A GENERALIZATION OF THE BIXON AND ZWANZIG HYDRODYNAMIC APPROACH RESULTING IN CORRECT SHORT-TIME BEHAVIOUR

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By using the "reduced" model theory it is possible to introduce a hydrodynamical approach within the context of the Mori theory. In the new theory, autocorrelation functions exhibit a correct behaviour at both short and long times.

Hydrodynamics has been successfully applied by Zwanzig and Bixon [1] to evaluate the velocity correlation function in liquids. A minor error in their calculation has been corrected by Metiu et al. [2].

According to Alder and Wainwright [3], the hydrodynamic approach provides the correct $t^{-3/2}$ time behaviour at long times, whereas the velocity correlation function exhibits a linear decay at short times, rather than the correct parabolic one [1,2].

Metiu et al. [2] emphasized that the breakdown of the hydrodynamic theory at large frequencies could affect the ability of the theory to describe vibrational spectra. The problem of obtaining correct time behaviour at both short and long times must then be regarded as an important question which is still to be clarified.

The main aim of this letter is to show that the "reduced" model theory (RMT) [4–6] can afford a simple solution to this difficult problem. The RMT provides indeed a rigorous justification [6] for mechanical models such as the "itinerant oscillator" [7,8]. These mechanical models result, in turn, in correlation functions exhibiting correct behaviour at short times [7,8]. Furthermore, by virtue of such a mechanical analogy, hydrodynamics can be included straightforwardly in the Mori theory. The procedure is outlined below.

According to Mori theory [9], it is possible to express the velocity autocorrelation function, $C(t)$, in the following exact form (in this paper we denote by $\mathbf{v}$ the translational velocity)

$$C(t) = \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega \cos\omega t \times\left\{\left[-\mathrm{i}\omega + \frac{\Delta_1^2}{-\mathrm{i}\omega + \Delta_2^2/[-\mathrm{i}\omega + \xi_M(\omega)]}\right]^{-1}\right\}. \quad (1)$$

In eq. (1), and in the following similar ones, we mean to take the real part of the term in curly brackets (frequency spectrum). The RMT [5] shows that a mechanical model, resulting in the same "memory kernel" as the one providing the relaxation of $C(t)$, is expressed by the following system of integro-differential equations. For each component of $\mathbf{v}$

$$\dot{v} = \ddot{x} = -(k/m)(x-y)\,, \quad (2)$$

$$\dot{w} = \ddot{y} = (k/M)(x-y) - \int_0^t \xi_M(t-\tau)w(\tau)\mathrm{d}\tau\,, \quad (2')$$

where

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$$k/m = \Delta_1^2 \,, \tag{3}$$

$$k/M = \Delta_2^2 \,, \tag{4}$$

$$\xi_M(t) = \mathcal{L}^{-1}\{\hat{\xi}_M(\omega)\} \,. \tag{5}$$

We denote by a the radius of the "real" particle of mass m, whereas the "virtual" particle of mass M can be regarded as a sphere of radius R. In the spirit of refs. [1,2], we assume that this sphere is suffering a dissipation process described by the memory kernel

$$\hat{\xi}_M(\omega) = (4\pi R/3M) f(R, \eta_s^0, \eta_\ell^0, \tau_s, \tau_\ell, \rho_0, \beta, \omega) \,, \tag{6}$$

obtained by using the hydrodynamic properties of the real fluid. In eq. (6), f is a function of R, η_s^0 and η_ℓ^0, the shear and longitudinal viscosities, respectively; τ_s and τ_ℓ, the shear and longitudinal relaxation times, respectively; ρ_0, the particle density, a parameter β, and ω. The explicit form of f can be determined by comparing eq. (6) with eq. (2.13) of ref. [2].

