Memory expansion for diffusion coefficients

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We present a memory expansion for macroscopic transport coefficients such as the collective and tracer diffusion coefficients D_C and D_T, respectively. The successive terms in this expansion for D_C describe rapidly decaying memory effects of the center-of-mass motion, leading to fast convergence when evaluated numerically. For D_T, one obtains an expansion of similar form that contains terms describing memory effects in single-particle motion. As an example we evaluate D_C and D_T for three strongly interacting surface systems through Monte Carlo simulations, and for a simple model diffusion system via molecular dynamics calculations. We show that the numerical method provides a speedup of about two orders of magnitude in computational time as compared with the standard methods, when collective diffusion is concerned. For tracer diffusion, the speedup is not quite as significant. Our studies using the memory expansion provide information of the nature of memory effects in diffusion and suggest a nontrivial power-law behavior of memory terms at intermediate times. We also discuss the application of the present approach to studies of other transport coefficients. [S0163-1829(98)04828-0]

I. INTRODUCTION

Transport phenomena such as diffusion, thermal conduction, and viscous flow are of both fundamental and practical interest. In the macroscopic hydrodynamic regime they are characterized by transport coefficients such as the diffusion coefficient or the thermal conductivity. Using the Green-Kubo approach,[1–3] these coefficients can be expressed in terms of equilibrium time-dependent correlation functions, which have been the basis of many analytical and numerical simulation studies. However, the transport coefficients are defined in the hydrodynamical limit of long times and large length scales. In the numerical calculation of multiparticle quantities such as the collective diffusion for adsorbates on surfaces[4] and the shear viscosity for fluids,[5] this becomes a major problem due to the lack of self-averaging.[6] Therefore, for many interesting systems characterized by large time-scale separations and strong interactions, accurate studies of transport properties using the standard methods[4,7] are extremely tedious.

The purpose of this article is to present a memory expansion for transport coefficients that overcomes these difficulties. We illustrate the method by considering the collective and tracer surface diffusion coefficients D_C and D_T, respectively. The collective diffusion coefficient describes the macroscopic density fluctuations on a surface and has relevance in, e.g., annealing processes after surface sputtering and spreading of molecular layers on surfaces.[8] The tracer diffusion coefficient in turn characterizes single-particle motion as is evident in surface growth under MBE conditions, for example. In the formalism for collective diffusion, the center-of-mass of the system (c.m.) is viewed as performing diffusive motion. The leading contribution to this expansion corresponds to a random motion of the c.m. with no correlations between the displacements in successive time intervals. The same idea holds true for the successive displacements of a single particle, when tracer diffusion is concerned. The memory effects in D_C and D_T are then included systematically through a summation of suitable correlation functions over different time intervals.

This formulation is particularly suited for numerical Monte Carlo (MC) and molecular dynamics (MD) simulation studies. We have applied the expansion to evaluate D_C and D_T for a variety of strongly interacting systems using both MC and MD simulation techniques. In all the cases studied, this method speeds up the computation of D_C over conventional methods[4] by about two orders of magnitude, while for D_T the speedup is not quite as significant. We find that in all cases studied here, the temporal behavior of memory terms in the diffusion coefficients can be described rather well by a power law with some effective exponent at intermediate times. At long times, the memory effects decay exponentially. Finally, as discussed below, we would like to stress that the present method can be applied to studies of other transport coefficients such as shear and longitudinal viscosities, or thermal conductivity.[9]

II. MEMORY EXPANSION

Our starting point is the Green-Kubo response function formalism[9] in which a transport coefficient $T_{\mu\nu}$ can be expressed in terms of time correlations of the spatial μ, ν components of a ''current flux'' $\vec{J}(t)$:

$$T_{\mu\nu} = A \int_0^\infty dt \langle J_\mu(t) J_\nu(0) \rangle. \qquad (1)$$

In Eq. (1), A is a thermodynamic factor and $\langle \ \rangle$ denotes an ensemble average. For isotropic systems, T can be characterized by the scalar quantity $\langle \vec{J}(t) \cdot \vec{J}(0) \rangle$. The explicit form of $\vec{J}(t)$ depends on the specific transport coefficient under consideration, such as viscosity, electric conductivity, or diffusion coefficient. In this work, we focus on surface diffusion of adparticles at finite densities. We then need to distinguish between two different diffusion coefficients. The tracer diffusion coefficient D_T is related to the motion of a single tagged particle, while the collective diffusion coefficient D_C describes macroscopic density fluctuations. Although the expansion proposed here is very similar for both diffusion coefficients, we wish to clarify the discussion by presenting the two cases separately.

