Classical, Microscopic, Liquid Poisson Oscillator

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We report on the atomic dynamics of a simulated Lennard-Jones liquid confined in a plane micropore when the density profile approximates to two dense slabs with a low-density region between. The atomic motion parallel to the slit is essentially diffusional. The atomic motion across the slit comprises statistically independent, very fast, but infrequent, jumps of atoms from one slab to the other, a novel observation in this field. These atomic dynamical events accurately obey Poisson statistics but are consistent with the static density profile in the gap. This system is proposed as a model classical (as opposed to quantum mechanical) microscopic physical system which obeys Poisson statistics.

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The density profile of microscopic liquids in confined geometry has been widely studied for many years by the method of computer simulation (for an excellent account, see Ref. 1), including work from this laboratory on liquids confined between plane walls[2] and inside spherical containers.[3,4]

The *dynamics* of atomic motion in liquids in microscopic confinement has been less studied until recently, e.g., 4 pages of 400 in Ref. 1. Almost all of this work includes attempts to explain the atomic motion in terms of diffusion concepts and/or modifications of classical diffusional behavior.[5–13] We shall use a different and novel approach.

In this paper we report on simulations of a Lennard-Jones (LJ) liquid for which the potential between atoms with centers r apart is

$$\phi(r)=\begin{cases}4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], & r<r_c=3.0\sigma,\\ 0, & r>r_c,\end{cases}$$

where ε is an energy parameter (the attractive energy) and σ a length parameter (the atomic diameter). The liquid is constrained to remain between the two plane walls by an external potential,

$$\phi_e(z)=\phi_w(z)+\phi_w(w-z),$$

where

$$\phi_w(z)=\tfrac{1}{9}\,\varepsilon(\sigma/z)^9;$$

i.e., the external potential is repulsive and is infinite for $z\le 0$ and $z\ge w$, so w is the distance between the "walls." The potential $\phi_w(z)$ is the repulsive part of the conventional "summed" LJ 12-6 potential (see Ref. 1, p. 83). Most simulations have been for one wall or when w is large enough that there is an almost homogeneous liquid in the central region (e.g., in Ref. 13, $w=15\sigma$) but there is substantial variation in the liquid density near the walls where it "oscillates" with a period of about σ.

Atomic motion parallel to the walls is effectively unrestricted. For times larger than the velocity autocorrelation time τ_v, the motion corresponds closely to classical two-dimensional diffusion. The mean-squared distance diffused in the plane determines the diffusion coefficient D through

$$\langle x^2+y^2\rangle=4D_{\parallel}t+\gamma(z_0).$$

This is true wherever the atom starts from, although that may affect the value of γ, since it eventually samples the whole cross section between $z=0$ and w, and the density variation is of no direct relevance.[8,13]

Atomic motion perpendicular to the walls cannot be described by diffusion, except approximately for atoms in the central quasihomogeneous region—if there is one—and for limited elapsed time. This is true even allowing for the confining boundary conditions. In fact, it is formally shown in Ref. 13 that the diffusion equation, even with a tensor, space-dependent diffusion coefficient, corresponds to a uniform equilibrium density, which is manifestly not the case for a confined liquid. If there is not even an approximately uniform density region within the liquid confined by parallel walls, then, if $w\gg\sigma$ (mesopores), we have suggested elsewhere[13] that the transverse atomic motion is quite well described by a rate-equation formalism which is a generalization of a diffusional one.

We report on the atomic motion in a liquid between plane parallel repulsive walls which are a distance of only a few σ apart (micropores), in fact, $w=3.0\sigma$. The fluid is then very strongly perturbed by the external potential everywhere. In this case even a rate-equation approach is inadequate. The density profile $\rho(z)$ is shown in Fig. 1. Also shown is the density profile for the corresponding perfect gas with the same number of atoms for which

$$\rho(z)\propto\exp[-\phi_w(z)/k_BT].$$

The number of particles N_p is 1020 and the total energy per particle was -2ε. The lateral replicating dimen-

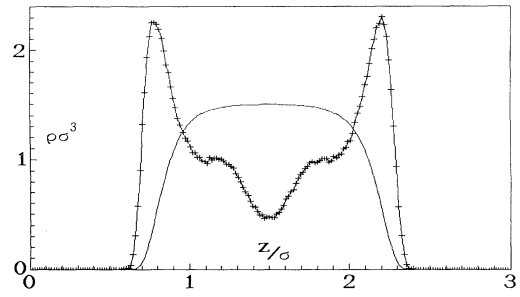

FIG. 1. The density profile for a Lennard-Jones liquid between repulsive walls at $z=0$ and 3.0σ. The curve without points is for the corresponding perfect gas.

