On the Velocity Autocorrelation in a Classical Fluid*

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The evaluation of the velocity autocorrelation function and of its frequency spectrum in a classical liquid is discussed in the framework of the formalism developed by Tjon for the spin autocorrelation function. This is based on an integrodifferential equation involving a memory function, and is shown to be equivalent to the well-known approach based on the time expansion of the correlation function. The use of a Guassian memory function leads to fair agreement with the results of Rahman's numerical experiments for liquid argon.

I. INTRODUCTION

THE calculation of the velocity autocorrelation function of an atom in a liquid is a difficult and as yet an unsolved problem. In a real fluid this function is not a simple exponential but has a negative part as its characteristic feature. Recent work of Nijboer and Rahman[1] has shown that the representation of this function by means of its time expansion is far from satisfactory because the expansion converges very slowly. Thus the correlation function does not even become negative when one includes the t^4 term in the time expansion. This term already involves the fourth moment of the frequency spectrum of the velocity autocorrelation, a quantity which can in principle be evaluated from a knowledge of the interatomic potential but is in fact very poorly known.

In this paper we follow a method which was used by Tjon[2] to calculate the spin autocorrelation function and is equivalent to summing the time expansion to infinite order, though approximately. The method consists in evaluating the velocity autocorrelation function from a linear integrodifferential equation whose kernel has the meaning of a memory function. The memory function is taken to be a simple Gaussian whose parameters are related to the diffusion coefficient and to the second moment of the frequency spectrum. An explicit calculation of the velocity autocorrelation function and of its frequency spectrum for liquid argon at two temperatures yields fair agreement with the numerical experiments of Rahman. A detailed discussion of the integrodifferential equation, and applications based on an exponential kernel, have been presented recently by Berne, Boon, and Rice.[3]

II. THEORETICAL DISCUSSION

The integrodifferential equation for the normalized velocity autocorrelation function $\Phi(t)$ is[2]

$$\frac{d\Phi(t)}{dt}=\int_0^t \alpha(\tau)\Phi(t-\tau)d\tau, \tag{1}$$

where

$$\Phi(t)=\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle_T/\langle v^2\rangle_T. \tag{2}$$

The frequency spectrum $f(\omega)$ is defined by the Fourier transform

$$f(\omega)=\frac{2}{\pi}\int_0^\infty \Phi(t)\cos(\omega t)dt. \tag{3}$$

The time expansion of the correlation function, therefore, reads

$$\Phi(t)=\sum_{n=0}^{\infty}(-1)^n\frac{\langle\omega^{2n}\rangle_{\mathrm{av}}}{(2n)!}t^{2n}, \tag{4}$$

where $\langle\omega^{2n}\rangle_{\mathrm{av}}$ are the even moments of the frequency spectrum.

Equation (1) implies the following recurrence relationship[2] between the even moments of $f(\omega)$ and the even moments $\alpha^{(2k)}$ of the Fourier transform of the kernel $\alpha(t)$:

$$\langle\omega^{2n}\rangle_{\mathrm{av}}=-\sum_{k=1}^{n}\langle\omega^{2(n-k)}\rangle_{\mathrm{av}}\alpha^{(2k-2)}. \tag{5}$$

Conversely, starting from the time expansion (4) and using the recurrence relationship (5) and the identity

$$\int_0^1 x^n(1-x)^m dx=n!m!/(n+m+1)!,$$

one can establish Eq. (1) in a straightforward manner. Equations (1) and (4), therefore, provide two equivalent formulations of the problem, which are connected by the relationship (5). The advantage of using the former approach is that one can guess a reasonable functional form for the kernel $\alpha(t)$, which has the physical meaning of a memory function.

The frequency spectrum $f(\omega)$ can also be evaluated directly from the Laplace transform of the kernel $\alpha(t)$ for imaginary argument. Indeed, by multiplying both members of Eq. (1) by $e^{\pm i\omega t}$ and integrating over time, one finds

$$f(\omega)=-\frac{1}{\pi}\left[\frac{1}{\hat{\alpha}(i\omega)+i\omega}+\frac{1}{\hat{\alpha}(-i\omega)-i\omega}\right], \tag{6}$$

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
[1] B. R. A. Nijboer and A. Rahman, Physica **32**, 415 (1966).
[2] J. A. Tjon, Phys. Rev. **143**, 259 (1966).
[3] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).

where

$$\hat{\alpha}(\pm i\omega)=\int_0^\infty \alpha(t)e^{\pm i\omega t}dt. \tag{7}$$

