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Computer studies of Brownian motion in a Lennard-Jones fluid: The Stokes law

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Molecular dynamics calculations have been carried out on a system of identical particles interacting through a Lennard-Jones potential containing a heavy test particle. It is shown that the autocorrelation function of the total force can be used to compute the friction constant, if an appropriate cutoff is introduced. In the limit of large mass and density, the test particle behaves as a Brownian particle, with a friction constant that is mass independent and obeys the Stokes law.

This paper is devoted to the study of Brownian motion by means of molecular dynamics calculations. In particular, we will be concerned with a system of identical particles containing a heavy test particle. Our interest in this problem was motivated by the following considerations. The stochastic motion of a particle in a fluid can be described by the Langevin equation

$$M\frac{d\mathbf{V}(t)}{dt} = -\xi\mathbf{V}(t) + \mathbf{F}'(t)\,, \tag{1}$$

where M and $\mathbf{V}(t)$ are the mass and the velocity of the particle, ξ is the friction constant, and $\mathbf{F}'(t)$ is some random force with zero mean average that is usually assumed to be Gaussian. The first microscopic expression for ξ was proposed by Kirkwood,[1] and had the general structure of a time correlation formula

$$\xi = \frac{1}{3K_B T}\int_0^{\tau_0} d\tau\, \langle\, \mathbf{F}(\tau)\cdot\mathbf{F}(0)\rangle\,, \tag{2}$$

where K_B is the Boltzmann constant, T is the temperature of the system, the angular brackets denote equilibrium ensemble average, and $\mathbf{F}(\tau)$ is the total force exerted on the Brownian particle by the fluid. The upper limit of the integral τ_0 is not specified by the theory. It cannot be replaced by infinity, because in this limit the whole integral vanishes. As it was remarked by Zwanzig,[2] the main implication of this fact is that physical intuition is required when using expression (2).

On the other hand, using projection operator methods it is possible to derive[2,3] an exact formal equation for the evolution of the velocity of the Brownian particle:

$$M\frac{d\mathbf{V}(t)}{dt} = -\int_0^t d\tau\, K(\tau)\,\mathbf{V}(t-\tau) + \mathbf{F}^*(t)\,, \tag{3}$$

where

$$K(\tau) = \frac{1}{3K_B T}\langle \mathbf{F}^*(\tau)\cdot\mathbf{F}^*(0)\rangle \tag{4}$$

and $\mathbf{F}^*(t)$ is a "projected" force having the properties

$$\langle\mathbf{F}^*(t)\rangle = 0, \quad \langle\mathbf{F}^*(t)\mathbf{V}(0)\rangle = 0\,,$$
$$\mathbf{F}^*(0) = \mathbf{F}(0)\,. \tag{5}$$

The particular case of a Brownian particle much heavier than the surrounding particles of the fluid has been studied by Lebowitz and Rubin,[4] Lebowitz and Resibois,[5] Zwanzig,[6] and many others after them. They found that in the limit

$$\gamma \equiv \left(\frac{m}{M}\right)^{1/2} \ll 1\,, \tag{6}$$

where m is the mass of the fluid particles, the friction coefficient is given by

$$\xi = \int_0^\infty d\tau \lim_{\gamma\to 0} K(\tau) \tag{7}$$

$$= \frac{1}{3K_B T}\int_0^\infty d\tau \lim_{\gamma\to 0}\langle\mathbf{F}(\tau)\cdot\mathbf{F}(0)\rangle\,. \tag{8}$$

In the last expression the time correlation function must be evaluated in a reference system with the Brownian particle fixed in space. The difference between this correlation function and the one appearing in Eq. (2) must be noticed.

