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Many-particle diffusion in continuum: Influence of a periodic surface potential

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Many-particle diffusion in continuum: Influence of a periodic surface potential

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We study the diffusion of Brownian particles with a short-range repulsion on a surface with a periodic potential through molecular dynamics simulations and theoretical arguments. We concentrate on the behavior of the tracer and collective diffusion coefficients $D_T(\theta)$ and $D_C(\theta)$, respectively, as a function of the surface coverage θ. In the high friction regime we find that both coefficients are well approximated by the Langmuir lattice-gas results for up to $\theta \approx 0.7$ in the limit of a strongly binding surface potential. In particular, the static compressibility factor within $D_C(\theta)$ is very accurately given by the Langmuir formula for $0 \leqslant \theta \leqslant 1$. For higher densities, both $D_T(\theta)$ and $D_C(\theta)$ show an intermediate maximum which increases with the strength of the potential amplitude. In the low friction regime we find that long jumps enhance blocking and $D_T(\theta)$ decreases more rapidly for submonolayer coverages. However, for higher densities $D_T(\theta)/D_T(0)$ is almost independent of friction as long jumps are effectively suppressed by frequent interparticle collisions. We also study the role of memory effects for many-particle diffusion. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1467908]

I. INTRODUCTION

The dynamics of Brownian particles in confined geometries, and in 2D in particular, is an important theoretical problem with applications in surface science and colloidal systems. In the ideal case of no external potential, the density dependent diffusion coefficients of 2D hard disk particles have been recently determined using both numerical simulations[1,2] and various theoretical approximations.[2–5] While the single-particle Brownian limit in the ideal case is trivial, no exact analytic results exist for finite densities, however. For adparticles on real surfaces even the single-particle limit becomes nontrivial due to the interactions with the substrate atoms. This leads to complicated many-body effects that manifest themselves through memory effects in the motion of the adparticle.[6,7] In the Markovian limit of a constant friction (delta function in time), there exist analytic solutions for the single-particle diffusion coefficient in various limits.[7,8] In this case, the surface can be described by a periodic adiabatic potential where the adparticles diffuse. When this potential becomes strongly binding, the lattice-gas (LG) picture of single-particle diffusion becomes a good approximation.[8,9] The LG approach has been immensely useful in diffusion studies due to its conceptual simplicity, and for finite coverages there exists a wealth of analytic and numerical diffusion studies for LG models of various systems.[7,8,10–16] However, the range of validity of the LG approximation with regard to the continuum limit has only been examined in the one-particle limit.[9]

An unusual feature of Brownian particles in the 2D ideal continuum case is that the collective diffusion coefficient $D_C(\rho)$ is solely determined by the static compressibility of the system, since the center-of-mass (CM) mobility is strictly independent of the particle density ρ. This result no longer holds when there is an external potential in the system. In fact, in the LG limit, it is an exact result for a Langmuir gas of hard-core particles (with an on-site exclusion interaction only) that $D_C(\theta)$ itself remains independent of the surface coverage θ up to $\theta = 1$.[17] In this case, both the compressibil-

ity of the LG adlayer and its CM mobility depend on θ but cancel out each other.[15] For a Langmuir gas there also exists accurate analytic estimates of $D_T(\theta)$ which is a nontrivial, monotonously decaying function of θ.[10,11]

In this work, our purpose is to study some of the fundamental issues of many-particle diffusion in continuum. To this end, we consider a collection of Brownian particles that mutually interact with a short-range repulsive potential in a separable 2D periodic potential. The interparticle interaction has been chosen to be such that it mimics a hard-core exclusion interaction within each potential minimum. There are two main issues that we address here. The first concerns the range of validity of the LG approximation for many-particle diffusion, and the second the influence of friction. To this end, we first study the density dependence of the tracer and collective diffusion coefficients in the high friction limit, varying the relative strength of the potential amplitude. In this way we can interpolate between the continuum hard disk case studied in detail in Ref. 2, and the LG limit of a strong adsorption potential. The continuum approach also allows us to consider coverages $\theta > 1$, corresponding to the case where particles are added to a system where every actual adsorption site (potential minimum) has already been occupied. To study the effect of friction, we repeat the calculations in the low friction limit and compare the results in both density regimes. Finally, we also study the role of memory effects in many-particle diffusion.

