COLLECTIVE COORDINATES IN CLASSICAL SYSTEMS*

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Let $\vec r_j, \vec v_j$, $j=1,\cdots,N$, denote the positions and velocities, respectively, of a classical system of N particles, each of mass M; Zwanzig[1] has suggested that

$$J_{\vec\kappa}(t)=N^{-1/2}\sum_{j=1}^{N}(\vec\kappa\cdot\vec v_j)\exp(i\vec\kappa\cdot\vec r_j) \qquad (1)$$

should have characteristics of a collective coordinate, i.e., it should have a damped oscillatory behavior.

In this communication we shall consider the properties of the function

$$C(\vec\kappa,t)=\langle J_{\vec\kappa}(0)J_{-\vec\kappa}(t)\rangle_T, \qquad (2)$$

which is called the autocorrelation of the coordinate $J_{\vec\kappa}(t)$; $\langle\cdots\rangle_T$ denotes thermal averaging. It will be shown that (i) the spectral function of $C(\vec\kappa,t)$, i.e., its Fourier transform, can be obtained directly from inelastic neutron scattering experiments; (ii) this spectral function is peaked at a nonzero value of frequency, i.e., $C(\vec\kappa,t)$ has an oscillatory behavior, for all systems; (iii) molecular-dynamics[2] calculations on liquid argon show that the oscillatory behavior of $C(\vec\kappa,t)$ is intimately related to $S(\vec\kappa)$, the Fourier transform of the pair correlation function.

Consider first the coordinate

$$Q_{\vec\kappa}(t)=N^{-1/2}\sum_{j=1}^{N}\exp[i\vec\kappa\cdot\vec r_j(t)].$$

Let its autocorrelation, namely $\langle Q_{\vec\kappa}(0)Q_{-\vec\kappa}(t)\rangle_T$, be denoted by $F(\vec\kappa,t)$. Then the Fourier transform of $F(\vec\kappa,t)$ is the scattering law $S(\vec\kappa,\omega)$ which, in the first Born approximation, gives the probability of scattering a plane wave off the system with a momentum change $\hbar\vec\kappa$ and energy change $\hbar\omega$. It follows, therefore, that

$$-\ddot F(\vec\kappa,t)=\int_{-\infty}^{+\infty}\exp(i\omega t)\omega^2S(\vec\kappa,\omega)d\omega. \qquad (3)$$

Using $\dot Q_{\pm\vec\kappa}(t)=\pm iJ_{\pm\vec\kappa}(t)$ and the fact that in equilibrium all thermal averages are independent of the origin of time, we get

$$\begin{aligned}\dot F(\vec\kappa,t)&=-i\langle Q_{\vec\kappa}(0)J_{-\vec\kappa}(t)\rangle_T\\&=-i\langle Q_{\vec\kappa}(-t)J_{-\vec\kappa}(0)\rangle_T.\end{aligned}$$

Hence

$$\begin{aligned}\ddot F(\vec\kappa,t)&=(-i)^2\langle J_{\vec\kappa}(-t)J_{-\vec\kappa}(0)\rangle_T\\&=-\langle J_{\vec\kappa}(0)J_{-\vec\kappa}(t)\rangle_T\\&=-C(\vec\kappa,t).\end{aligned} \qquad (4)$$

or, inversely, since $\dot F(\vec\kappa,0)=0$, we have

$$F(\vec\kappa,t)=F(\vec\kappa,0)-\int_0^t(t-u)C(\vec\kappa,u)du. \qquad (5)$$

From (3) and (4) we see that $\omega^2S(\vec\kappa,\omega)$ is the spectral function of $C(\vec\kappa,t)$, i.e.,

$$C(\vec\kappa,t)=\int_{-\infty}^{+\infty}\exp(i\omega t)\omega^2S(\vec\kappa,\omega)d\omega. \qquad (6)$$

Thus, using inelastic neutron scattering data we can get $\omega^2S(\vec\kappa,\omega)$; then, for given value of $\vec\kappa$, its Fourier transform will show the oscillatory behavior of $C(\vec\kappa,t)$. Note that $C(\vec\kappa,o)=\kappa^2k_BT/M$ and $\int_{-\infty}^{+\infty}C(\vec\kappa,t)dt=0$.

It is important to realize that $\omega^2S(\vec\kappa,\omega)$ will show a maximum in its dependence on ω at a certain $\omega(\vec\kappa)$ for all systems, including an ideal gas. In this sense $C(\vec\kappa,t)$ is oscillatory for all systems; however, the manner in which the oscillatory character depends on $\vec\kappa$ is what makes $C(\vec\kappa,t)$, and hence $\omega^2S(\vec\kappa,\omega)$, a very useful function to consider. The results for an ideal gas are instructive. In the classical limit, for an ideal gas, $S(\kappa,\omega)=(M/2\pi k_BT\kappa)^{1/2}\times\exp(-M\omega^2/2\kappa^2k_BT)$, and hence $\omega^2S(\kappa,\omega)$ has a maximum in ω at

$$\omega(\kappa)=\kappa(2k_BT/M)^{1/2}. \qquad (7)$$

Since for large enough κ (short-wavelength limit), $S(\vec\kappa,\omega)$ tends to the ideal gas form for all systems, it follows that Eq. (7) gives the large-κ behavior of $\omega(\vec\kappa)$ for all systems.

