Frequency-Dependent Friction Constant Analysis of Diffusion in Simple Liquids*

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A simple discussion of the self-diffusion motions of an atom in a simple liquid is given. The discussion, based mainly on fluctuation-dissipation theorems, dispersion relations, and sum rules, provides a rigorous framework in which a number of phenomenological descriptions are examined. Specific results for liquid argon are compared with computer molecular dynamics calculations. It is shown that the use of simple frequency-dependent friction constants leads to reasonable calculations of the velocity autocorrelation function and of the self-diffusion coefficient.

THE analysis of time autocorrelation functions in a simple liquid by computer studies[1] provides one with a variety of data which one may hope to explain by approximate theories of more or less phenomenological character. The purpose of this paper is to explain in simple, but rigorous, terms the phenomenological description which has been proposed in different guises, and to examine the validity of some simple assumptions which have been used to obtain numerical results within this rigorous framework. A secondary purpose is to strip some of this analysis from its formal framework and to make it more comprehensible to those who wish to analyze their data from this viewpoint.

To motivate the rigorous phenomenological discussion of correlation functions and their properties we begin by considering the classical description of a simple oscillator embedded in a medium. The oscillator, with mass m and a spring constant ω_0, is subjected to an arbitrarily weak external disturbance, $F^{\text{ext}}(t)$, which vanishes for $t<t_0$. The average behavior of the oscillator is rigorously described by the microscopic equation

$$m\langle\ddot{x}(t)\rangle_{\text{n.e.}}+m\omega_0^2\langle x(t)\rangle_{\text{n.e.}}=\langle F^{\text{int}}(t)\rangle_{\text{n.e.}}+F^{\text{ext}}(t)\,, \quad (1)$$

where $\langle\ \rangle_{\text{n.e.}}$ denotes an average taken over a thermodynamic equilibrium ensemble appropriate to the system prior to t_0. If the external force is arbitrarily weak, we can write the linear response as

$$\langle x(t)\rangle_{\text{n.e.}}=\int_{-\infty}^{\infty}dt'\tilde{\chi}(t-t')F^{\text{ext}}(t')\,, \quad (2)$$

where

$$\tilde{\chi}(t-t')=\int_{-\infty}^{\infty}(d\omega/2\pi)\chi(\omega)e^{-i\omega(t-t')}$$

$$=\int_{-\infty}^{\infty}(d\omega/2\pi)[\chi'(\omega)+i\chi''(\omega)]e^{-i\omega(t-t')} \quad (3)$$

is the ratio of the displacement to the external, infinitesimal impulsive force $F^{\text{ext}}(t)=F_0^{\text{ext}}\delta(t-t_0)$. Because the response is causal, $\chi'(\omega)$ and $\chi''(\omega)$ satisfy Kramers-Kronig relations, and we can therefore deduce that

$$\chi(\omega)=\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\chi''(\omega')}{\omega'-(\omega+i\epsilon)}\,. \quad (4)$$

We may also show[2,3] that if there is no magnetic field or rotation of the medium the imaginary (absorptive) response $\chi''(\omega)$ is real and odd, and has a definite sign, i.e.,

$$\omega\chi''(\omega)=-\omega\chi''(-\omega)\geq 0\,. \quad (5)$$

For a classical system, the Nyquist theorem states that the fluctuation spectrum $S(\omega)$ defined by

$$\langle x(t)x(t')\rangle_{\text{eq.}}-\langle x(t)\rangle_{\text{eq.}}\langle x(t')\rangle_{\text{eq.}}=\int_{-\infty}^{\infty}(d\omega/2\pi)S(\omega)e^{-i\omega(t-t')} \quad (6)$$

is given by[3]

$$S(\omega)=(2/\beta\omega)\chi''(\omega)\,, \quad (7)$$

where β is the reciprocal temperature in energy units. Since the oscillator kinetic energy $\frac{1}{2}m\langle\dot{x}^2(t)\rangle_{\text{eq.}}$ is $(2\beta)^{-1}$, we have

$$\langle\dot{x}^2(t)\rangle_{\text{eq.}}=\frac{1}{m\beta}=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^2S(\omega)$$

or

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2\left[\frac{\chi''(\omega)}{\omega}\right]=\frac{1}{m}\,. \quad (8)$$

Equation (8) is correct even if the oscillator is quantum mechanical, but Eq. (7) would have to be slightly

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[1] A. Rahman, Phys. Rev. **136**, A405 (1965); B. R. A. Nijboer and A. Rahman, Physica **32**, 415 (1966).

