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Toward a Microscopic Basis for the de Gennes Narrowing

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It is pointed out that recent work on the high-frequency behavior of the neutron scattering function $S(k, \omega)$ in liquids indicates that at fixed ω there is a dip at a value of k very close to the maximum of $S(k)$ (first diffraction peak). This dip is due to the configurational average over pairs of particles and scales as the inverse particle radius.

KEY WORDS: de Gennes narrowing; neutron scattering in liquids; time correlation functions; hard core limit; neutron scattering at high frequencies.

The shape of the coherent inelastic neutron scattering function $S(k, \omega)$ in simple liquids has been the object of considerable study. It was suggested in 1959 by de Gennes,[1] on the basis of sum rule arguments, that a line narrowing should occur at certain k values, in particular near the first diffraction maximum (at about $2\ \text{Å}^{-1}$ in argon). This effect is observed in neutron experiments.[2] No completely satisfactory microscopic derivation of this result has appeared. Here we contribute to a solution of this problem by pointing out that a recent detailed kinetic analysis[3] of the high-frequency behavior of $S(k, \omega)$ provides a partial microscopic basis for the line narrowing.

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The value k_0 at which $S(k)$ is a maximum is determined mainly by the particle diameter σ, or effective hard sphere size, and seems to be essentially a packing effect. Generally one finds k_0 to be slightly larger than $2\pi/\sigma$ with only a weak dependence on the thermodynamic state.[4] It is shown in Ref. 3 that this radius also determines the k value at which a dip in the high-frequency part of $S(k, \omega)$ appears. Since one has

$$S(k) = \int (d\omega/2\pi) S(k, \omega) \tag{1}$$

this result implies a connection between the high-frequency behavior and that of the rest of the spectrum. Furthermore, the dip is due only to a static configurational average, being almost independent of the dynamical behavior. This is responsible for its absence in the tail of the self-correlation function, for which the line narrowing[5] is much less marked.[2]

The reason for a line narrowing at the first diffraction peak seems intuitively obvious. The pairs of particles sampled at k_0 are at or close to the distance of the first coordination shell. Such pairs correspond to nearest neighbors in the solid—the first diffraction peak is the liquid analog of the first Bragg peak. Since the pairs "prefer" this separation, one expects them to move more slowly, implying more weight in $S(k, \omega)$ at low frequencies.[3] In the solid case, the phonon energy is reduced at the corresponding k value, even going to zero in certain directions.

De Gennes'[1] argument for a line narrowing runs as follows. Define a normalized scattering function

$$\Sigma(k, \omega) \equiv S(k, \omega) \Big/ \int (d\omega/2\pi) S(k, \omega) = S(k, \omega)/S(k) \tag{2}$$

Then consider the ratio

$$R(k) \equiv \tfrac{1}{3} \left[\int (d\omega/2\pi) \omega^4 \Sigma(k, \omega) \right] \Big/ \left[\int (d\omega/2\pi) \omega^2 \Sigma(k, \omega) \right]^2 \tag{3}$$

One also needs the classical counterpart of the f sum rule:

$$\int (d\omega/2\pi) \omega^2 S(k, \omega) = k^2/\beta m \tag{4}$$

Using Eqs. (3) and (4) and the sum rule[1]

$$\begin{aligned} M_4(k) &\equiv \int (d\omega/2\pi) \omega^4 S(k, \omega) \\ &= (3k^4/\beta^2 m^2) + (k^2/\beta m^2) \\ &\quad \times \rho \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k}\cdot\mathbf{r})(\hat{k}\cdot\nabla)^2 V(r) \end{aligned} \tag{5}$$

[2] Neither our argument nor that of Ref. 1 predicts a line narrowing in this case.
[3] We are indebted to Prof. S. Yip for this argument.

where $g(r)$ is the pair correlation function and $V(r)$ the interparticle potential, we find

$$R(k) = \left[1 + (\rho\beta/3k^2) \times \int d\mathbf{r}\, g(r)(1 - \cos \mathbf{k}\cdot\mathbf{r})(\hat{k}\cdot\nabla)^2 V(r)\right] S(k) \tag{6}$$

Using experimental values for $S(k)$ in liquid argon, de Gennes showed that at k_0 the second moment of $\Sigma(k, \omega)$ has a minimum while $R(k)$ has a maximum, indicating a line narrowing.