Notice that the use of eq. (6) results in correct behaviour of $C(t)$ at long times. Since $\xi_M(\omega) \approx a\,\omega^{1/2} + b$ for $\omega \to 0$, from eq. (1) we obtain

$$C(t \to \infty) \approx \frac{2}{\pi} \int_0^\infty d\omega \{\Delta_2^2/\Delta_1^2 \hat{\xi}_M(\omega)\} \cos \omega t$$

$$\approx \frac{2}{\pi} \int_0^\infty d\omega \{\Delta_2^2/\Delta_1^2 \{b + a\omega^{1/2}\}\} \cos \omega t$$

$$\approx A t^{-3/2} \,. \tag{7}$$

In the context of the hydrodynamic approach [1,2], $C(t)$ is written as

$$C(t) = \frac{2}{\pi} \int_0^\infty d\omega \{[-i\omega + \hat{\xi}_H(\omega)]^{-1}\} \cos \omega t \,, \tag{8}$$

where

$$\hat{\xi}_H(\omega) = (4\pi a/3m) f(a, \eta_s^0, \eta_\ell^0, \tau_s, \tau_\ell, \rho_0, \beta, \omega) \,. \tag{9}$$

Since the generalized hydrodynamic approach, given by eq. (1), and the standard one [1,2], given in eq. (8), both result in correct behaviour at small frequencies, then by using eqs. (3) and (4) we obtain

$$R f(R, \eta_s^0, \eta_\ell^0, \tau_s, \tau_\ell, \rho_0, \beta, \omega \to 0)$$

$$= a f(a, \eta_s^0, \eta_\ell^0, \tau_s, \tau_\ell, \rho_0, \beta, \omega \to 0) \,. \tag{10}$$

Eq. (10) is satisfied for

$$R = a \,, \tag{11}$$

which fixes unequivocally the radius of the "virtual" particle.

As far as the mass M of the virtual particle is concerned, it can be evaluated, in principle, by means of eqs. (3) and (4), as

$$M = m\,\Delta_1^2/\Delta_2^2 \,. \tag{12}$$

The calculation of Δ_1^2 and Δ_2^2 can be performed by using the following relations [10]

$$\Delta_1^2 = \langle \omega^2 \rangle \,, \tag{13}$$

$$\Delta_2^2 = (\langle \omega^4 \rangle - \langle \omega^2 \rangle^2)/\langle \omega^2 \rangle \,. \tag{14}$$

In ref. [10] it is shown that the moments $\langle \omega^2 \rangle$ and $\langle \omega^4 \rangle$ can be related to the dynamic structure factor, $S(q, \omega)$, which in part determines the coherent scattering cross section in thermal neutron scattering experiments in liquids. For the sake of simplicity, however, we assume for Δ_1^2 values close to the "experimental" one, $\Delta_1^2 = 0.50 \times 10^{26}\ s^{-2}$ [11], and we introduce

$$p = m/M \tag{15}$$

as a fitting parameter.

From fig. 1 it appears that the elastic nature of the mechanical model allows a correct description of the frequency spectrum without any need for regarding the fluid as being viscoelastic. This also provides a bound to the p values. For $p > 2$, the results improve significantly compared to the experimental situation, and become almost independent of p. We have determined that for $p < 2$ the frequency spectrum form is largely incorrect.

Fig. 2 shows that the behaviour of the velocity correlation function is significantly improved at short times with respect to the standard hydrodynamical theory [1,2], whereas at intermediate times our results are comparable to those of ref. [2].

Fig. 3 shows that the experimental second minimum which occurs below the t-axis is a feature that can appear in the context of the present theory, provided that the liquid viscoelasticity is taken into account. Such a second minimum, of course, has to be related to the second structural feature of the frequency spectrum (fig. 4). The existence of this structure has been clearly emphasized by Rahman [12]. The present

