ferconi and Tosi is established.

KEY WORDS: Jump model, frequency spectrum, direct correlation function.

1 INTRODUCTION

Earlier work of Brown and March¹ used the so-called Green–Kubo relations (see Eq. (1.4) below) to treat the self-diffusion coefficient D , and the viscosities, at the melting temperature T_m of liquid metals. In this work, sum rules on the self function $S_s(q, \omega)$ and the van Hove dynamical structure factor $S(q, \omega)$ were employed, together with general arguments on the frequency range of S_s and S and on the relation between them via the static structure factor $S(q)$.

The present work is in the same general area, but it takes account of progress in the theory of transport coefficients by Zwanzig², the relation of whose work to the treatment of Ref. 1 was established by one of us (N.H.M.)³. Zwanzig's approach to obtain the self-diffusion constant D is here generalized to obtain the frequency spectrum $g(\omega)$, which is the Fourier transform of the velocity auto-correlation function $\langle v(0) \cdot v(t) \rangle$:

$$g(\omega) = \frac{k_B T}{m\pi} \int_0^\infty \frac{\langle v(0) \cdot v(t) \rangle}{\{v(0)\}^2} \cos \omega t \, dt. \quad (1.1)$$

Alternatively, $g(\omega)$ is related to the self function S_s referred to above by

$$g(\omega) = \omega^2 \lim_{k \rightarrow 0} \frac{S_s(k, \omega)}{k^2}. \quad (1.2)$$

The sum rule on $S_s(k, \omega)$ for classical liquids yields for the ‘normalization’ of the frequency spectrum $g(\omega)$:

$$\int_{-\infty}^{\infty} g(\omega) d\omega = \frac{k_B T}{m} \quad (1.3)$$

where m is the ionic mass, while D is given by

$$\frac{D}{\pi} = \lim_{\omega \rightarrow 0} \omega^2 \lim_{k \rightarrow 0} \frac{S_s(k, \omega)}{k^2} = g(\omega = 0), \quad (1.4)$$

the second step in Eq. (1.4) following immediately from Eq. (1.2).

One other piece of information on $g(\omega)$ follows from hydrodynamics and in particular from the long-time tail of the velocity auto-correlation function, namely a term of the form $t^{-3/2}$ at long time. This in turn yields for $g(\omega)$ at small ω the expansion

$$g(\omega) = \frac{D}{\pi} - A\omega^{1/2} + \dots \quad (1.5)$$

where A is given by⁴

$$A = (2\pi)^{1/2} \frac{2}{3\rho} \left[4\pi \left(D + \frac{\eta}{\rho m} \right) \right]^{-3/2} \frac{k_B T}{m\pi}. \quad (1.6)$$

This shows that both D and the shear viscosity η enter the form of $g(\omega)$ at small ω . Immediately below, in Section 2, we generalize Zwanzig’s work² to obtain $g(\omega)$. Though, as anticipated above, D and η enter in a basic way, the model used is not capable of yielding the long-time tail in $\langle v(0) \cdot v(t) \rangle$, and hence the cusp at $\omega = 0$ revealed in Eq. (1.5) is absent from our model result for $g(\omega)$.

2 MODEL OF FREQUENCY SPECTRUM $g(\omega)$

Zwanzig² sets out four assumptions that define his picture of a liquid-state dynamical model. Following Stillinger and Weber⁵, the configuration space of the many-particle assembly is viewed as divided into cells, each one of which is associated with a local minimum on the potential energy surface of the assembly. The picture is then that the configuration of the liquid remains in one of these cells for some time, performing approximately harmonic oscillations about the local minimum, until suddenly a

saddlepoint or bottleneck on the potential surface is located, and a 'jump' occurs to another cell.

Using this same picture, we now calculate $g(\omega)$ from Eq. (1.1) in terms of the collective normal modes with dispersion relation ω_q . Zwanzig's result for D then generalizes to read:

$$g(\omega) \propto \int_0^\infty dt [\cos(\omega + \omega_q)t + \cos(\omega - \omega_q)t] \exp\left(-\frac{t}{\tau}\right) \quad (2.1)$$

where $\exp(-t/\tau)$ represents the waiting time distribution for cell jumps, with τ being evidently a lifetime. Evaluating the time-integral in Eq. (2.1) and utilizing Zwanzig's result for D : namely

