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Diffusion in a Two-Dimensional System

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The velocity autocorrelation in a two-dimensional Lennard-Jones system is obtained by the molecular-dynamics method. At moderate densities the autocorrelation function decays slowly, proportional to the inverse time whereas it decays rapidly at high density. The model is compared with monolayers of methane adsorbed on the basal plane of graphite. The influence of the substrate on the diffusion is small and the calculated and experimentally obtained diffusion constants agree at high density.

Molecular-dynamics calculations of the velocity autocorrelation function (v.a.c.) in a two-dimensional system of hard disks¹ show that the v.a.c. decays inversely proportional to the time at least at intermediate densities. This "non-Langevin" behavior can lead to a logarithmic divergence in the expression for the diffusion coefficient for the two-dimensional system.² Recently there has been published³ some experimental data for diffusion in monolayers of methane on the basal plane of graphite. The diffusion constants were obtained from quasielastic scattering of neutrons on the monolayers and assuming Brownian movements of the interacting methane molecules. The conclusion from the experiments was that the monolayers behaved "two dimensionally" and in accordance with other experimental data of monolayers of simple molecules adsorbed on solid surfaces.⁴ This film can be described by a two-dimensional Lennard-Jones system^{5,6} and the purpose of the present calculations is to analyze the decay in this system of the v.a.c. and to compare the resulting diffusion with the experimental data from Ref. 3.

The molecular-dynamics calculations are performed for two basic systems of $N = 256$ and $N = 576$ Lennard-Jones particles, respectively, and with periodic boundaries. The program is written in double precision and the calculations are carried out using the Verlet algorithm⁷ with a reduced-time step $\Delta t^* = (\Delta t)(\epsilon_{gg}/m)^{1/2}2^{-1/6}\sigma_{gg}^{-1} = 0.005$, where ϵ_{gg} and σ_{gg} are the potential parameters in the Lennard-Jones potential for the pair interaction between the particles in the two-dimensional system and m is the mass of the particles. We have compared the calculations with the experimental data for methane and used the values⁸ $\sigma_{gg} = 3.783 \text{ \AA}$ and $\epsilon_{gg}/k = 148.9 \text{ K}$. With these values of the energy parameters the reduced-time step corresponds to $7.6 \times 10^{-15} \text{ s}$, which is found to be sufficient.

The present calculations are performed with and without an external potential, $u_1(\vec{r})$, which simulates the underlying solid substrate. Steele⁹ has derived an expression for $u_1(\vec{r})$ as a Fourier series in multiple of the reciprocal-lattice vectors \vec{b}_1 and \vec{b}_2 . To second order in the expansion he finds that

$$u_1(\vec{r}) = -2a_1\{\cos(2\pi\vec{b}_1 \cdot \vec{r}) + \cos(2\pi\vec{b}_2 \cdot \vec{r}) + \cos[2\pi(\vec{b}_1 + \vec{b}_2) \cdot \vec{r}]\} \\ + 4a_2\{\cos[2\pi(\vec{b}_1 + 2\vec{b}_2) \cdot \vec{r}] + \cos[2\pi(2\vec{b}_1 + \vec{b}_2) \cdot \vec{r}] + \cos[2\pi(\vec{b}_1 - \vec{b}_2) \cdot \vec{r}]\}, \quad (1)$$

where $\vec{b}_1 = (1, -1/\sqrt{3})/\sigma_{ss}$, $\vec{b}_2 = (0, 2/\sqrt{3})/\sigma_{ss}$, and the carbon-carbon distance, σ_{ss} , in the graphite surface is taken to be 1.42 Å. The constant a_1 and a_2 are complicated functions of the distance to the basal plane of graphite and of the energy parameters, ϵ_{gc} and σ_{gc} , between the adsorbed particles and the carbon atoms in the graphite. The energy parameters, ϵ_{gc} and σ_{gc} , are obtained from the corresponding energy parameters for the carbon-carbon (*c*) interaction and the methane-methane (*g*) interaction using the Lorentz-Berthelot rules. For the carbon-carbon interaction we use $\sigma_{cc} = 3.40$ Å and $\epsilon_{cc}/k = 28$ K.⁹ With these values of the energy parameters the two first coefficients in the expansion are $-2a_1 = -0.02535\epsilon_{gg}$ and $4a_2 = 0.00030\sigma_{gg}$, respectively.