II. THE MODEL

The model system we consider here consists of an ensemble of 2D particles in presence of a periodic surface potential. The particles interact with each other through a strongly repulsive, short-range potential of the form,

$$V(r) = \epsilon \left(\frac{\sigma}{r} \right)^n , \tag{1}$$

where r is the separation between the particles. For n we have chosen here the frequently used value of 12 and ε was chosen to be unity. This allows a direct comparison with previous calculations on a smooth surface.[2] A cutoff at $r_c = 2\sigma$ was used in the simulations. The adiabatic surface potential is explicitly given by

$$V_A(x,y) = V_0 \left(\cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a} \right), \tag{2}$$

where a is the separation between two nearest minima and $2V_0$ is the potential barrier between the minima. The minima of this potential form a square lattice on the surface. Three different values for the barrier were used in the simulations: $V_0 = 0.02$, $V_0 = 0.2$, and $V_0 = 0.3$. The separation, or the lattice constant, a we have chosen to be 2σ so that two particles in neighboring wells interact very little with one another, but repel each other if they try to occupy the same minimum. In this way, for large V_0 the system mimics the Langmuir gas case.

We define the surface coverage θ in the present model as the relative number of particles in the minima. Thus $\theta = 1$ means that there are equally many particles in the system as there are minima. When comparing the results to our previous smooth surface results[2] it is important to notice that θ in the present case is not restricted to values below unity. In fact $\theta = 1.0$ is a rather low density of particles corresponding to $\rho = 0.25$ in units of particles per unit area. The lattice gas model, on the other hand, is of course defined only up to $\theta = 1$.

In the present work, for numerical studies we use a combination of molecular dynamics (MD) and Monte Carlo (MC) simulation techniques. All dynamical quantities here have been computed with MD, while MC sampling has been used to obtain static averages such as the thermodynamic factor described below. The system size used in MD simulations was $L = 100\sigma$, and $L = 240\sigma$ in the MC simulations with periodic boundary conditions in both cases. The details of the simulations are as in our previous work.[2] The equation of motion of each particle in the system is given by the Langevin equation,[18]

$$\frac{d}{dt}\mathbf{p}(t) = -\eta \mathbf{p}(t) + \mathbf{f}(t) + \mathbf{F}(t), \tag{3}$$

where $\mathbf{p}(t) = m\mathbf{v}(t)$ is the 2D momentum of the particle, η is the friction coefficient, t is time, and $\mathbf{f}(t)$ is the total interaction force with the other particles. The mass m was chosen to be unity. The remaining random term $\mathbf{F}(t)$ is the driving force for the motion of the Brownian particles, and it obeys the standard fluctuation-dissipation relation.[18] The equation of motion is integrated using the velocity Verlet algorithm.[18] We have set $k_B T = 0.1$ which means that the ratio of the barrier height to temperature is 0.4, 4.0, and 6.0. For the two latter values the single particle diffusion coefficient $D_0 \equiv D_T(\theta = 0)$ is well within the activated Arrhenius regime, and the motion of the particle in the high friction limit follows the simple picture of uncorrelated jumps between nearest neighbor minima through the saddle points.[8]

In the present paper we study diffusion both in the high and low friction regimes.[8,19] In the high friction limit $\eta/\omega_0 \gg 1$, where $\omega_0 = \pi/\sigma\sqrt{V_0/m}$ is the frequency of the vibrational mode and we choose $\eta/\omega_0 = 10$. In coverages below $\theta = 1.0$ this means that the particles only jump from one minimum to the adjacent ones along the x and the y directions, and there are virtually no double jumps or recrossing events. Also in this high friction limit an exact analytic solution for the single-particle diffusion coefficient can be found[8] in case of a separable potential such as in Eq. (2). When we increase the surface potential amplitude we expect the LG approximation to become more accurate.[9] In the low friction regime, we set $\eta/\omega_0 = 0.1$. In this case longer jumps become possible,[19] and analytic solutions for D_0 exist, too.[7] The single-particle case in continuum with a separable and nonseparable surface potentials for a wide range of values of friction has been studied by Chen *et al.*[19–21]