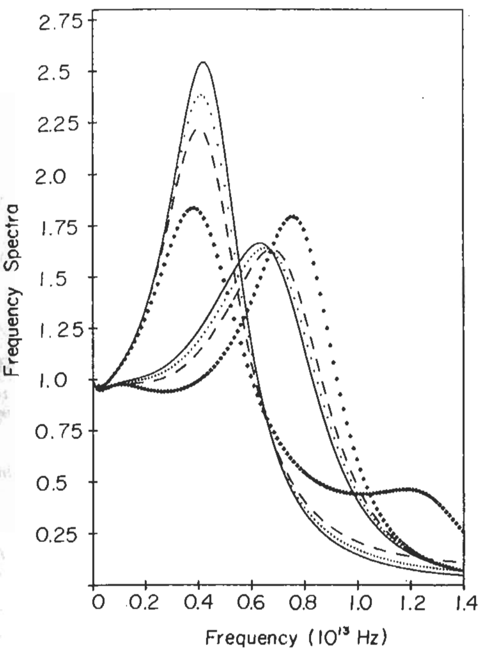

Fig. 1. Frequency spectra of eq. (1) normalized to unity at zero frequency. The curves peaking at lower frequency do not include viscoelasticity ($\tau_s = \tau_\ell = 0$), whereas those peaked at higher frequencies do ($\tau_s = 2.5 \times 10^{-13}$ s, $\tau_\ell = 2 \times 10^{-13}$ s [2]). R = 1.4 Å and $\Delta_1^2 = 0.45 \times 10^{13}\ s^{-2}$. The parameter p [eq. (15)] is 100 for the solid lines, 10 for the dotted lines, 5 for the dashed lines, and 2 for the crossed lines.

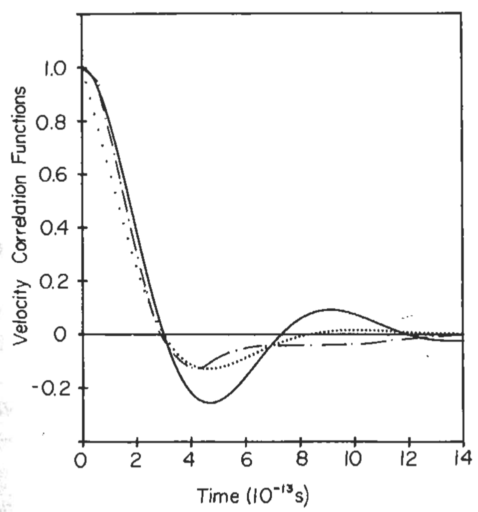

Fig. 2. Solid line: velocity autocorrelation function as given in eq. (1), corresponding to the solid line of fig. 1 without viscoelasticity. Dotted line: same function as calculated in ref. [2] by means of eq. (8). Dash–dotted line: "experimental" function as given by Rahman [13].

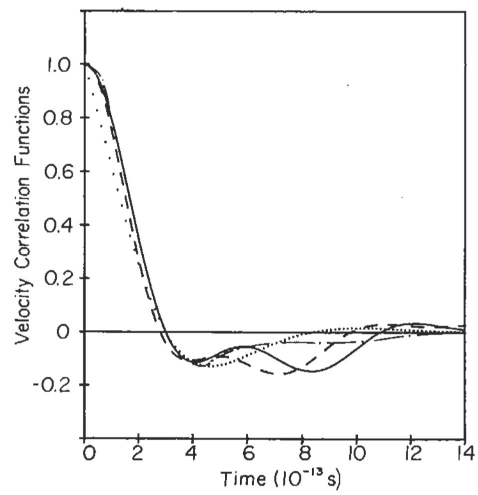

Fig. 3. Velocity autocorrelation functions for the viscoelastic case. Solid line: R = 1.6 Å, $\Delta_1^2 = 0.45 \times 10^{-13}\ s^{-2}$, p = 1.4; dashed line: R = 1.8 Å, $\Delta_1^2 = 0.55 \times 10^{-13}\ s^{-2}$, p = 1.6; dotted line: ref. [2]; dash–dotted line: ref. [13].

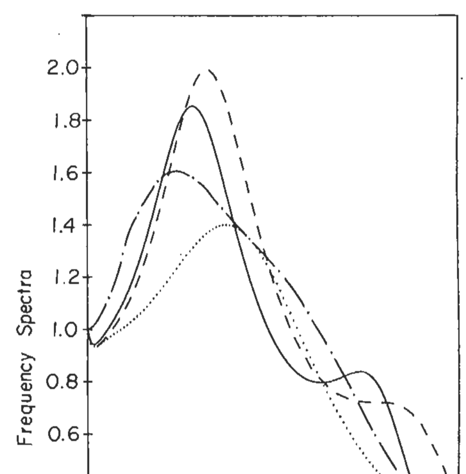

Fig. 4. Frequency spectra corresponding to the velocity autocorrelation functions of fig. 3.

theory accounts for such a structure, even though in too exaggerated a manner for the range of parameters used here.

In conclusion, even though a quantitative reproduction of the "experimental" results deserves further studies, it seems that the RMT can afford a full explanation of the most relevant feature exhibited by Rahman's results [13].

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