[2] Much of the formal properties we quote here are discussed in L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) **24**, 419 (1963). A detailed discussion of the general formalism, as well as the oscillator example, can be found in P. C. Martin, in *1967 Les Houches Lectures* (Gordon and Breach Science Publishers, Inc., New York, 1968).

[3] See, for example, R. Kubo, in *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959).

modified. In addition, we have from (6) and (7) the relations

$$\beta\langle \dot{x}^2(t)\rangle=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^4\left[\frac{\chi''(\omega)}{\omega}\right]\equiv\frac{1}{m}\langle\omega_{vv}^2\rangle\,, \qquad (9)$$

$$\beta\langle \ddot{x}^2(t)\rangle=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^6\left[\frac{\chi''(\omega)}{\omega}\right]\equiv\frac{1}{m}\langle\omega_{vv}^4\rangle\,, \qquad (10)$$

as well as higher-order moment relations which will not be considered. If quantum-mechanical corrections are included, Eqs. (9) and (10) would be only slightly changed.

All of the above results are rigorous. To understand the rigorous analysis we have suggested, however, it is useful to recall some nonrigorous phenomenological analyses. The simplest such analysis is based on the replacement of the internal force due to the medium by a frictional force:

$$\langle F^{\rm int}(t)\rangle_{\rm n.e.}\simeq -m\gamma\langle\dot{x}(t)\rangle_{\rm n.e.}\,, \qquad (11)$$

where the friction constant $\gamma>0$, so that Eq. (1) becomes

$$m\langle\ddot{x}(t)\rangle_{\rm n.e.}+m\omega_0^2\langle x(t)\rangle_{\rm n.e.}+m\gamma\langle\dot{x}(t)\rangle_{\rm n.e.}=F^{\rm ext}(t)\,. \qquad (1')$$

For this simple model, Eq. (3) gives

$$\tilde{\chi}(t-t')=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{e^{-i\omega(t-t')}}{m(\omega_0^2-\omega^2-i\gamma\omega)}$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\left\{\frac{\omega_0^2-\omega^2}{m[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]}+i\frac{\gamma\omega}{m[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]}\right\}e^{-i\omega(t-t')}\,. \qquad (3')$$

The statement corresponding to Eq. (4) is

$$\frac{1}{m(\omega_0^2-\omega^2-i\gamma\omega)}=\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{1}{\omega'-\omega-i\epsilon}\times\frac{\gamma\omega'}{m[(\omega_0^2-\omega'^2)^2+(\gamma\omega')^2]}\,, \qquad (4')$$

and the absorption (or power spectrum) of the oscillator is seen to be

$$\frac{\gamma\omega^2}{m[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]}\geq 0\,, \qquad (5')$$

which is consistent with Eq. (5). Inspection of the other properties shows that Eq. (8) is the statement

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\gamma\omega^2}{m[(\omega_0^2-\omega^2)^2+(\gamma\omega)^2]}=\frac{1}{m}\,, \qquad (8')$$

and it is also correct. However, Eqs. (9) and (10) are not satisfied by the assumption, Eq. (11). They fail because the model implies that the internal force is instantaneously out of phase with the displacement, whereas at short times these must be in phase. For this reason, Maxwell[4] and Drude[5] proposed a somewhat better nonrigorous phenomenological description.

Instead of the assumption, Eq. (11), we may postulate that

$$\langle F^{\rm int}(t)\rangle_{\rm n.e.}=-m\int_{-\infty}^{\infty}dt'\tilde{\gamma}(t-t')\langle\dot{x}(t')\rangle_{\rm n.e.}\,, \qquad (12)$$

where

$$\tilde{\gamma}(t-t')=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\gamma(\omega)e^{-i\omega(t-t')}$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[\gamma'(\omega)+i\gamma''(\omega)]e^{-i\omega(t-t')}\,, \qquad (13)$$

and where $\gamma(\omega)$ satisfies an equation like Eq. (4):

$$\gamma(\omega)=\lim_{\epsilon\to 0}\int_{-\infty}^{\infty}\frac{d\omega}{\pi i}\frac{\gamma'(\omega')}{\omega'-(\omega+i\epsilon)}\,. \qquad (14)$$

As a consequence of Eq. (12), we obtain

$$\chi^{-1}(\omega)=m[\omega_0^2-\omega^2-i\omega\gamma(\omega)]\,. \qquad (15)$$