Hauge and Martin-Löf[7] have derived the Langevin equation using fluctuating phenomenological hydrodynamics, and they get as a necessary condition for the validity of Eq. (1) that the density of the fluid must be small as compared with the density of the Brownian particle, i.e.,

$$\gamma' \equiv \left(\frac{\rho_f}{\rho_B}\right)^{1/2} \ll 1\,. \tag{9}$$

Of course, conditions (6) and (9) are equivalent if M is the only big parameter in the problem, although the distinction between them can be significant in practice.[7] A careful study of the Brownian motion, starting from the Liouville equation and using perturbation methods[8] as shown that *both* conditions, (6) and (9), are needed to guarantee the validity of Eq. (8).

Beyond the formal theories, there is still the problem of explicitly evaluating the friction constant for a given system. It is usually acknowledged that one can use the familiar Stokes law

$$\xi = c\pi\eta R\,, \tag{10}$$

where η is the shear viscosity of the fluid, R the radius of the Brownian particle, and c a constant factor which is equal to 6 for the "stick" boundary conditions and 4 for the "slip" boundary conditions. However, as far as we are aware of, the only satisfactory derivations of Eq. (10) correspond to a *macroscopic* sphere moving in a fluid. Recent work by van Beijeren and Dorfman,[9] who use kinetic theory to describe the fluid, is shedding some light on this problem.

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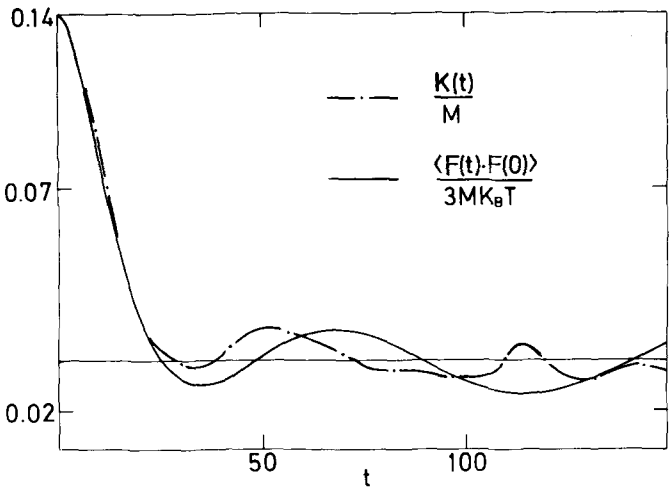

FIG. 1. The memory function and the correlation function of the total force for the case $M = 50\ m$ and $\sigma^*_{fB} = 1.5$. Time is in units of $h = 10^{-14}$ s.

Three of the main questions we have analyzed with our computer experiments are the following:

(1) The possibility of using Eq. (2) to calculate the friction constant ξ. This expression is simpler than the others because it contains the real total force acting on the Brownian particle. Lagar'kov and Sergeev[10] claim that in the approximation in which Eq. (8) holds, the friction constant can also be found from Eq. (2) with τ_0 being the smallest time verifying

$$\langle \mathbf{F}(t) \cdot \mathbf{F}(t+\tau_0) \rangle = 0. \tag{11}$$

(2) The relevance of the conditions (6) and (9). Some study in this direction has been carried out by Bishop and Berne[11] who showed, for a special monodimensional system, that $K(\tau)$ becomes mass independent when γ is small enough.

(3) The validity of the Stokes law (10) to describe the experimental data. Prior work in this direction will be discussed later on.

We now briefly describe the model and the method we have used. The model consists of 863 identical particles and a test particle whose mass and size have been modified in the different experiments. The particles interact via a pairwise, additive, truncated Lennard-Jones potential. As usual we will use reduced units in which σ_{ff}, ϵ, and $(m\sigma_{ff}^2/48\epsilon)^{1/2}$ are taken as units of length, energy, and time, respectively. Here σ_{ff} and ϵ are the Lennard-Jones parameters characterizing the interaction between equal particles. For the interaction of the test particle with the other particles we use the same value of ϵ but the parameter σ_{fB} is determined by the Lorentz rule

$$\sigma_{fB} = \frac{\sigma_{ff} + \sigma_{BB}}{2}\ , \tag{12}$$

where σ_{BB} is the parameter corresponding to the test particle. We have used periodic boundary conditions and the potential has been truncated at a distance 2.5 σ^*_{ij}, where the star indicates reduced units. In all the cases the density and temperature of the system were $n^* = 0.6$ and $T^* = 2.95 \pm 0.05$.