In the case of substances for which the incoherent neutron scattering cross section is not negligible (argon, sodium, etc.), the observed $\omega^2S(\vec\kappa,\omega)$ will be the transform of an appropriately weighted sum of $C(\vec\kappa,t)$ and $C_s(\vec\kappa,t)$, where $C_s(\vec\kappa,t)$ is the autocorrelation of $(\vec\kappa\cdot\vec v)\exp(i\vec\kappa\cdot\vec r)$, $\vec r$ and $\vec v$ being the position and velocity of any one particle. Hence, under favorable circumstances, we may even observe two peaks in $\omega^2S(\vec\kappa,\omega)$, one arising out of the transform of the "self" part $C_s(\vec\kappa,t)$ and the other from the

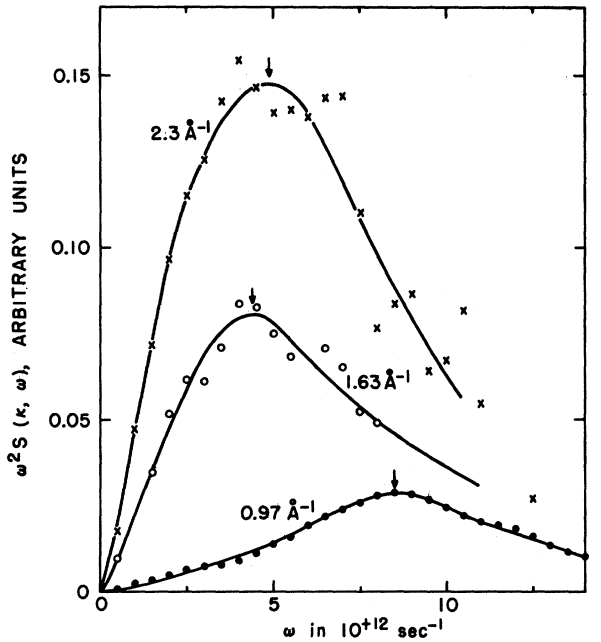

FIG. 1. $\omega^2 S(\kappa,\omega)$ for liquid argon, obtained from molecular dynamics data; arrow indicates $\omega_{\max}(\kappa)$, the position of the maximum.

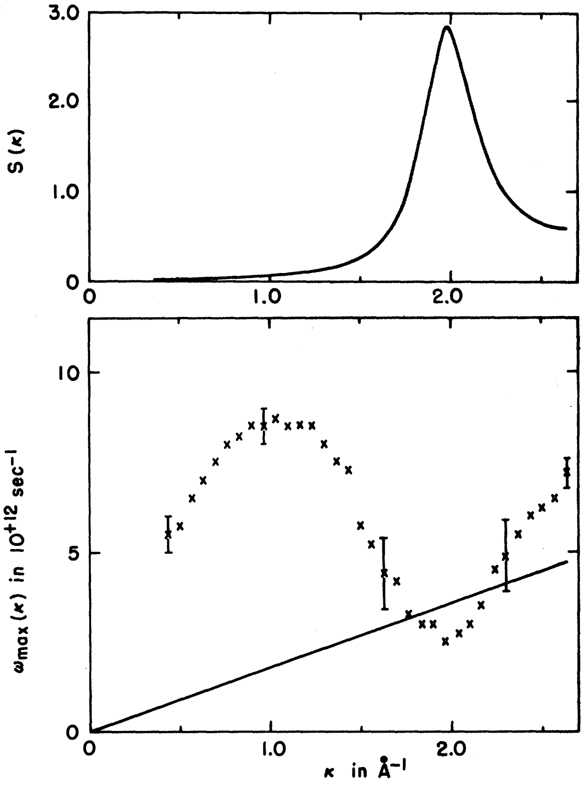

FIG. 2. The structure factor $S(\kappa)$ and $\omega_{\max}(\kappa)$ shown as a function of κ. The straight line has the slope $(2k_BT/M)^{1/2}$.

collective part $C(\vec{\kappa},t)$.

Molecular dynamics[2] gives us the positions and velocities of the particles as a function of time for a system of a few hundred particles; this is just the information required to calculate correlations like $F(\vec{\kappa},t)$ and $C(\vec{\kappa},t)$. A calculation on liquid argon, at a density of 1.407 g/cc and temperature 76°K, has been made and the data analyzed to obtain $F(\kappa,t)$; no oscillatory behavior is found in $F(\kappa,t)$. On the other hand, $\omega^2 S(\kappa,\omega)$, shown in Fig. 1 as a function of ω for a few values of κ, has a well-defined peak at some $\omega(\kappa)$. In Fig. 2 we have plotted $\omega(\kappa)$ for all the κ for which the calculation was made; also shown in Fig. 2 is the structure factor $S(\kappa)[\equiv F(\kappa,t=0)]$ which is the Fourier transform of the pair correlation function $g(r)$. In another paper we shall present the results in greater detail.

In conclusion we note that a treatment of a collective coordinate, like, e.g., $J_{\vec{\kappa}}(t)$ of Eq. (1), as a dynamical variable always involves the linearization of the equation of motion; the approximations involved in the linearization are usually hard to assess or to justify. On the other hand, a correlation like $C(\vec{\kappa},t)$ of Eq. (2) is seen to have a peaked spectral function without recourse to any approximation; the fact that this function, namely $\omega^2 S(\vec{\kappa},\omega)$, is a directly observable quantity adds further interest to a theoretical analysis of $C(\vec{\kappa},t)$.

It is fruitless to discuss whether the behavior of $C(\vec{\kappa},t)$ discussed above proves the existence of "phonons" in liquids. Whether or not the position-density fluctuations in a system have an oscillatory behavior, we have shown that the momentum-density fluctuations always have an oscillatory behavior and hence have a spectral function peaked at a nonzero frequency. We recall that in the theory of liquid helium, too, it is the momentum density which is a well-defined oscillatory collective coordinate.

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[1] R. Zwanzig, Phys. Rev. 156, 190 (1967).

[2] A. Rahman, Phys. Rev. 136, A405 (1964).