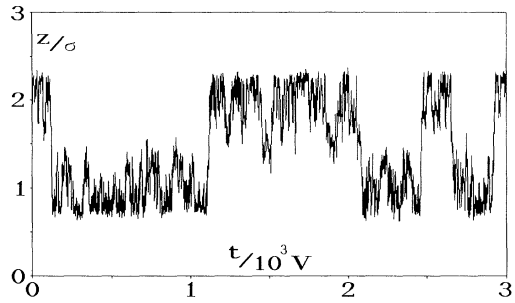

FIG. 2. The transverse coordinate z of one atom as a function of time for an arbitrarily chosen initial time. Note that the duration of a jump is much shorter than the time between jumps although the trajectory is by no means free.

sions $L_x=L_y=L$ were fixed so that the mean overall density was the same as in Ref. 13, $\rho_m=0.6451\sigma^{-3}$, so that $L=22.96\sigma$. After equilibration the temperature was $T=0.854\varepsilon/k_B$, which for the corresponding homogeneous coexisting liquid is a typical liquid temperature for the LJ 12-6 fluid.[14]

The unit of time is the Verlet[15] unit $V\equiv(m\sigma^2/48\varepsilon)^{1/2}$, where m is the mass of the atom. For the conventional values used for argon $V=3.1\times10^{-13}$ s. In order to ensure an accurate computation we chose the time step $\Delta t=0.02V$, in our fifth-order Gear predictor-corrector algorithm, which is less than $\tau_v/20$.

We, therefore, have a situation where the confined liquid takes the approximate conformation of two slabs of thickness about 0.5σ with a rather low density between; at the midpoint it is $0.48\sigma^{-3}$. A rather similar system has been studied previously[8] but for a different wall potential and not interpreted in the way we do in the following.

The atomic motion in a direction parallel to the constraining planes is diffusional. Fitting by the equation above we find that $D_{\parallel}=46\times10^{-4}\sigma^2/V$. This is a low value compared with that in the homogeneous coexisting liquid at the same temperature when $\rho=0.78\sigma^{-3}$ for which, using published data,[16] we estimate that $D\simeq100\times10^{-4}\sigma^2/V$. On the other hand, the fluid density is very high in the layers, about 1.5, say, and roughly $D\propto\rho^{-2}$ which gives a very rough estimate $D\simeq30\times10^{-4}\sigma^2/V$, so the observed value is much as to be expected. It was in part the low diffusion constant encountered in the slabs, and the consequent small values of τ_v, which caused us to use the unusually small value of Δt. Together with the well-known very slow equilibration of inhomogeneous systems which demands very long elapsed simulation times, this made the simulations very expensive to perform even using seventeen T800 transputers in parallel. Typically the number of production steps was 150000, i.e., $T=3000V$. The actual computing time per time step was 1.8 s.

For the transverse, z, motion of the atoms it is manifestly ridiculous to think in terms of diffusion, or, indeed, even of a rate-equation approach.[13] We have studied the transverse motion of each of the 1020 atoms for the simulation period T. We recorded the actual motion for eight atoms chosen at random and the times of the transitions for all 1020 atoms. A plot of the z position of one atom as a function of time is shown in Fig. 2 and is typical of the behavior of any one of the 1020 atoms.

We see that the atom tends to remain in one layer or the other and makes sudden rapid jumps from one to the other. As a closer inspection shows, the atom suffers a small number of collisions with other atoms during the transition but, by and large, once it clearly starts across the gap it gets across. The mean time of transition, $\langle t_t\rangle$, is less than 10% of the average time between transitions, $\langle t\rangle$, so that the jumps either way can be regarded as discrete "events" at well identified times. We assumed that if an atom got to $z=1.8\sigma$ when transitting to the right and $z=1.2\sigma$ when transitting to the left, it had completed a transit and this was counted by the algorithm as an event.