It should be emphasized here that Eq. (12) does not represent an approximation because Eq. (15), where $\gamma(\omega)$ is finite as $\omega\to 0$, can be deduced directly from Eqs. (4) and (5). In the more formal discussion ω_0^2 is no longer the spring constant, but appears simply as the value of $[m\chi(0)]^{-1}$. (Clearly the medium might contain other springs, and the division into a particular spring and the rest of the medium is arbitrary.) Equation (15) enables us to relate the various properties of $\chi(\omega)$ and $\gamma(\omega)$. In particular, Eqs. (9) and (10) are equivalent to the statements that

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\gamma'(\omega)=\langle\omega_{vv}^2\rangle-\omega_0^2\,, \qquad (16a)$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2\gamma'(\omega)=\langle\omega_{vv}^4\rangle-(\langle\omega_{vv}^2\rangle-\omega_0^2)^2\,. \qquad (17a)$$

To introduce the phenomenological description of Maxwell and Drude, one assumes that

$$\gamma(\omega)=\gamma_R(\omega)=\frac{\gamma_R}{1-i\omega\tau_R}\,, \qquad (18)$$

and thus

$$\gamma_R'(\omega)=\frac{\gamma_R}{1+(\omega\tau_R)^2}\,, \qquad (19a)$$

$$\gamma_R''(\omega)=\frac{\omega\gamma_R\tau_R}{1+(\omega\tau_R)^2}\,. \qquad (20)$$

[4] J. C. Maxwell, Phil. Trans. Roy. Soc. London **157**, 49 (1967).
[5] P. Drude, Ann. Phys. **1**, 56 (1900); **3**, 369 (1900).

This assumption is compatible with Eqs. (5) and (8) as before, and in addition we can satisfy Eq. (9) by requiring the identity

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\gamma_R'(\omega)=\frac{\gamma_R}{\tau_R}=\langle\omega_{vv}^2\rangle-\omega_0^2 \tag{16b}$$

to hold. Notice that Eqs. (16b) and (18) imply that the velocity autocorrelation function

$$f(\omega)=\frac{2}{\pi}\int_0^{\infty}dt\cos\omega t\frac{\langle v(t)v(0)\rangle}{\langle v^2(0)\rangle}=\frac{m\beta\omega^2}{\pi}S(\omega)$$

is of the form

$$f(\omega)=\frac{2}{\pi}\frac{\omega^2\gamma_R/[1+(\omega\tau_R)^2]}{\{\omega^2-\omega_0^2-\gamma_R\tau_R\omega^2/[1+(\omega\tau_R)^2]\}^2+\{\omega\gamma_R/[1+(\omega\tau_R)^2]\}^2}$$
$$=\frac{2}{\pi}\frac{\omega^2\tau_R(\langle\omega_{vv}^2\rangle-\omega_0^2)[1+(\omega\tau_R)^2]}{[\omega^2-\omega_0^2-(\omega\tau_R)^2(\omega^2-\langle\omega_{vv}^2\rangle)]^2+[\omega\tau_R(\langle\omega_{vv}^2\rangle-\omega_0^2)]^2}. \tag{21}$$

Physically, the model description introduces an additional effective spring or cage with spring constant $\langle\omega_{vv}^2\rangle-\omega_0^2$, which relaxes in time τ_R. The fact that Eq. (18) corresponds to the assumption of a relaxing cage can also be seen by going back to Eq. (12) and letting $\tilde{\gamma}'(t)$ be the even function of t equal to $\frac{1}{2}\tilde{\gamma}(t)$ for $t>0$. We then find[6]

$$\tilde{\gamma}_R'(t)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\gamma_R'(\omega)e^{-i\omega t}=\frac{\gamma_R}{2\tau_R}e^{-|t|/\tau_R}. \tag{22a}$$

Even though Eq. (18) is a more realistic assumption than Eq. (11), it does not permit us to satisfy Eq. (10), or equivalently Eq. (17a), because the second moment of $\gamma_R'(\omega)$ diverges.