III. RESULTS

A. Numerical results for tracer diffusion

The tracer diffusion coefficient of individual particles D_T is defined as

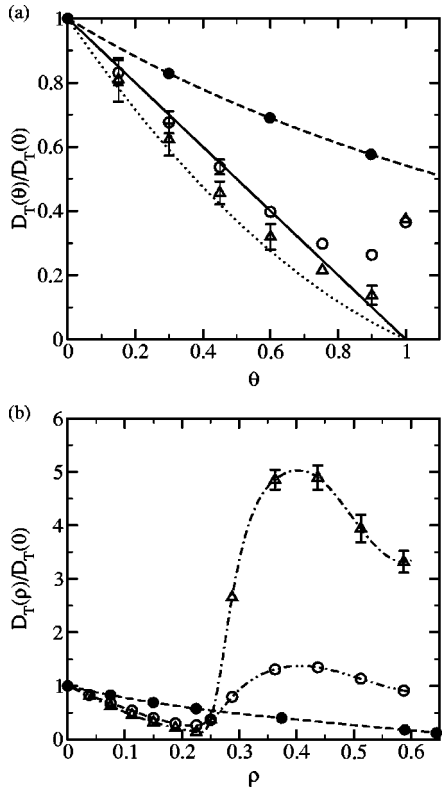

FIG. 1. The normalized tracer diffusion coefficient in the high friction regime (a) for coverages below $\theta=1$ and (b) for higher densities. The solid circles are smooth surface data $V_0=0$ from Ref. 2, the solid line is the mean field result $1-\theta$, and dotted line indicates the results of Ref. 11 for the Langmuir gas. Triangles are the present simulation data for $V_0=0.3$ and open circles for $V_0=0.2$. The data for $V_0=0.02$ are so close to the smooth surface data that they are omitted. Other lines are guides to the eye. In this and all the other figures the error bars are of the same size as the symbols or smaller, when not explicitly shown.

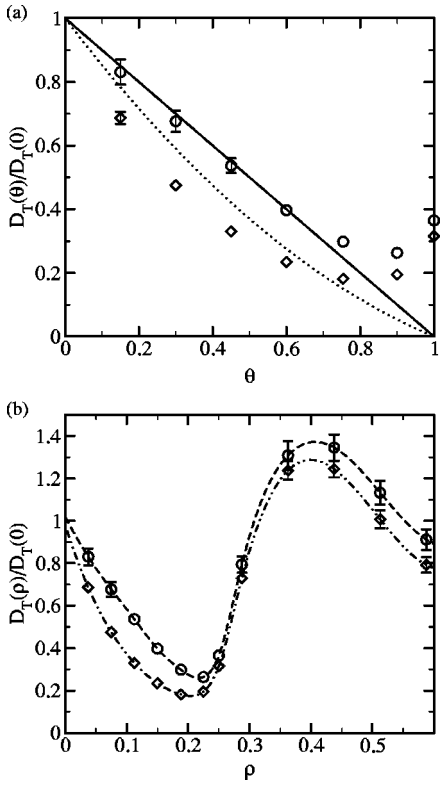

FIG. 2. The effect of friction on D_T for $V_0=0.2$ (a) for coverages below $\theta=1$ and (b) for higher densities. The solid line is the mean field result $1-\theta$ and dotted line is the result of Ref. 11 for the Langmuir gas (other broken lines are guides to the eye). The open circles are the present simulation results in the high friction regime and the diamonds in the low friction regime.

$$D_T=\frac{1}{2d}\lim_{t\to\infty}\frac{1}{t}\left\langle\frac{1}{N}\sum_{i=1}^{N}|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2\right\rangle$$
$$=\frac{1}{d}\int_0^\infty\left\langle\frac{1}{N}\sum_{i=1}^{N}\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\right\rangle dt, \tag{4}$$

where $d=2$ is the dimension of the system and $\mathbf{r}_i(t)$ is the position vector of particle i at time t, and $\mathbf{v}_i(t)$ its velocity. The quantity $\phi(t)\equiv\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle$ is the velocity autocorrelation function associated with the tracer particle. In evaluating the diffusion coefficients during the simulations we employ the memory expansion method[22] which has been shown to be an efficient way to evaluate D_T.

We first check that the one particle diffusion coefficient is in agreement with the known analytic results.[8] In the high friction limit we have

$$D_0=\frac{k_BT}{m\eta}\left[I_0\left(\frac{V_0}{k_BT}\right)\right]^{-2}, \tag{5}$$

where I_0 is the hyperbolic Bessel function of order zero. Our simulation result is within 2% of the analytic result, as expected. In the low friction case, our numerical result deviates about 20% from the approximate 1D formula given in Ref. 23.