We have evaluated the various mean times given below for 33941 events in 1020 trials,

$$\langle t_t\rangle/V=27.5,\quad \langle t\rangle/V=327,$$

and

$$\langle t^2\rangle/\langle t\rangle^2=2.08,\quad \langle t^3\rangle/\langle t\rangle^3=6.50,\quad \langle t^4\rangle/\langle t\rangle^4=27.1.$$

The ratios above immediately establish, with little doubt, that the probability distribution of the events is Poisson[17,18] for which $\langle t^n\rangle/\langle t\rangle^n=n!$; i.e., the above three numbers, in the limit of an indefinitely large number of events, would be 2, 6, and 24, respectively.

This is why we call our system a liquid Poisson oscillator.

The above moment method of determining the statistics of events is never used, as far as we are aware, in the analysis of physical systems. This is presumably because of, first, the difficulty and expense of measuring and recording the actual times of the events or even of the time intervals t (as remarked by Rutherford, Geiger, and

TABLE I. Conventional test for Poisson statistics. $w=3.0\sigma$, $T=2995.4V$, $N=N_p=1020$.

k	N_k Simulation	Poisson
0	0	0.2
1	1	1.3
2	8	5.9
3	16	17.4
4	45	38.2
5	72	67.4
6	81	98.9
7	123	124.4
8	146	137.0
9	139	134.1
10	120	118.1
11	96	94.6
12	58	69.4
13	42	47.1
14	27	29.6
15	22	17.4
16	15	9.6
17	1	5.0
18	3	2.4
19	4	1.1
20	0	0.5
21	1	0.2
>22	0	0.1

Bateman[19]). This is not a real problem for the computer model in these days of massive storage facilities. Second, the interval T has to be long enough that $T/\langle t\rangle \gg 1$. This is usually a tedious requirement experimentally, but it is not too onerous for us. However, we also perform the conventional analysis. The best known such experiment is Rutherford, Geiger, and Bateman's measurements of radioactive decay by α-particle emission (see Ref. 19, p. 149 of Ref. 17, and Ref. 18). The other well-known example is the statistics of the emission of photons.[20,21] It may be noted that both these are quantum mechanical which is peculiarly partial to events in the strict sense. The number of particles (events) is recorded for a large number N of identical intervals of time T. Then if exactly k events are found N_k times, the mean number of events is

$$\langle k\rangle=\sum_{k=0}^{\infty} kN_k/N\,,$$

and if the statistics are Poisson, the expected number of times that exactly k events are observed in T, for $N\rightarrow\infty$, is given by

$$N_k=N\langle k\rangle^k\exp(-\langle k\rangle)/k!\,.$$

$\langle k\rangle$ is usually a small, but not too small, number. This happens to be so for our time intervals. For the particular sample in Fig. 2, $k=6$ and, in fact, $\langle k\rangle=8.18$. The observed values of N_k are compared in Table I with the expected values for an infinite Poisson process. This increases our confidence that the process is rather accurately Poisson.

As is well known,[17,18] a Poisson distribution corresponds to the probability p of an individual event being vanishingly small, but that there are a very large number of attempts n in the time interval available and that np, called $\langle k\rangle$ above, is of moderate size. The physical situation which led us to expect a Poisson distribution in our system is that a particular atom has a very small probability p of both being in a suitable position, say, on the inner side of one of the two main density peaks, *and* having a suitably high z component of velocity in the correct direction so as to cross the gap without serious hindrance by other atoms in the gap. It makes many attempts n when the conditions happen to be unfavorable. We can use the events in T for all the N_p atoms because they are effectively statistically independent.

Nevertheless, at any given moment quite a large number of atoms are crossing the gap somewhere in the plane of area L^2. In fact, there are some 100 atoms in the gap at any moment. The mean density of atoms in the gap, assumed to be of width g, is given by

$$\rho_g=(\langle t_t\rangle/\langle t\rangle)N_p/gL^2\,.$$

Assuming that $g=\frac{1}{2}\sigma$ (see Fig. 1) the formula yields the value $\rho_g=0.4\sigma^{-3}$. This is as consistent as one could reasonably expect with the observed density in the gap; see Fig. 1. Thus the atomic *dynamics* is consistent with the static property, the density profile.

Explaining the values of the parameters observed in terms of the theory of confined liquids is, of course, a more difficult matter.

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