We can, however, go further in an *ad hoc* manner, introducing two other two-parameter descriptions which do not violate Eq. (17a). In particular we may consider a simple exponential form for $\gamma'(\omega)$,

$$\gamma_E'(\omega)=\gamma_E\exp(-2|\omega|\tau_E/\pi), \tag{19b}$$

which corresponds to a cage which relaxes as t^{-2}:

$$\tilde{\gamma}_E'(t)=\gamma_E\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-2|\omega|\tau_E/\pi}e^{-i\omega t}=\frac{\gamma_E}{2\pi}\frac{(2\tau_E/\pi)}{t^2+(2\tau_E/\pi)^2}, \tag{22b}$$

or we may consider a simple Gaussian form,

$$\gamma_G'(\omega)=\gamma_G\exp(-\omega^2\tau_G^2/\pi), \tag{19c}$$

which corresponds to a cage with a Gaussian relaxation[7]

$$\tilde{\gamma}_G'(t)=\gamma_G\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-\omega^2\tau_G^2/\pi}e^{-i\omega t}=\frac{\gamma_G}{2\tau_G}e^{-\pi t^2/\tau_G^2}. \tag{22c}$$

Two relations governing the parameters γ and τ are provided by Eqs. (16a) and (17a). For the present assumptions these become

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\gamma_E'(\omega)=\frac{\gamma_E}{\tau_E}=\langle\omega_{vv}^2\rangle-\omega_0^2, \tag{16c}$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\gamma_G'(\omega)=\frac{\gamma_G}{\tau_G}=\langle\omega_{vv}^2\rangle-\omega_0^2, \tag{16d}$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2\gamma_E'(\omega)=\frac{\pi^2}{2\tau_E^2}[\langle\omega_{vv}^2\rangle-\omega_0^2]=\langle\omega_{vv}^4\rangle-(\langle\omega_{vv}^2\rangle-\omega_0^2)^2, \tag{17b}$$

$$\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\omega^2\gamma_G'(\omega)=\frac{\pi}{2\tau_G^2}[\langle\omega_{vv}^2\rangle-\omega_0^2]=\langle\omega_{vv}^4\rangle-(\langle\omega_{vv}^2\rangle-\omega_0^2)^2. \tag{17c}$$

A third relation between the two parameters is given by

$$D=(m\beta\gamma)^{-1}, \tag{23}$$

where D is the self-diffusion coefficient. With the single relaxation model, Eqs. (16b) and (23) determine γ_R and τ_R, and Eq. (17a) cannot be satisfied. With the exponential and Gaussian models, γ and τ can be determined from Eqs. (16a) and (17a) as indicated, and these values in turn provide a calculation[8] of D. The calculated values of D depend on the quantities $\langle\omega_{vv}^4\rangle$, $\langle\omega_{vv}^2\rangle$, and ω_0^2, the first two being known equilibrium properties. ω_0 may be taken to be zero for a liquid.

We have applied the approximations represented by Eqs. (19a), (19b), and (19c) to liquid argon for which the velocity autocorrelation function has been determined by computer molecular dynamics experiments.[1] A comparison of our phenomenological calculations

[6] The approximation, Eq. (18), is equivalent to the assumption of an exponential memory function as discussed by B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966). This model also has been used in the analysis of inelastic neutron-scattering experiments on liquid argon by R. C. Desai and S. Yip, Phys. Rev. (to be published).

[7] The equivalent assumption, that of a Gaussian memory function, has been recently discussed by K. S. Singwi and M. P. Tosi, Phys. Rev. **157**, 153 (1967).

[8] Alternatively, we may use a three-parameter description which would then accommodate the correct values for D, $\langle\omega_{vv}^2\rangle$, and $\langle\omega_{vv}^4\rangle$.

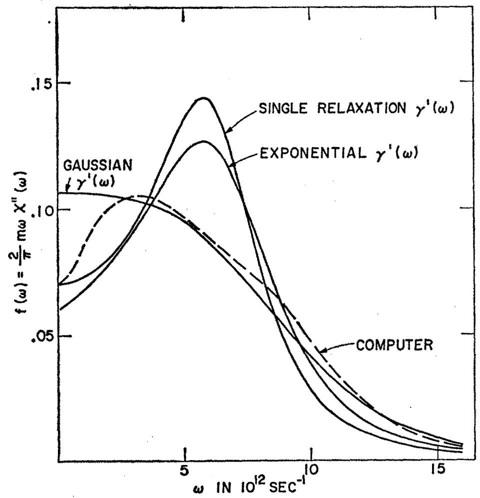

FIG. 1. Spectral distribution of the velocity autocorrelation function in liquid argon at 1.407 g/cm^3 and 85.5°K. In the exponential and Gaussian approximations $f(\omega)$ is computed from

$$f(\omega)=\frac{2}{\pi}\gamma'(\omega)\bigg/\left\{\omega^2\left[1+P\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{\gamma'(\omega')}{\omega'^2-\omega^2}\right]^2+\gamma'^2(\omega)\right\},$$

and in the single relaxation approximation this expression is equivalent to Eq. (21). The phenomenological friction constants $\gamma'(\omega)$ used are those given in Fig. 2. The computer $f(\omega)$ is shown here as the dashed curve, from which we find $\langle\omega_{vv}^2\rangle\simeq 47\times10^{24}$ sec^{-2} and $\langle\omega_{vv}^4\rangle\simeq 6750\times10^{48}$ sec^{-4}.