In particular, one has

$$f(0)=-\frac{2}{\pi}\left[\int_0^\infty \alpha(t)dt\right]^{-1}. \tag{8}$$

One sees immediately from Eq. (1) that, when $\alpha(t)$ is a delta function, $\Phi(t)$ is an exponentially decaying function corresponding to the motion of a particle governed by the Langevin equation. On the other hand, if $\alpha(t)$ is a constant, $\Phi(t)$ is an oscillatory function of time corresponding to the case of an Einstein oscillator. Thus the two limiting cases are contained in Eq. (1) for appropriate choices of the memory function. A simple and reasonable choice for the memory function in a liquid, which leads to the two limiting cases for appropriate choices of the parameters, is a Guassian form,

$$\alpha(t)=-Ae^{-Bt^2}. \tag{9}$$

We note that the adoption of an exponentially decaying memory function is not consistent with the relationship (5), since only the zeroth moment of its Fourier transform exists. However, this form of the kernel will become correct at large time.[3]

For a Gaussian kernel, the frequency spectrum $f(\omega)$ tends to zero at high frequencies as $\omega^{-2}\exp(-\omega^2/4B)$. On the other hand, at small frequencies $f(\omega)$ has the form

$$f(\omega)=f(0)\left\{1+\frac{\omega^2}{4B}\left[1-\frac{16}{\pi}\left(\frac{B}{A}-\frac{1}{2}\right)^2\right]\right\}. \tag{10}$$

Therefore, $f(\omega)$ will have a positive slope in this limit

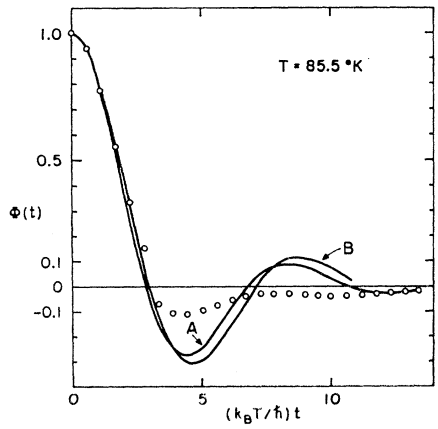

FIG. 1. Velocity autocorrelation in liquid argon at 85.5°K. Curve A: $\langle\omega^2\rangle_{\rm av}=50\times10^{24}$ sec^{-2}, $D=1.88\times10^{-5}$ cm^2 sec^{-1}. Curve B: $\langle\omega^2\rangle_{\rm av}=45\times10^{24}$ sec^{-2}, $D=1.88\times10^{-5}$ cm^2 sec^{-1}. The circles are from B. R. A. Bijboer and A. Rahman, Ref. 1.

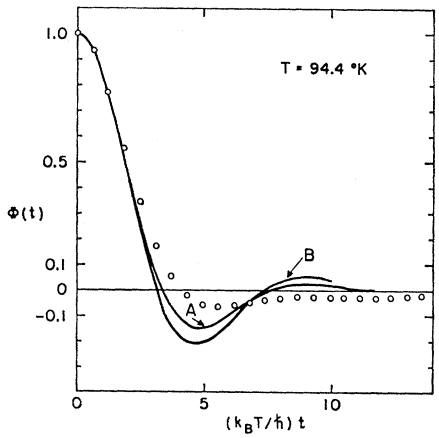

FIG. 2. Velocity autocorrelation in liquid argon at 94.4°K. Curve A: $\langle\omega^2\rangle_{\rm av}=55\times10^{24}$ sec^{-2}, $D=2.43\times10^{-5}$ cm^2 sec^{-1}. Curve B: $\langle\omega^2\rangle_{\rm av}=55\times10^{24}$ sec^{-2}, $D=2.19\times10^{-5}$ cm^2 sec^{-1}. The circles are from A. Rahman, Ref. 4.

if the parameters satisfy the condition

$$0.057\leqslant B/A\leqslant 0.943. \tag{11}$$

The parameters A and B of the Gaussian kernel can be fixed from experimental data by means of Eq. (5) for $n=1$ and of Eq. (8). These give

$$A=\langle\omega^2\rangle_{\rm av} \tag{12}$$

and

$$B^{1/2}/A=\tfrac{1}{4}\pi^{3/2}f(0). \tag{13}$$

Now,

$$\langle\omega^2\rangle_{\rm av}=(1/3M)\int g(r)\nabla^2\varphi(r)d\mathbf{r} \tag{14}$$

and

$$f(0)=2MD/\pi k_BT. \tag{15}$$

Here, $g(r)$ is the pair distribution function, $\varphi(r)$ is the interatomic potential, M the atomic mass, and D the diffusion coefficient.

III. APPLICATION TO LIQUID ARGON

We have evaluated the velocity autocorrelation function and its frequency spectrum for liquid argon at 85.5 and 94.4°K, using the data of Rahman.[1,4] These are $\langle\omega^2\rangle_{\rm av}=50\times10^{24}$ sec^{-2} [This value should be preferred to the other values reported in Ref. (1) (A. Rahman, private communication).] and $D=1.88\times10^{-5}$ cm^2 sec^{-1} at 85.5°K, and $\langle\omega^2\rangle_{\rm av}=55\times10^{24}$ sec^{-2} and $D=2.43\times10^{-5}$ cm^2 sec^{-1} at 94.4°K. We have also investigated the effects of small changes (by $\pm10\%$) in these numerical values. The results are presented in Figs. 1 to 4, together with the results obtained in the numerical experiments of Rahman.[1,4,5]

[4] A. Rahman, Phys. Rev. **136**, A405 (1964).
[5] A. Rahman, J. Chem. Phys. **45**, 2585 (1966).