The memory function $K(\tau)$ can be calculated from the equation

$$\partial_t \Psi(t) = -M^{-1} \int_0^t d\tau\, K(\tau)\, \Psi(t-\tau)\,, \tag{13}$$

where $\Psi(t)$ is the velocity autocorrelation function of the test particle. This relation follows from Eqs. (3) and (5). Once $K(\tau)$ is known, the friction constant is given by Eq. (8). Nevertheless, this procedure has the drawback that, in addition to inverting Eq. (13), we have to consider the evolution of the system during very long periods of time. These difficulties are not present in Eq. (2), because the total force $\mathbf{F}(\tau)$ is given directly by the molecular dynamics data. Thus, we have compared the memory function per unit of mass $K(\tau)/M$ computed from Eq. (13) with $(3MK_BT)^{-1}\langle \mathbf{F}(\tau) \cdot \mathbf{F}(0) \rangle$ for different values of M and σ_{BB}. Figure 1 shows both functions for the case $M/m = 50$ and $\sigma^*_{fB} = 1.5$. We see that they behave in a similar way for small times but, when the time increases, $K(\tau)$ fluctuates faster and with smaller amplitude than the total force autocorrelation function. The area under the latter up to its first zero is equal to 0.055 in reduced units. On the other hand, the area under $K(\tau)$ up to a time 40 h, including the initial decay and the first region of negative contribution, also gives 0.055. If we extend the integral up to 109 h, now including also the next oscillation, we get 0.058. Finally upon adding another oscillation the re-

TABLE I. Mass and radius dependence of ξ, given by Eq. (2). The values of the parameters $\gamma = (m/M)^{1/2}$ and $\gamma' = (\rho_f/\rho_B)^{1/2}$ are also indicated.

σ_{BB}	$\frac{M}{m} = 20$ ($\gamma = 0.22$)		$\frac{M}{m} = 50$ ($\gamma = 0.14$)		$\frac{M}{m} = 75$ ($\gamma = 0.12$)		$\frac{M}{m} = 100$ ($\gamma = 0.1$)	
σ_{ff}	γ'	ξ	γ'	ξ	γ'	ξ	γ'	ξ
1	0.125	77.9	0.079	60.5	0.065	74.9	0.056	64.3
1.2	0.165	101.4	0.104	103.0	0.085	99.1	0.074	102.5
1.4	0.207	117.7	0.131	138.2	0.107	138.1	0.093	125.5
1.8	0.303	140.8	0.192	142.9	0.156	141.8	0.136	148.6
2	0.355	210.4	0.224	131.0	0.183	167.9	0.158	159.0
2.2			0.258	177.8	0.211	189.3	0.183	164.8
2.4			0.295	170.6			0.209	209.2
2.6							0.235	206.2

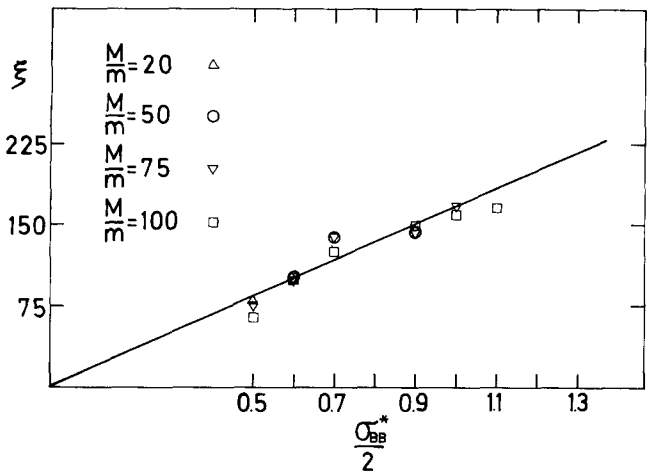

FIG. 2. Radius dependence of the relevant values of ξ obtained by using Eq. (2).

sult is 0.054. We conclude that it is plausible to assume that future contributions also cancel and the total area under $K(\tau)$ is approximately 0.054. Similar results hold for all the cases we have studied. As a consequence, Eq. (2) with τ determined by Eq. (11) can be considered as a good approximation for the integral from zero to infinity of $K(\tau)$. This answers question (1).