$$D = (k_B T/3mN) \sum_{\omega_q} \tau/(1 + \omega_q^2 \tau^2), \quad (2.2)$$

where there are a total of $3N$ normal mode frequencies, one obtains

$$g(\omega) = \frac{k_B T}{2\pi(3mN)} \sum_{\omega_q} \left[\frac{\tau}{1 + (\omega + \omega_q)^2 \tau^2} + \frac{\tau}{1 + (\omega - \omega_q)^2 \tau^2} \right] \quad (2.3)$$

which evidently reduces to D/π with D as in Eq. (2.2), in the limit $\omega \rightarrow 0$. Replacing the sum over frequencies by an integral over \mathbf{q} , with the usual density of states factor, and defining a Debye cut-off q_0 in the usual way by

$$(4\pi/3)(q_0/2\pi)^3 = N/V \quad (2.4)$$

where N/V is the number density of the liquid, the \mathbf{q} integration can be completed with the assumption of a Debye spectrum, following Zwanzig's evaluation of the limit $\omega \rightarrow 0$. Using the abbreviations

$$a = c^2 q_0^2 \tau^2, \quad b = \omega c q_0 \tau^2, \quad C = 1 + \omega^2 \tau^2, \quad (2.5)$$

one readily obtains, with $Q = q/q_0$:

$$g(\omega) = \text{constant} \left[\frac{Q}{a} - \frac{b}{2a^2} \ln|X| + \frac{b^2 - 2aC}{2a^2} \frac{2}{(4aC - b^2)^{1/2}} \tan^{-1} \frac{2aQ + b}{(4aC - b^2)^{1/2}} \right]_0^1 \quad (2.6)$$

when $4aC > b^2$. Here X has been written for $aQ^2 + bQ + C$. Zwanzig neglects the \tan^{-1} term, and reaches then, taking both longitudinal and transverse frequencies, the result

$$g(0) = \frac{D}{\pi} = (k_B T/3\pi^2)(3N/4\pi V)^{1/3}(1/\rho c_l^2 \tau + 2/\rho c_t^2 \tau) \quad (2.7)$$

where c_l and c_t represent longitudinal and transverse sound velocities. Then $\rho c_l^2 \tau$ and $\rho c_t^2 \tau$ are interpreted simply as longitudinal and shear viscosities η_l and η respectively.

One has presumably not automatically satisfied the sum rule (1.3); this could then be used to relate the lifetime τ to other properties of the liquid, though admittedly by a complicated implicit equation. While Eq. (2.6) represents the generalization we were seeking of the Zwanzig result (2.7), we note next that as ω becomes sufficiently large, Eq. (2.3) yields a slow decay of $g(\omega)\alpha\omega^{-2}$. This slow rate of decay seems to be a limitation inherent in this model, and may well need to be removed by multiplication by either as factor such as $\exp(-\alpha\omega)$ or $\exp(-\beta\omega^2)$: with again a relation between τ and exponent α or β following from the sum rule (1.3). As noted in Ref. 3, the Zwanzig formula (2.7) reduces, as a special case, to the relation between D and η given by Brown and March at the melting temperature of liquid metals.

Having discussed the frequency spectrum $g(\omega)$ associated with the self-function $S_s(q, \omega)$ in the jump model summarized above, we turn next to a more detailed study of the dispersion relation ω_q for collective modes in liquid metals near the melting point and in the corresponding hot solids. Then we shall consider the relation of $S_s(q, \omega)$, $S(q, \omega)$ and ω_q to the static structure $S(q)$.

3 DISPERSION RELATION ω_q FOR LIQUID METALS AT T_m AND IN HOT SOLID METALS

Let us start from the apparently drastic assumption that the dynamics of liquid metals at T_m , and the corresponding hot solid metals near freezing, are governed by an effective pair interaction, which has a Fourier transform, say $\tilde{\phi}(q)$. We will refer briefly below to the relation of $\tilde{\phi}(q)$ to the true pair potential in a liquid metal like Na.