This argument can be further analyzed as follows. Define the frequencies

$$\omega_h \equiv \left[\int (d\omega/2\pi)\omega^4\Sigma(k, \omega)\right]^{1/4}, \qquad \omega_i \equiv \left[\int (d\omega/2\pi)\omega^2\Sigma(k, \omega)\right]^{1/2} \tag{7}$$

Then ω_h is a typical "high" frequency—that is, one at or near which $\Sigma(k, \omega)$ contributes most to its fourth frequency moment. Likewise, Eq. (7) uses the second moment to define a typical "intermediate" frequency. One can see that these definitions are meaningful, by multiplying the experimental values for $S(k, \omega)$ by the appropriate power of ω and noting that the resulting curve is (roughly) localized in frequency. Such curves for $\omega^2 S(k, \omega)$ can be seen in Figs. 10 and 11 of Ref. 7. Now we take the fact that ω_h (or ω_i) decreases as k approaches k_0 to mean that $\Sigma(k, \omega)$ is decreasing at high (or intermediate) frequencies. Since Σ is normalized to one, this means it must be increasing at lower frequencies; hence there is a line narrowing at this k value. This reasoning assumes a simple line shape; we suppose that there does not exist, for instance, a strongly k-dependent shoulder in the spectrum. No such feature is observed in neutron measurements of $S(k, \omega)$. With this interpretation R gives a measure of the relative rate at which Σ decreases at high and intermediate frequencies. Denoting the derivative with respect to k at k_0 by a prime, we have

$$R' = \omega_i' = \omega_h' = 0 \tag{8}$$

and

$$R'' < 0, \qquad \omega_i'' > 0, \qquad \omega_h'' > 0 \tag{9}$$

(The last inequality can be shown by a numerical computation of M_4 using experimental data or by the results given below.) Now by direct computation

$$R'' = 4R[(\omega_h''/\omega_h) - (\omega_i''/\omega_i)] \tag{10}$$

Hence $R'' < 0$ implies

$$\omega_i''/\omega_i > \omega_h''/\omega_h \tag{11}$$

This indicates that as k nears k_0, $\Sigma^{1/2}$ will decrease more rapidly in the intermediate-frequency region than $\Sigma^{1/4}$ does at high frequencies.

We now show that the line narrowing can be derived by a different argument. Our analysis considers $S(k, \omega)$ rather than $\Sigma(k, \omega)$. We argue from Eqs. (1) and (4) and the fact—shown below—that at high ω, $S(k, \omega)$ dips as a function of k at or very near k_0. Since $S(k)$ has a maximum at k_0 and the second moment has no extremum, it follows that $S(k, \omega)$ must be increasing at low frequencies as k_0 is approached. Here as above we must assume a simple line shape. The new feature of this argument is the explicit microscopic analysis of the large-ω behavior of $S(k, \omega)$. Using this, the line narrowing is at least partially derived in terms of the dynamics of the constituent particles of the system. The implications drawn above for the behavior at high and intermediate frequencies are of course not altered by taking this viewpoint.

It should be noted that the frequency region where the "dip" is calculated is for ω near ω_h and is just that responsible for almost all of the oscillatory (second) term in $M_4(k)$. The dynamical processes involved also cause $M_4(k)$ to diverge if one lets the repulsive part of $V(r)$ become infinitely hard.[8]

In what follows we give a condensed version of the derivation of the high-frequency behavior of the scattering function. Further details are contained in Ref. 3.

Consider the second derivative of the intermediate scattering function [the Fourier transform of $S(k, \omega)$]:

$$(\partial^2/\partial t^2)F(k, t) = -(1/N) \sum_{i,j=1}^{N} \langle \mathbf{k}\cdot\mathbf{v}_i(0)\{\exp[i\mathbf{k}\cdot\mathbf{r}_i(0)]\} \times \mathbf{k}\cdot\mathbf{v}_j(t) \exp[-i\mathbf{k}\cdot\mathbf{r}_j(t)]\rangle \tag{12}$$

The events causing it to vary most rapidly at short times are collisions involving the repulsive forces. Since the repulsive part of the potential is almost a hard core, it is a good approximation to consider two-body collisions only. This is because the duration of a "close-in" two-body collision, though finite, is very short for a realistic potential (it goes to zero in the hard core limit) so that there exists a frequency range for which many-body collisions can be neglected. For argon this is $\omega \gtrsim 10^{+13}\ \mathrm{sec}^{-1}$. This step reduces the calculation to a two-body problem and defines the time interval over which it is valid. Furthermore, as long as k is not too large, we can replace $\mathbf{r}_i(t)$ by $\mathbf{r}_i(0)$, thereby neglecting the change in position during a collision as compared to the change in velocity.