Using expression (2) we have computed the value of ξ for different values of σ_{BB}/σ_{ff} and M/m. The results are given in Table I, where the values of γ and γ' are indicated for each case. Based on these data we get the following conclusions:

(i) For a given value of σ_{BB}/σ_{ff}, the value of ξ becomes independent of the mass beyond a given value of γ. This result confirms and extends the result previously obtained by Bishop and Berne with their monodimensional model.[11]

(ii) The value of γ for which ξ reaches a stationary value is not always the same. For instance, for $\sigma_{BB}/\sigma_{ff} \geq 1.4$ and $\gamma = 0.22$ the values of ξ are rather different from the ones obtained for smaller values of γ, i.e., bigger values of M. (The value corresponding to $\sigma_{BB}/\sigma_{ff} = 1.8$ seems to be accidental.)

(iii) The above behavior can be explained if we take into account the parameter γ' defined in Eq. (9). The anomalous values correspond to values of $\gamma' > 0.2$. We can conclude that only for smaller γ' the Langevin description (i) is valid.

So, when $\gamma \ll 1$ and $\gamma' \ll 1$ we have a value of ξ that looks mass independent. This answers question (ii).

In Fig. 2 the significant values of ξ, i.e., those corresponding to $\gamma' < 0.2$, are represented as a function of $\sigma^*_{BB}/2$. They show a linear dependence, qualitatively agreeing with Stokes' law (10). To put this result on a more quantitative basis, we need the shear viscosity of the fluid at the conditions we are considering. Using again molecular dynamics techniques and applying the time correlation expression we have found that

$$\eta^* = 7.7 \pm 1.5. \tag{14}$$

As the particles in the system are not hard spheres but they interact through a Lennard-Jones potential, there is no well-defined radius for the Brownian particle. We define an effective radius as $\lambda\sigma_{BB}/2$ and determine λ by assuming that Stokes' law holds in the form

$$\xi = 4\pi\eta\lambda \frac{\sigma_{BB}}{2}. \tag{15}$$

When this is done, one finds the value $\lambda = 1.7 \pm 0.4$, that is quite near unity. Then, the Stokes' law gives a good description of our system. This completes our program.

The concept of effective radius has been used by Verlet[12] to describe the equilibrium properties of a fluid consisting of identical particles. If we extrapolate his results to a system of particles at the temperature and density we are considering, it is roughly found that $\lambda_V = 0.97$. The difference between this value and the one we have got can not be considered as surprising. The idea, when introducing the effective radius, is to incorporate in a hard-sphere description the effects coming from the attractive part of the potential, and these effects depend quite a lot on the particular physical phenomenon under consideration. In this sense, we make the conjecture that the attractive part of the potential must bring about an increase in the friction constant, because it contributes to the slowing down force that the fluid exerts on the Brownian particle.

Now we want to refer to some results in a related problem. Using the Stokes' law, Einstein[13] derived a relation between the diffusion coefficient D for Brownian particles in a fluid and the viscosity of the fluid:

$$D = \frac{K_B T}{c\pi\eta R}. \tag{16}$$

A number of authors have used self-diffusion and viscosity data for simple fluids to test the validity of this relation, known as the Stokes–Einstein law. The data have been obtained from experiments[14] as well as from molecular dynamics calculations.[15] Their conclusion is that Eq. (16) holds over a remarkably wide range[16] with c corresponding to slip boundary conditions, i.e., $c = 4$.

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