The experimentally obtained diffusion constants are given for different coverages, $\theta = \rho/\rho_{c1}$, of the monolayer of the graphite, where ρ_{c1} is the density at full coverage of the surface. For ρ_{c1} we use the relation $\rho_{c1}\sigma_{gg}^2 \approx 2^{2/3}3^{-1/2}$ for the particles in the monolayer packed in a triangular lattice and have⁵ $\rho\sigma_{gg}^2 = 0.9165\theta$. The diffusion coefficients at the temperature $T = 90$ K, above the critical temperature, are measured at the coverages $\theta = 0.45, 0.7, \text{ and } 0.9$, respectively. Since the external potential must be periodic over the basic system we cannot, with $N = 256$, perform the calculations exactly for these values of θ . The calculations are performed for the reduced densities $\rho\sigma_{gg}^2 = 0.3964, 0.6050, \text{ and } 0.7770$, which correspond to the coverages $\theta = 0.433, 0.660, \text{ and } 0.848$, respectively.

After an initial time of 4000 time steps where the system is temperature calibrated to $T = 90\epsilon_{gg}/k$ K by scaling the velocities, the velocity autocorrelation function, $A(t)$, is obtained from the records of the velocities (stored after every 40 time steps) for the subsequent time interval τ as

$$A(t) = \frac{\langle \sum_i^N \vec{v}_i(\tau') \vec{v}_i(\tau' + t) \rangle}{\langle \sum_i^N \vec{v}_i^2(\tau') \rangle}, \quad (2)$$

where the mean, indicated by the bracket, is performed over the whole time interval τ , as described by Rahman.¹⁰ The diffusion constant D is related to $A(t)$ by²

$$D = \lim_{\tau \rightarrow \infty} \frac{1}{2d\tau} \langle \sum_i^N [\vec{r}_i(\tau) - \vec{r}_i(0)]^2 \rangle \quad (3a)$$

$$= \lim_{\tau \rightarrow \infty} \frac{1}{d} \int_0^\tau dt A(t), \quad (3b)$$

where d is the dimension of the system. The molecular-dynamics program was tested by com-

paring the diffusion constant (for $\rho\sigma_{gg}^2 = 0.7708$, $kT/\epsilon_{gg} = 1.341$) with the corresponding value obtained by Fehder, Emeis, and Futrelle¹¹ and they were found to agree within the statistical error.

In Fig. 1 is shown the result of the calculation for $N = 256$ and for the three different values of the coverages: $\theta = 0.433, 0.660, \text{ and } 0.848$. The system is exposed to the graphite potential given by (1). The three functions are obtained from 9000, 17 000, and 9000 time steps, respectively, and the statistical uncertainties are from 0.005 to 0.01. Thus at the reduced time corresponding to 5×10^{-12} s the uncertainties are larger than or of the same order as $A(t)$. At low coverage the v.a.c. has a long tail, whereas $A(t)$ at the high coverage value are short ranged and with a slope similar to the v.a.c. at high density in three-dimensional systems.¹⁰ Also shown on the figure, with full line, is the Langevin expression for $A(t)$ with the value $D = 13 \times 10^{-5}$ cm² s⁻¹ found in Ref. 3. As can be seen from the figure, $A(t)$ deviates systematically from this expression.

In order to determine the functional form of the tail of $A(t)$, we have, in Fig. 2, plotted $A(t)$ as a function of the reduced inverse time and for the medium coverage $\theta = 0.660$. The circles are for $N = 256$ and without the external potential (1), the triangles are the corresponding values of $A(t)$ when the system is exposed to the external potential. The squares are for a system of $N = 576$ particles and without (1). The values are obtained

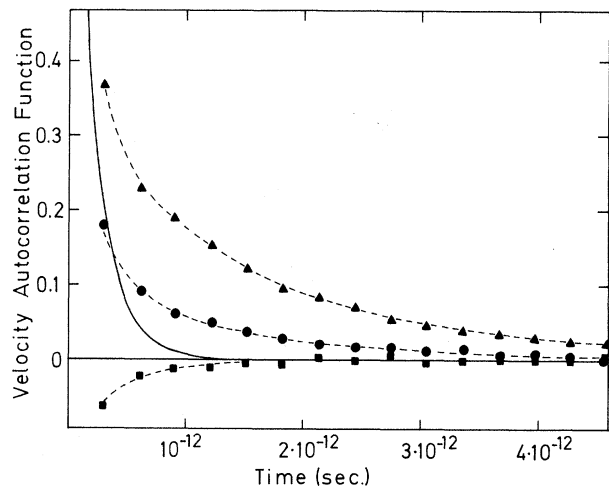


FIG. 1. The velocity autocorrelation function for a two-dimensional Lennard-Jones system on a graphite-like surface. The three sets of data are for the coverages $\theta = 0.43$ (filled triangles), 0.660 (filled circles), and 0.848 (filled squares), respectively. The Langevin-type exponential function is also shown (full line).