with the computer results is shown in Figs. 1 and 2 for argon at 1.407 g/cm^3 and 85.5°K. The corresponding values of D are

$$D_R=D_{\text{computer}}=1.88\times10^{-5}\ \text{cm}^2/\text{sec},$$
$$D_E=1.67\times10^{-5}\ \text{cm}^2/\text{sec},$$
$$D_G=2.95\times10^{-5}\ \text{cm}^2/\text{sec}.$$

One should note that all of these procedures which set

$$m\beta/D=\gamma=(\langle\omega_{vv}^2\rangle-\omega_0^2)\tau$$

are quite different from the procedure employed by Kirkwood[9] and his followers who effectively take

$$\gamma\approx[\langle\omega_{vv}^2\rangle-\omega_0^2]^{1/2}.$$

The latter procedure amounts to taking, in the quite similar problem of electrical conductivity,

$$\sigma\approx\omega_p,$$

instead of

$$\sigma\approx\omega_p^2\tau,$$

since ω_p^2 corresponds quite closely to $\langle\omega_{vv}^2\rangle$.

Having indicated how the quantity $\gamma'(\omega)$ or $\tilde{\gamma}(t)$ plays a central role in phenomenological descriptions, we may turn the problem around. We may ask for $\gamma(\omega)$ given the response function $\chi(\omega)$, or in view of Eqs. (4) and (7), given the position autocorrelation function $S(\omega)$, or the velocity autocorrelation function $f(\omega)$. Once we know $\gamma(\omega)$ we may also find $\tilde{\gamma}(t)$. There is reason to expect, from our phenomenological models, that $\gamma(\omega)$ and $\tilde{\gamma}(t)$ may be simpler than $S(\omega)$.

As Figs. 1 and 2 show, this expectation that $\gamma(\omega)$ and $\tilde{\gamma}(t)$ are simpler than $\chi(\omega)$ and $\tilde{\chi}(t)$ appears to be borne out. Even when a simple, smooth function like $\gamma_R(\omega)$ is used and ω_0 is set equal to zero, $\chi''(\omega)$ may still peak away from $\omega=0$ and $\tilde{\chi}(t)$ may exhibit oscillatory structure. To put it differently, the solutions to the differential equation for the displacement are more varied than the friction constant. The conduction analog would state that the conductivity is a less variable quantity than the electric field which is determined by the differential equation in which the conductivity appears. The reanalysis of the data therefore seems to hold promise.

Lest the reader be tempted to apply these conclusions too generally, however, it would be well for him to recall the conductivity example, to which we have alluded, in more detail. It is certainly true that $\langle\omega_{vv}^2\rangle$ plays the role of ω_p^2. Consequently, in a normal conductor, where we take $\omega_0=0$,

$$\sigma(\omega)\approx\omega_p^2\tau/(1-i\omega\tau).$$

Furthermore, in a superconductor we have [with $\omega_0^2\to\omega_p^2(n_s/n)$ and $n_s+n_n=n$]

$$\sigma(\omega)-\frac{\omega_0^2}{i\omega}=\left(\frac{n_n}{n}\right)\frac{\omega_p^2\tau}{1-i\omega\tau}-\frac{\omega_p^2}{i\omega}\left(\frac{n_s}{n}\right).$$

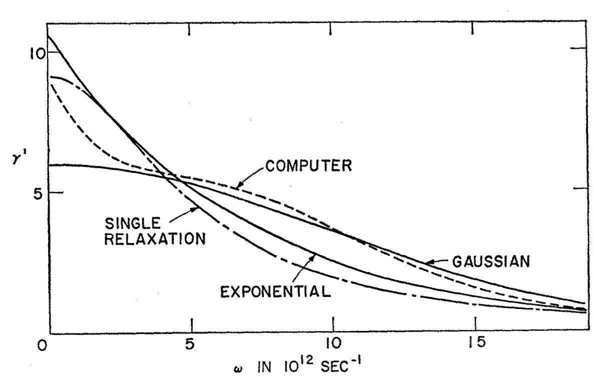

FIG. 2. Frequency-dependent friction constant $\gamma'(\omega)$ for liquid argon as calculated [similar results have been obtained independently by L. Verlet (private communication)] from the computer $f(\omega)$ of Fig. 1. Also shown are the single relaxation, exponential, and Gaussian approximations: $\gamma_R'(\omega)=9.4/[1+(0.2\omega)^2]$, $\gamma_E'(\omega)=10.6e^{-0.144|\omega|}$, $\gamma_G'(\omega)=5.98e^{-(0.072\omega)^2}$, with ω in units of 10^{12} sec^{-1}.