In Fig. 1 we show D_T for different surface potential amplitudes in the high friction case. At lower coverages, below $\theta=1.0$, when all the minima are not yet filled the tracer diffusion coefficient is a decreasing function of coverage. In the case of high friction as the surface potential amplitude increases the behavior changes from that of a completely smooth surface[2] towards that of a Langmuir gas.[11] The agreement with the LG results seems to be very good up to coverages of $\theta\approx0.7$ for the strongest potential studied here. For higher densities, there is a strong intermediate peak at $D_T(\theta)$ whose relative magnitude increases with increasing potential amplitude.

The effect of friction is illustrated in Fig. 2 for the case $V_0=0.2$. In the low friction case as the particles are more mobile also the blocking effect is enhanced and the decrease of the tracer diffusion coefficient as a function of coverage is more rapid. Interestingly, for high densities the normalized diffusion coefficient is almost independent of friction. As shown below, this is due to interparticle collisions that increase the effective friction.

In Fig. 3 we show the normalized distribution function $P(l)$ of jumps of length l for integer multiples of the lattice spacing a in the low friction regime. Here we have used the same definition for a jump as Chen *et al.*,[19] that is a jump begins when the energy of the particle exceeds the energy of the diffusion barrier and ends when the energy has dropped $3k_BT$ below the saddle point. In the single-particle limit, the

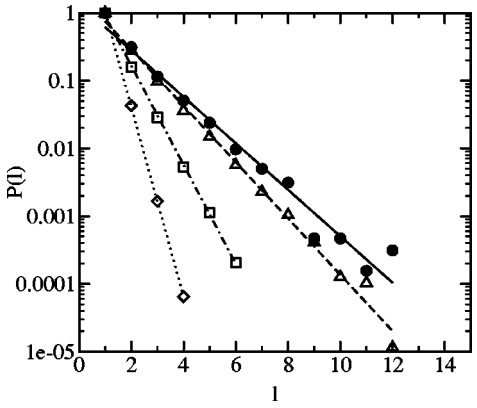

FIG. 3. The distribution function $P(l)$ for jumps of length l in the low friction case and $V_0=0.2$. Solid circles are for the single-particle case, triangles for $\theta=0.15$, squares $\theta=0.6$, and diamonds $\theta=1.0$. Only integer values of l are shown in the figure. The lines are exponential fits to the data.

average jump length is $\bar{l}\equiv\langle l\rangle=1.7$, with a standard deviation of $\sigma_l=1.2$. This is in good agreement with Ref. 24, where jump length distributions were calculated directly from the corresponding 1D Klein–Kramers equation for slightly different set of parameters. When the density increases, this number quickly drops towards unity, and for $\theta=1.0$, $\bar{l}=1.1$, with $\sigma_l=0.3$. This shows that the interparticle collisions lead to an increase in the effective friction which suppresses the long jumps.

As mentioned above, at higher densities when the number of particles approaches and exceeds the number of minima, both D_T and the CM mobility D_{cm} display interesting behavior. In the presence of the surface potential they display a dramatic *increase* relative to D_0. This is a somewhat surprising result since the surface potential tends to decrease the mobility of the particles by trapping them in the minima of the potential. In the case that the number of particles on the surface is slightly higher than the number of minima, most particles are trapped by these wells and the rest are in interstitial positions. In our case when the lattice spacing is set at $a=2\sigma$ the distance of the trapped particles from each other is larger than what it would be on a smooth surface. The interstitial atoms, on the other hand, are drawn closer to the trapped particles by the surface potential than what they would be without it. This results into enhancement of the mobility of these particles and into increase of the dynamic coefficients influenced by the repulsive interaction between the particles.

To check out the role of the interstitial particles, we have carried out additional simulations in the high friction regime with $V_0=0.3$ in which we increased the lattice parameter a. If the lattice spacing increases also the distance between particles increases, and this decreases the effect of the repulsive interaction between the particles resulting in lower diffusion coefficients. This is exactly what we observe. Even a relatively small increase of about 10% in the lattice parameter from its original value of 2σ leads to a dramatic decrease of over 50% in the diffusion coefficient at high densities.

