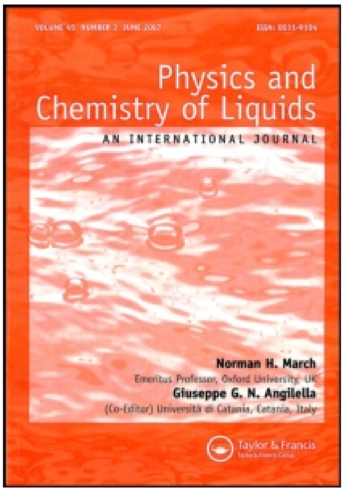

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Letter

Relation Between Spectral Functions for Diffusion and Sound-wave Attenuation in Both Liquid Metals and Charged Colloidal Liquids Near Freezing

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Spectral functions for diffusion and sound-wave attenuation, related to self and van Hove dynamical structure factors in the long wavelength limit, can be related directly by approximate classical theories of liquids. The interest in testing such a relationship experimentally, both in liquid metals and in charged colloidal liquids near freezing, is stressed.

Key Words: Spectral functions, diffusion, sound-wave attenuation.

In this work, the question is addressed as to whether there is an intimate relationship in dense liquid metals and in charged colloidal liquids, near their respective freezing points, between the spectral functions $z(\omega)$ and $s(\omega)$ for diffusion and for sound wave attenuation respectively. These functions are defined in terms of the self correlation function $S_s(k, \omega)$ and the van Hove dynamical structure factor $S(k, \omega)$ by

$$z(\omega) = \lim_{k \to 0} \frac{\omega^2}{k^2} S_s(k, \omega) \tag{1}$$

and

$$s(\omega) = \lim_{k \to 0} \frac{\omega^4}{k^4} S(k, \omega). \tag{2}$$

In the low frequency limit $\omega \to 0$, transport coefficients can be extracted from these spectral functions according to the Kubo–Green formulae[1]

$$z(0) = D/\pi \tag{3}$$

and

$$s(0) = \frac{\Gamma k_B T}{\pi M^2 \rho} \tag{4}$$

where D is the self-diffusion coefficient, $\Gamma = \frac{4}{3}\eta + \zeta$ the sound wave attenuation coefficient, η and ζ being the shear and bulk viscosities respectively.

Starting with the pioneering work of Vineyard[2], there have been a number of theories of increasing degrees of sophistication which attempt to construct $S(k, \omega)$ from the, assumed given, self function $S_s(k, \omega)$ and the static structure factor $S(k)$. Thus the collective mode theory due to Hubbard and Beeby[3] has been subsequently modified by Gyorffy and March and shown by them[4] to then yield

$$s(\omega) = \frac{k_B T}{MS(k=0)}\left[z(\omega) - \frac{1}{2}\omega\frac{\mathrm{d}z(\omega)}{\mathrm{d}\omega}\right] \tag{5}$$

To reveal somewhat more clearly the analytic structure of this approximate theory, one can integrate Eq. (5) to obtain the result, after insertion of the appropriate physical boundary condition:

$$z(\omega) = \frac{2MS(0)}{k_B T}\,\omega^2\left[\int_\omega^\infty \frac{s(\omega)}{\omega^3}\,\mathrm{d}\omega\right] \tag{6}$$

Though the philosophy in Refs 3 and 4 was to construct $S(k, \omega)$ from $S_s(k, \omega)$ and the static structure factor $S(k)$, the somewhat surprising form (6) means that one could input $s(\omega)$, if it could be obtained by suitable extrapolation from neutron plus light scattering measurements of $S(k, \omega)$, and hence generate from Eq. (6) an approximate spectral function $z(\omega)$. This is essentially the Fourier transform of the velocity correlation function, namely

$$z(\omega) = \frac{k_B T}{M\pi}\int_0^\infty \frac{\langle v(0)\cdot v(t)\rangle}{\langle v(0)^2\rangle}\cos\omega t\,\mathrm{d}t. \tag{7}$$

One feature of $z(\omega)$ which is known exactly is its small ω expansion. Specifically, Gaskell and March[5] have shown that

$$z(\omega) = \frac{D}{\pi} + d_1\omega^{1/2} + d_2\omega + \cdots \tag{8}$$

where

$$d_1 = -(2\pi)^{1/2}\frac{2}{3\rho}\left[4\pi\left(D + \frac{\eta}{\rho M}\right)\right]^{-3/2}\frac{k_B T}{M\pi} \tag{9}$$

with ρ denoting the number density and M the atomic mass. Therefore it is plain that D and η are intimately involved in any relation between $s(\omega)$ and $z(\omega)$, even somewhat away from the low frequency limit $\omega = 0$. Apart from the precise result (8) for the spectral function $z(\omega)$, the general features of the velocity correlation function are well established in simple liquids. Therefore, it would be of interest to test the approximate relation (6) in the manner outlined above for suitable liquid metals, e.g. Rb or Al, near the freezing point, where it is known from the work of Brown and March[6] that the transport coefficients D and η are related at least semi-quantitatively by the form (5) applied at $\omega = 0$, namely

$$\Gamma = \tfrac{4}{3}\eta + \zeta \doteqdot \frac{3DM\rho}{S(0)}. \tag{10}$$

However, in addition to the above interest in liquid metals, current studies[7] on charged colloidal liquids prompt us to emphasize the potential interest also of a relation between the spectral functions $s(\omega)$ and $z(\omega)$ of the polyions in such a system. Of course, the correlated motions of the polyions are now taking place in a solvent, characterized by a dielectric constant entering the Debye length, which in turn fixes the repulsive Yukawa forces between the polyballs, and damping forces arising from the solvent viscosity. Whereas for a simple classical liquid like Ar, Brown and March[6] have exhibited explicitly the mass scaling properties of $S_s(k, \omega)$ and $S(k, \omega)$, their argument, of course, needs modification in the presence of such solvent damping. The work of Lindsay *et al.*[7] suggests that, at least in strongly interacting charged colloidal liquids, the mass dependence of shear viscosity is substantially altered. The simplicity of the results of Lindsay *et al.*[7] for shear viscosity has prompted Hone *et al.*[8] to propose a formula for the self-diffusion coefficient D in these strongly interacting colloidal liquids near the freezing point.

In summary, it would seem to be of considerable interest to study experimentally the relation between the spectral functions $s(\omega)$ and $z(\omega)$ for sound-wave attenuation and diffusion, both in liquid metals such as Rb and Al, and also in strongly interacting colloidal liquids, near their respective freezing points. In the latter case, the additional variables provided by the solvent, and by the mass of the polyions, should enable existing theories relating self and van Hove correlation functions to be fully tested and ought to point the directions in which these theories need modification or refinement.

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