The present approach clearly reproduces semiquantitatively some of the features of Rahman's results. Thus the velocity autocorrelation function becomes negative at approximately the correct time and has a well-defined minimum; it reaches, however, a deeper negative value and undergoes some additional oscillations of small amplitude. Small changes in the parameters do not affect these features markedly. The theoretical frequency spectrum has a peak in approximate correspondence to the shoulder in Rahman's spectrum, and the high-frequency tail of the spectrum is also approximately reproduced. The low-frequency peak in Rahman's spectrum is missed entirely. Small changes in the parameters affect markedly the height of the peak and, to a lesser extent, its position and the high-frequency tail. A decrease in the diffusion coefficient or in the second moment of the spectrum heightens and narrows the peak in $f(\omega)$ and strengthens the oscillations in $\Phi(t)$; this behavior is consistent with the analysis given in Sec. II.

Our results at 94.4°K, for the values of the parameters quoted above, can be compared with the results obtained by Berne *et al.*,[3] at the same temperature and for the same values of the parameters, but with an exponential kernel. The curves for $\Phi(t)$ and the broad features of $f(\omega)$ are essentially the same. The peak in $f(\omega)$ obtained with a Gaussian kernel is, however, lower and more spread out.

We have also evaluated $\Phi(t)$ and $f(\omega)$ for values of B/A just outside the bounds (11). For small values of this ratio $f(\omega)$ has a very high and narrow peak, and $\Phi(t)$ undergoes many slightly damped oscillations; the particle is clearly being described as an Einstein oscillator with a very small damping. For large values of B/A $f(\omega)$ decreases continuously from its value at zero frequency, but $\Phi(t)$ still undergoes some strongly damped oscillations. Substantially larger values of B/A are necessary to completely eliminate the oscillations.

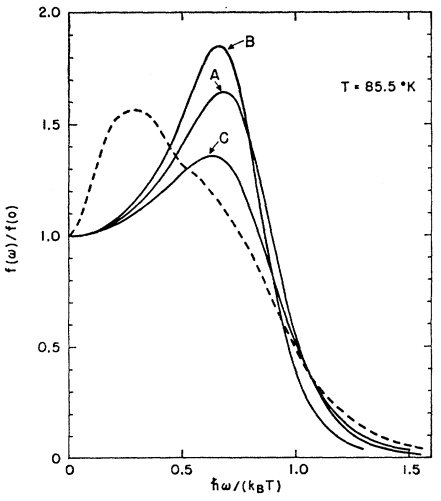

FIG. 3. Frequency spectrum of velocity autocorrelation in liquid argon at 85.5°K. Curves A and B: data as in Fig. 1. Curve C: $\langle\omega^2\rangle_{av}=50\times10^{24}$ sec^{-2}, $D=2.07\times10^{-5}$ cm^2 sec^{-1}. The broken curve is from A. Rahman, Ref. 5.

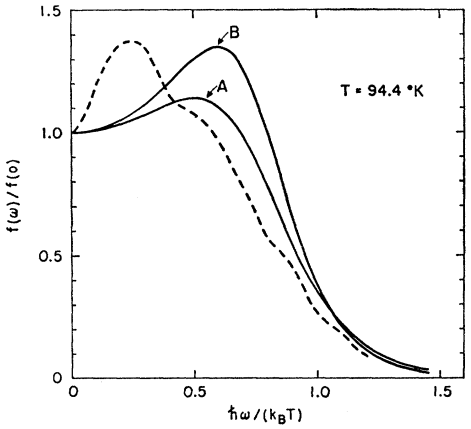

FIG. 4. Frequency spectrum of velocity autocorrelation in liquid argon at 94.4°K. Curves A and B: data as in Fig. 2. The broken curve is from A. Rahman, Ref. 4.

IV. CONCLUDING REMARKS

While the present approach clearly represents a substantial improvement in the description of the velocity autocorrelation over the use of the Langevin picture or of a truncated time expansion, it is also clear that the use of a simple memory function oversimplifies the problem. The motion of a particle in a liquid involves a diffusive component as well as a damped vibratory component; the former contributes mostly to the low-frequency part of the spectrum while the latter is expected to lead to a peak in the region of the shoulder in Rahman's spectrum.[5,6] By fitting the parameters of the kernel to the diffusion coefficient and to the second moment of the spectrum one is taking into account both components in an approximate manner. Our comparison with Rahman's results suggests that the present approach is actually giving more weight to the second component, and may, therefore, be describing the liquid as more "solidlike" than it really is. A better description could be developed in this framework by using a more complicated kernel, at the expense of increasing the number of parameters in the model.

ACKNOWLEDGMENT

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[6] K. S. Singwi, Physica **31**, 1257 (1965).