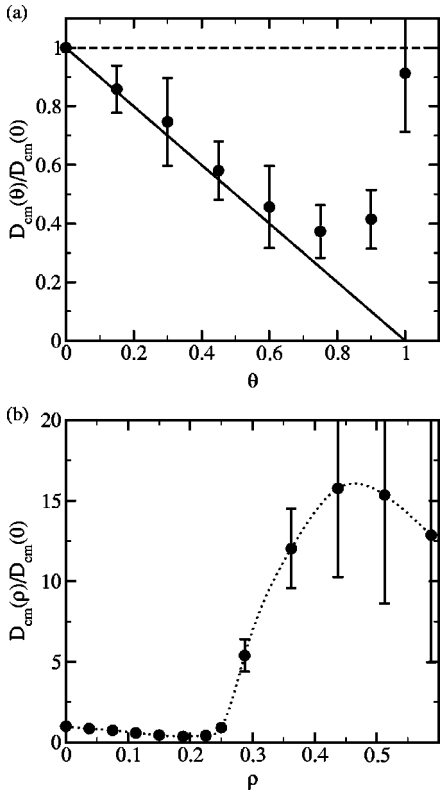

FIG. 4. The normalized CM mobility (a) for coverages below $\theta=1$ and (b) for higher densities. The constant dashed line is the exact result for the smooth surface case ($V_0=0$), the solid line is the exact analytic result $1-\theta$ for the Langmuir gas, and the solid circles present the simulation data for $V_0=0.3$. The dotted line is a guide to the eye.

B. Collective diffusion

In addition to tracer diffusion of single particles, an interesting question concerns the behavior of collective density fluctuations in surface systems. The collective diffusion coefficient $D_C(\rho)$ characterizing these fluctuations can be defined by means of the diffusion equation,

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t}=\nabla\cdot[D_C(\rho)\nabla\rho(\mathbf{r},t)]. \tag{6}$$

Another equivalent way is through the Green–Kubo equation,

$$D_c=\xi D_{\mathrm{cm}}=\xi\lim_{t\to\infty}\frac{1}{2dNt}\langle|\mathbf{R}(t)|^2\rangle, \tag{7}$$

where $\xi=\langle N\rangle/[\langle N^2\rangle-\langle N\rangle^2]$ is the thermodynamic factor (proportional to the inverse of the compressibility κ_T), and $\mathbf{R}(t)=\Sigma_{i=1}^{N}[\mathbf{r}_i(t)-\mathbf{r}_i(0)]$ is the CM displacement.[15]

In the case of Brownian hard spheres on a smooth surface, it is an exact result that the CM mobility D_{cm} is independent of the density ρ.[3] This is because the interparticle interactions preserve the CM momentum, and thus $D_{\mathrm{cm}}(\rho)=D_{\mathrm{cm}}(0)=D_0$. However, with the surface potential in place this argument does not hold. On the other hand, in the LG limit the behavior of the CM mobility can be solved analytically for a Langmuir gas and it decreases linearly as a function of coverage as $D_{\mathrm{cm}}(\theta)=D_0(1-\theta)$.

In Fig. 4 we show the CM mobility as a function of

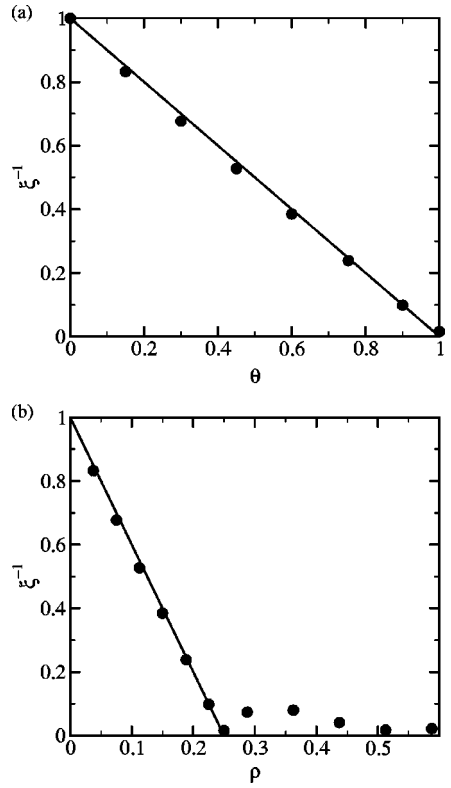

FIG. 5. The inverse thermodynamic factor of Eq. (7) (a) for coverages below $\theta=1$, and (b) for higher densities. The solid line is the exact result for the Langmuir gas ($\xi^{-1}=1-\theta$), and the solid circles present our simulation data for $V_0=0.3$.