In a classical system, the initial velocity average is Maxwellian. Thus our approximation allows the calculation of all parts of Eq. (12) except the pair correlation function $g(r)$ at small r, which enters as an unknown. It is just a measure of the probability that a given "close-in" pair configuration

will occur. If we now introduce relative coordinates for the pair and keep only those parts of Eq. (12) that vary most rapidly, we find

$$(\partial^2/\partial t^2)F(k, t) = -\tfrac{1}{4}\rho \int d\mathbf{r}\langle \mathbf{k}\cdot\mathbf{v}(0)\mathbf{k}\cdot\mathbf{v}(t)\rangle(1 - \exp i\mathbf{k}\cdot\mathbf{r})g(r) \tag{13}$$

where $\mathbf{v}(t)$ is the relative velocity of two particles whose initial separation is r and the brackets indicate averaging over initial velocities. Note that the factor $\exp i\mathbf{k}\cdot\mathbf{r}$ is due to the off-diagonal terms in Eq. (12) and hence would be absent for the self-correlation function. Arguing further that head-on collisions are the most import and taking the time Fourier transform gives

$$S(k, \omega) = \tfrac{1}{4}\rho \int d\mathbf{r}[A(\omega, r)/\omega^2][\mathbf{k}\cdot\mathbf{r})^2/r^2] \times (1 - \exp i\mathbf{k}\cdot\mathbf{r})g(r) \tag{14}$$

where $A(\omega, r)$ is the Fourier transform of $\langle v(0)v(t)\rangle_r$. In Ref. 3 we show that for smooth, repulsive potentials a good approximation for A is

$$A(\omega, r) = (2\pi)^{1/2}(2/\beta m)[1/\omega(r)] \exp\{-\tfrac{1}{2}[\omega/\omega(r)]^2\} \tag{15}$$

where

$$\omega(r) \equiv [(2/m)V''(r)]^{1/2} \tag{16}$$

and $V''(r)$ is the second derivative of the potential. This Ansatz fits the zeroth and second frequency moments of $A(\omega, r)$ exactly and compares well with the exact solution when $V(r)$ is an exponential plus a constant.

Now in Eq. (14) the frequency and wave vector dependences are completely decoupled for each value of $\mathbf{r}$. From the properties of $A(\omega, r)$ and $g(r)$ it is easy to see that the integration in Eq. (14) is in general restricted to a small range of r [of the order of the width of the repulsive part of $V(r)$], over which $\mathbf{k}\cdot\mathbf{r}$ does not change much. Hence we can bring the k-dependent factors out of the integral, obtaining (after integration over angles)

$$S(k, \omega) \cong (\pi/2)\rho C[kr_1(\omega)]^2 f_2(kr_1(\omega)) \tag{17}$$

where r_1 depends only slightly on ω and is always close to σ and C is independent of k. For hard spheres $r_1 = \sigma$, one can show that $C \propto \omega^{-4}$ and Eq. (17) gives the exact asymptotic form of $S(k, \omega)$. For other potentials the ω dependence is more complicated, involving the explicit behavior of $g(r)$ at small r via Eq. (14). The function $f_2(x)$ is defined by

$$f_2(x) = \int_{-1}^{+1} du\, u^2(1 - \cos xu) \tag{18}$$

Figure 1 is a plot of $x^2 f_2(x)$. The first dip comes at $x \cong 6.9$. Neutron measurements confirm the existence of this feature.[6]

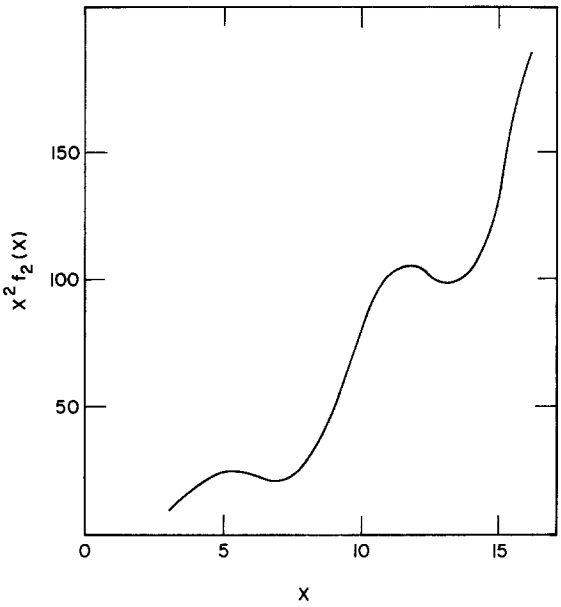

Fig. 1. The function $x^2 f_2(x)$ [cf. Eq. (18)].

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