Bardasis, Falk and Simkin⁶ have then discussed the collective modes of both crystals and fluids in terms of $\tilde{\phi}(q)$ introduced above. As the simplest example, the dilute fluid case then corresponds to a dispersion relation

$$\omega_q^2 = \left(\frac{\hbar q^2}{2m}\right)^2 + \frac{q^2 \rho}{m} \tilde{\phi}(q). \quad (3.1)$$

Setting $\tilde{\phi}(q) = 0$ will, of course, yield the usual free-particle dispersion relation. The same type of argument can be applied to liquids by the methods of Feynman and Cohen⁷. This leads naturally then to the question of how $\tilde{\phi}(q)$ is to be chosen in a dense liquid. Various workers⁸⁻¹⁰ have stressed in liquid-state theory the intimate connection between the direct correlation function $c(r)$ and the pair potential in units of $k_B T$. While pair potentials in dense liquids have relatively hard cores, $-k_B T c(r)$ has Fourier transform $-k_B T c(q)$ which exists for all q , since

$$c(q) = \frac{S(q) - 1}{S(q)}. \quad (3.2)$$

Since, at small q , in metals like Na and K, $S(q) \sim 0.02$, $c(q) \sim -1/S(q)$. Then, neglecting the free-particle term in Eq. (3.1), and making the identification, at melting temperature T_m to be definite:

$$-\tilde{\phi}(q) \rightarrow (k_B T c(q))_{T_m}, \quad (3.3)$$

one regains the Feynman-like result

$$\omega_q^2 \sim \left. \frac{k_B T q^2}{m S(q)} \right|_{T_m} \quad (3.4)$$

or the dispersion relation in the liquid metal in terms of the static structure factor. Eq. (3.4) has, in fact, been brought into direct contact with the measured dispersion relation ω_q for liquid Rb at T_m using the neutron studies of Copley and Rowe¹¹, by Matthai and March¹². The main features of the experiments are faithfully reflected by Eq. (3.4). However, it is not fully quantitative, and we shall return to this point below.

3.1 Longitudinal phonon dispersion relations in crystals

Having given evidence in favour of the choice of $\tilde{\phi}(q)$ in Eq. (3.3) in simple liquid metals at the melting temperature T_m , let us turn briefly to consider the dispersion of longitudinal phonons in simple s-p metals, like the alkalis Na, K and Rb, within the same theoretical framework. The result corresponding to Eq. (3.1) is then readily derived as^{6,13}:

$$\omega_q^2 = \frac{\rho}{m} \sum_{\mathbf{K}} \left[\left\{ \left[\frac{\mathbf{q}}{q} \cdot \mathbf{q} + \mathbf{K} \right]^2 \right\} \tilde{\phi}(\mathbf{q} + \mathbf{K}) - \left(\frac{\mathbf{q} \cdot \mathbf{K}}{q} \right)^2 \tilde{\phi}(\mathbf{K}) \right] \quad (3.5)$$

where the \mathbf{K} 's denote reciprocal lattice vectors.

While Eq. (3.5) is strictly a low temperature result, and the correspondence (3.3) is not therefore immediately appropriate, the recent work of Ferconi and Tosi¹⁴, by a substantially different route, using the free energy difference between a perfect crystal and a deformed crystal containing a 'phonon', is highly relevant here. Their result is equivalent to Eq. (3.5) when (i) a Debye-Waller factor is incorporated and (ii) $\tilde{\phi}(q)$ is replaced as in Eq. (3.3). Support for both (i) and (ii) is afforded by the good agreement they then obtain with the measured dispersion relations for hot solid K.

3.2 Dispersion relation for liquid metals at T_m based on fourth moment of $S(q, \omega)$

Having established the usefulness of the transformation (3.3) in liquid metals and in hot solids near the melting temperature T_m , we return to the discussion of Eq. (3.4) in relation to experiments in the liquid alkali metal Rb at T_m . As mentioned above, Eq. (3.4) is not fully quantitative. Since it rests on the assumption that the collective mode ω_q exhausts the second moment of $S(q, \omega)$, it is tempting to suppose that ω_q

based on satisfying the fourth moment theorem would be more quantitative. Such a theory of ω_q is afforded by the work of Hubbard and Beeby¹⁵. Their result, again based on the assumption of pair potential $\phi(r)$, is given by

$$\omega_q^2 = \frac{\rho}{m} \int \frac{\partial^2 \phi(r)}{\partial z^2} g(r) [1 - \cos qz] dr. \quad (3.6)$$

In earlier work, we evaluated Eq. (3.6) for model results for $g(r)$ and $\phi(r)$ for dense liquid Ar and for liquid Na near T_m . We noted there¹⁶ that one of the major problems of such a procedure resided in the poor velocity of sound predicted by such an approach for dense liquids. Our proposal here is to utilize Eq. (3.6) for liquid Na and K near T_m using the experimental structure factor S_q as measured by Greenfield, Wellendorf and Wiser¹⁷, but with ϕ replaced according to Eq. (3.3).