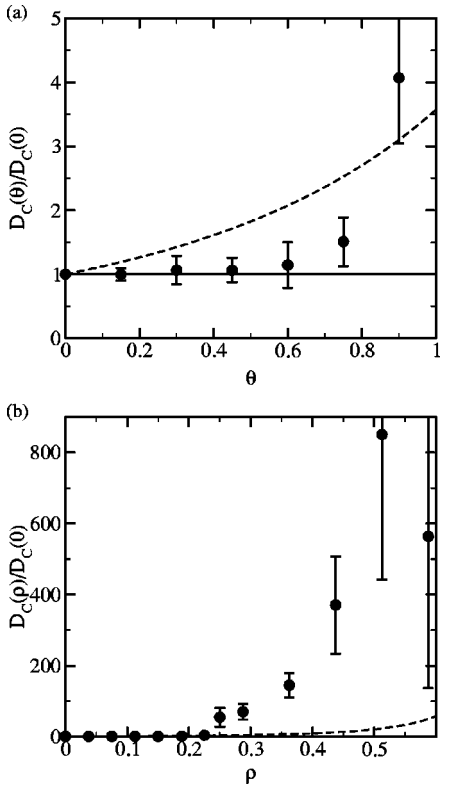

FIG. 6. The normalized D_C (a) for coverages below $\theta=1$ and (b) for higher densities. The dashed line is an approximate analytic result for the smooth surface from Ref. 36, the solid line indicates the Langmuir gas constant value, and the solid circles are present simulation data for $V_0=0.3$.

coverage in the present system in the high friction regime with different surface potential amplitudes. Again at lower coverages ($\theta\leqslant 0.7$) as the surface potential amplitude is increased we get very good agreement with the LG result. Similarly to the case of tracer diffusion, the CM mobility starts increasing at higher coverages due to the more mobile particles that cannot find unoccupied potential minima.

In Fig. 5 we show the behavior of the thermodynamic factor. Remarkably, according to our data it matches the Langmuir gas result almost perfectly for the whole coverage range up to $\theta=1$ [Fig. 5(a)]. The minimum of ξ^{-1} at $\rho=0.25$ corresponds to the minimum entropy state of fully occupied potential minima. Thus, we can conclude that the deviations of $D_C(\theta)$ from the LG limit are solely due to dynamical correlations between the particles. For higher densities, the dependence of ξ on ρ is rather weak. In Figs. 6(a) and 6(b) we show the complete $D_C(\theta)/D_C(0)$ for the two regimes. As expected, up to about $\theta=0.7$ it is in good agreement with the LG result, and then starts increasing due to the increasing CM mobility. For higher densities, the relative increase in D_C is much higher than for a smooth surface, and again this is essentially due to the CM mobility rather than the thermodynamic factor. The data indicate that D_C has a maximum at some intermediate value of the density contrary to the smooth surface case where it increases monotonously below freezing. However, due to lack of self-averaging in D_{cm} we have not studied how this depends on V_0.

For collective diffusion, we have not studied the influence of low friction. In Ref. 25 it has been shown, that for a Langmuir gas the possibility of long jumps induces a coverage dependence in D_C. However, this dependence is weak except for very low values of friction and furthermore, $D_C(\theta)$ approaches D_0 as a function of density as the long jumps are hindered by increasing coverage. In the continuum case, our results for $P(l)$ show that this happens at relatively low coverages already. Thus, we expect the effect of friction to be much weaker for the density dependence of D_C than for D_T.

C. Velocity autocorrelation functions

The velocity autocorrelation function $\phi(t)$ is a quantity of fundamental importance to the diffusion of adparticles as can be seen from the definition of D_T in Eq. (4). It is also readily accessible through STM experiments.[26] The time dependence of $\phi(t)$ has been studied in dense 3D Brownian liquids.[27–29] It was found that the deviations from exponential behavior were small, but increased with increasing density and in particular near the freezing transition.[27] More recent studies[28,30] have demonstrated that the temporal decay of $\phi(t)$ does not seem to follow simple exponential behavior, but rather a stretched exponential form. Recently, the temporal behavior of $\phi(t)$ (and its associated memory function to be defined below) have been studied in detail in a variety of strongly interacting 2D dissipative systems,[22,31–33] including a dense, viscous hard disk fluid.[34] It has been demonstrated that in many cases, $\phi(t)$ displays an *intermediate power law decay in time* $\propto t^{-x}$, where the value of the effective exponent x can be related to interaction and ordering