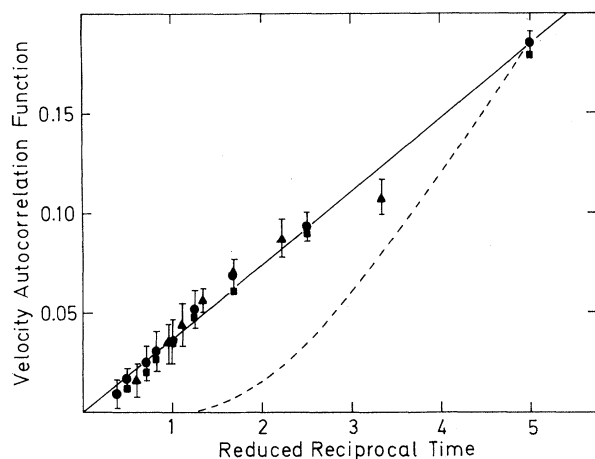


FIG. 2. The velocity autocorrelation function against the reduced reciprocal time for a two-dimensional Lennard-Jones system at medium density ($\theta \equiv 0.660$). The squares and circles are for a system of $N = 256$ particles and with and without an external graphitelike potential. The triangles are for a system of $N = 576$ particles without an external potential. The dashed line is the Langevin expression.

from 17,000, 17,000, and 9,000 time steps, respectively, and the uncertainties are shown by bars. The dashed line is the Langevin exponential form of v.a.c. The molecular-dynamics-calculated $A(t)$ varies proportionally with t^{-1} at least up to 5×10^{-12} s and does not follow an exponential function in this time interval for any value of the diffusion constant. If this functional form exists for longer time, the diffusion constant D , given by (3b), will diverge and indeed D , calculated from the records of the positions and using (3a), increases systematically as τ is increased up to 3×10^{-11} s.

The molecular-dynamics calculations make use of the "periodical-boundary" technique in order to simulate a macroscopic system. The influence on $A(t)$ on the size of the basic system can be determined by varying N , as is done here, and by calculating the time it takes a macroscopic sound wave to traverse the basic system.¹ From the relation for an adiabatic sound wave,

$$c = \left[\frac{C_p}{C_v} \left(\frac{\partial p}{\partial \rho} \right)_T \right]^{1/2} \approx \left\{ \left[1 + k \left(\frac{\partial u}{\partial T} \right)_\rho^{-1} \right] \left(\frac{\partial p}{\partial \rho} \right)_T \right\}^{1/2}, \quad (4)$$

we have estimated the velocity c from the energy per particle $u = kT + \langle u_2(T) \rangle$ and the equation of state $p(\rho)$ for the two-dimensional systems for $\theta \sim 0.660$ and $T = 90\epsilon_{gg}/k$ K to be $1.6(\epsilon/m)^{1/2}$, which corresponds to a traversal time $\sim 2 \times 10^{-11}$ s for the smallest system and (much) larger than the time intervals shown in Figs. 1 and 2. Consistent with this calculation, the autocorrelation functions for the small and the large system agree within the statistical uncertainty, as shown in Fig. 2.

At high coverage $\theta = 0.848$ $A(t)$ is short ranged and the diffusion constant D calculated by (3a) is independent of τ for τ greater than 2×10^{-12} s. The diffusion constants at this density and temperature are found to be 0.0399 and 0.0426, in units of $(\epsilon/m)^{1/2}\sigma_{gg}$ and for the system with and without the external graphite potential, which correspond to 4.2×10^{-5} cm² s⁻¹ and 4.5×10^{-5} cm² s⁻¹, respectively, in the case of CH₄. If we make correction for the lower coverage than that reported in Ref. 3 these values are in agreement with the value $(3.8 \pm 0.4) \times 10^{-5}$ cm² s⁻¹ obtained from a linear interpolation in the experimental values at $\theta = 0.7$ and $\theta = 0.9$.

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