4 $S(q, \omega)$ AND STATIC STRUCTURE $S(q)$ RELATED TO ω_q AND SELF MOTION

We consider here two aspects of the dynamical structure factor. First, in the light of the discussion of the Hubbard–Beeby form of ω_q , let us define in an analogous manner to Eq. (1.2) the frequency spectrum associated with $S(q, \omega)$ as

$$s(\omega) = \omega^4 \lim_{q \rightarrow 0} \frac{S(q, \omega)}{q^4} \quad (4.1)$$

Then, as noted by Gyorffy and March¹⁸, a modification of the Hubbard–Beeby theory yields a relation between $s(\omega)$ and $g(\omega)$ given by

$$s(\omega) = \frac{k_B T}{mS(0)} \left[g(\omega) - \frac{1}{2} \omega \frac{\partial g(\omega)}{\partial \omega} \right], \quad (4.2)$$

the original Hubbard–Beeby theory omitting the (large) factor $1/S(0)$ in a dense liquid metal. Using the jump model of $g(\omega)$ in Section 2, the form of $s(\omega)$ according to Eq. (4.2) is then determined.

4.1 *Static structure factor $S(q)$ related to ω_q*

The second aspect of the dynamical structure factor $S(q, \omega)$ to be considered is its zeroth moment, which is simply the static structure factor $S(q)$. Specifically, we examine the way one can use the structure of Eq. (3.6) to refine the approximations of Hubbard and Beeby in relation to static structure. As emphasized by March, Pathak and Ascough¹⁹, the shape of that theory is represented by

$$S(q) = \frac{k_B T}{m} q^2 \frac{Q(q, 0)}{(1 + \omega_q^2 Q(q, 0))}. \quad (4.3)$$

The result (3.4) is recovered by taking the limit $Q \rightarrow \infty$. In the Hubbard–Beeby theory, $Q(q, 0)$ is related to self-motion, but their approach, as they emphasized in the original paper, is poor for static structure, having been specifically designed to reproduce the second and fourth moments of $S(q, \omega)$.

In Ref. 19, using experimental values for $S(q)$ and ω_q^2 for liquid Rb at T_m , $[q^2 Q(q, 0)]^{-1}$ was extracted. It was found to rise from a finite long-wavelength limit to a maximum and subsequently to decrease monotonically. We merely note here that a model for the shape of $Q(q, 0)$ is given by Eq. (4.3), taking S_q from experiment for liquid Na and liquid K and using ω_q as in Eq. (3.6).

5 DISCUSSION AND SUMMARY

Evidence has been presented that simple theories of collective modes in liquid metals at the melting temperature T_m , based on the assumption of a pair potential with a Fourier transform $\phi(q)$, are very useful to gain physical insight provided that $\phi(q)$ is identified with $-(k_B T c(q))_{T_m}$ as in Eq. (3.3). The same conclusion is shown to follow from the recent work of Ferconi and Tosi¹⁴ on hot solid K near T_m , provided the Debye–Waller factor is correctly incorporated into Eq. (3.5).

Additional points investigated concern a model of the frequency spectrum $g(\omega)$ which correctly embodies the relation between self-diffusion coefficient D and shear viscosity η given by the work of Brown and March¹ and a treatment of static structure having the shape of Eq. (4.3). However, a quantitative theory relating the function $Q(q, 0)$ to the self motion remains a problem for further work.

A final point to be made concerns the relation of the work to the ‘real’ pair potential $\phi(r)$ extracted from the measured structure factor $S(k)$ —the so-called ‘inverse problem’—as posed originally by Johnson and March²⁰. The procedure has recently been brought to full fruition by the studies of Reatto and co-workers²¹ on liquid Na at T_m using the measured $S(q)$ from Ref. 17. We expect that if this potential is used in Newton’s equations in a full molecular dynamics study, the correct collective mode dispersion relation will be faithfully reproduced. However, the message of the present work is that simpler theories are also useful at T_m for liquid metals and their corresponding hot solids, provided the ‘pseudo pair potential’, $-(k_B T c(q))_{T_m}$ in Fourier transform is employed rather than $\phi(r)$. It is to be hoped in the future, that such simplifications will result in a fully quantitative, and largely analytical theory of $S(q, \omega)$, and in particular its relation to the self function $S_s(q, \omega)$ and the static structure $S(q)$. As to a theory of $S(q, \omega)$ in a crystal, it can be constructed from knowledge of the ω_q ’s as in Eq. (3.5), plus the polarization vectors²².

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