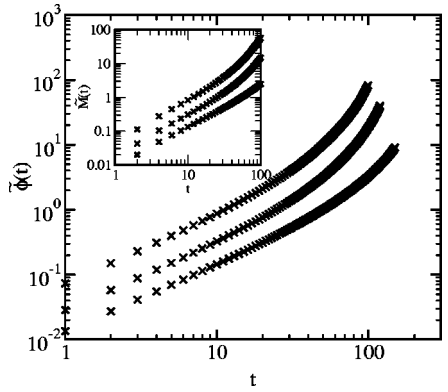

FIG. 7. The generalized velocity autocorrelation function $\tilde{\phi}(t) = [\phi(t)/\phi(0)]^{-1} - 1$ for $\theta = 1.0$ and three different potential amplitudes: $V_0 = 0.0$, $V_0 = 0.2$, and $V_0 = 0.3$ (from bottom to top, respectively). The inset shows the corresponding memory functions $\tilde{M}(t) = [M(t)/M(0)]^{-1} - 1$.

effects in the system.[32] In particular, if there are no ordered phases present, the value of x is typically about or larger than two for strongly repulsive and less than two for attractive systems.

In the present case we have studied this issue through the temporal behavior of $\phi(t)$ and the corresponding memory function $M(t)$ defined through[31]

$$\frac{d\phi(t)}{dt} = i\Omega_0 \phi(t) - \int_0^t M(t-s)\phi(s)ds, \tag{8}$$

where $i\Omega_0$ is the so-called frequency variable which vanishes in continuum. The intermediate time behavior of the velocity autocorrelation function can be in some cases well fitted by[32,33]

$$\phi(t) = \frac{\phi(0)}{1 + At^x}, \tag{9}$$

which leads to an algebraic decay $\phi(t) \sim t^{-x}$ for $At^x \gg 1$. In Fig. 7 we show the normalized velocity autocorrelation function as a function of time for three different surface potential amplitudes, including the smooth surface case,[2] and the inset shows the corresponding memory function. Fitting an effective power law to $\phi(t)$ gives $x \approx 1.0$ which is close to the values reported in the literature in similar systems,[34,32,2] and we can see that neither the overall form of $\phi(t)$ nor the value of x are affected by the adiabatic potential. Due to the relatively short range of the effective power law, it is difficult to pin down the value of x accurately, however. We have also studied the memory effects for the low friction case, and find qualitatively similar behavior. In this case, $\phi(t)$ shows pronounced oscillations in time for lower densities.

IV. SUMMARY AND DISCUSSION

In this paper we have presented a study of the diffusion of 2D repulsive Brownian particles on a rigid surface potential. We find that in such systems the dynamics of the continuum model at low densities approaches that of the Langmuir LG model as the strength of the binding potential increases. In particular, the static compressibility of the adlayer is accurately described by the LG result for the full coverage range up to almost $\theta = 1$, while the dynamic quantities show increasing deviations already before $\theta = 1$. At higher densities, where the comparison to the LG is no longer meaningful, the diffusion coefficients display nonmonotonic behavior unlike in the smooth surface case. Both $D_T(\theta)$ and $D_C(\theta)$ show large relative maxima due to the enhanced mobility of the particles at interstitial sites of the potential. We also show that in this regime, the relative values of the diffusion coefficients are only weakly influenced by the friction parameter η.

An interesting question remains regarding the validity of the LG approximation for particles with more realistic interactions, such as those e.g. mediated by a real substrate which may include attractive interactions, three-body forces etc. For such cases where the simplified Langmuir gas picture no longer holds, it is well known that within the LG approximation the diffusion coefficients explicitly depend on the form of the transition probabilities w_{ij} chosen to describe the jump events between sites i and j.[13,35] Recently, this issue has been addressed for LG models of some adsorption systems with strong interactions[32] where unphysical choices of w_{ij} may lead to qualitatively incorrect behavior of the diffusion coefficients near phase transition points. It would be of great importance to carry out a comparison such as presented here between the continuum case and its LG limit for cases with more complicated interactions than those considered here.

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