[9] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

On the other hand, in an insulator,

$$\sigma(\omega)=-i\omega[\epsilon(\omega)-1]\approx\omega_p{}^2\frac{i\omega}{\omega^2-\bar{\omega}^2+i\omega/\tau},$$

$$\sigma'(\omega)\approx\omega_p{}^2\frac{\omega^2/\tau}{(\omega^2-\bar{\omega}^2)^2+(\omega/\tau)^2}.$$

There is therefore no intrinsic reason for expecting $\sigma(\omega)$ or, in our parallel discussion, $\gamma(\omega)$, to be nonresonant. The even function $\gamma'(\omega)$ may be peaked at one (or several) nonvanishing frequencies $\bar{\omega}$. The variety of effects which may occur in γ is thus not necessarily much smaller than the variety of effects which can occur in χ. Nonetheless, at least in the simple fluid, the quantity $\gamma(\omega)$ and $\tilde{\gamma}(t)$ do appear simpler, and indeed, the assumption of a Gaussian or exponential form for $\gamma'(\omega)$ appears to give qualitatively reasonable values for D in dense fluids.

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Moments of the Momentum Density Correlation Functions in Simple Liquids*

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The fourth frequency moments of the longitudinal and transverse momentum correlation functions in a simple, classical liquid have been derived. Numerical results in the $k=0$ limit are given for a Lennard-Jones potential.

I. INTRODUCTION

The space-time correlations in the local momentum density of a simple fluid are perhaps its most fundamental properties. A complete knowledge of these correlations at all densities and temperatures in a classical fluid is sufficient to determine all the thermodynamic and transport properties of the fluid, as well as all the properties which could be investigated with ultrasonic, laser, and neutron-scattering studies. The difficulty, of course, is that there is no practical theory, other than machine solution of Newton's equations, for evaluating time-dependent correlation functions for a dense fluid from first principle. There are, however, a number of useful, calculable properties. Among these are the moment sum rules—expressions which relate the Fourier transform of the momentum correlation function to the interaction potentials and the instantaneous particle distribution functions. Since relatively reliable two-body potential functions are known (at least for gases), and since methods are available for computing equilibrium distribution functions in terms of these potentials, the direct evaluation of sum rules is feasible if laborious. The purpose of this paper is to extend the existing sum-rule calculations, and to present numerical results which may be useful in approximate calculations of the dynamic fluid response. Our own motivation for performing these calculations was an investigation of the shear viscosity discussed in the following paper.

Frequency moment analysis has long been recognized as a basic method in the study of correlation functions. For example, in inelastic neutron-scattering calculations the sum rules corresponding to the first four frequency moments of the density-density correlation function have been derived by Placzek.[1] Later deGennes[2] rederived the second and fourth moments (the zeroth and second moments of the longitudinal momentum correlation) more explicitly using classical arguments.[3] More recently, an expression for the fourth moment of the velocity autocorrelation function has been given by Nijboer and Rahman.[4] Corresponding moments have also been computed for spin systems and employed in a phenomenological treatment of spin diffusion.[5]

Studies of both transverse and longitudinal momentum correlation sum rules have thus far been directed only at the second frequency moment. Zwanzig and Mountain[6] pointed out that, in the limit of long

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[1] G. Placzek, Phys. Rev. **86**, 377 (1952).
[2] P. G. deGennes, Physica **25**, 825 (1959).
[3] Quantum-mechanical calculation of the first four moments has also been discussed by R. D. Puff [Phys. Rev. **137**, A406 (1965)] and applied to interacting Bose systems.
[4] B. R. A. Nijboer and A. Rahman, Physica **32**, 415 (1966).
[5] P. G. deGennes, J. Phys. Chem. Solids **4**, 223 (1958); H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962); H. S. Bennett and P. C. Martin, Phys. Rev. **138**, A608 (1965).
[6] R. Zwanzig and R. D. Mountain, J. Chem. Phys. **43**, 4464 (1965).