A. Collective diffusion

The first situation to be discussed concerns macroscopic density fluctuations. In this case, $T_{\mu\nu}$ in Eq. (1) is the collective diffusion coefficient $D_{C,\mu\nu}$, and the flux $\vec{J}(t)$ is then the total particle flux $\vec{J}(t) = \Sigma_{i=1}^N \vec{v}_i(t)$, where $\vec{v}_i(t)$ is the velocity of a particle $i = 1, \ldots, N$ at time t. The current flux correlation function in Eq. (1) can also be expressed in terms of the components of the center-of-mass coordinates of the adsorbate layer,[4] defined as $\vec{R}(t) = \Sigma_{i=1}^N [\vec{r}_i(t) - \vec{r}_i(0)]$, where $\vec{r}_i(t)$ is the position vector of particle i at time t. For the isotropic two-dimensional (2D) case then,[4]

$$D_C = \xi D_{\text{c.m.}} \equiv \xi \lim_{t\to\infty} \frac{1}{4Nt} \langle |\vec{R}(t)|^2 \rangle. \qquad (2)$$

In Eq. (2), which is sometimes called the Kubo-Green expression for collective diffusion, D_C is decomposed into two

factors. The first factor $\xi = \langle N \rangle / \langle (\delta N)^2 \rangle$ is determined by the number fluctuations of the overlayer in a grand canonical ensemble and is inversely proportional to the compressibility. The remaining part $D_{\text{c.m.}}$ describes the center-of-mass motion of the whole system, and is in fact the diffusion coefficient for a fictitious particle located at the c.m. position $\vec{R}(t)$ normalized by the total particle number N. $D_{\text{c.m.}}$ contains all the dynamical information for the collective diffusion coefficient D_C, and constitutes a numerical challenge in simulation studies of collective diffusion. Namely, to evaluate D_C accurately according to Eq. (1) or Eq. (2), one needs to go to the hydrodynamic long-time limit. Moreover, $\langle |\vec{R}(t)|^2 \rangle$ or $\langle \vec{J}(t) \cdot \vec{J}(0) \rangle$ are not self-averaging quantities in the sense that the computational effort always increases with larger system sizes.[6,10]

We now propose an alternate scheme, which is able to reduce this numerical problem to a great extent. In this approach for collective diffusion, one focuses on the motion of the c.m. at short time scales, instead of directly evaluating $D_{\text{c.m.}}$ from the long-time limit of Eq. (2). We divide the time t into M time intervals of equal length τ_0, and discretize the c.m. coordinate $\vec{R}$ correspondingly at times $t_m = m\tau_0$ with $m = 0, 1, \ldots, M$. Then $\vec{R}(t) \equiv \vec{R}(M\tau_0) = \Sigma_{m=1}^M \delta\vec{R}(t_m)$, where $\delta\vec{R}(t_m) = \vec{R}(t_m) - \vec{R}(t_{m-1})$ is the change in the position of the c.m. between two consecutive *observations* at times t_m and t_{m-1}. In the isotropic case, this leads to the expression

$$D_{\text{c.m.}} = \lim_{M\to\infty} \frac{1}{4NM\tau_0} \left[M\langle \delta\vec{R}(t_m) \cdot \delta\vec{R}(t_m) \rangle + 2 \sum_{k=1}^{M-1} (M-k) \right.$$
$$\left. \times \langle \delta\vec{R}(t_m) \cdot \delta\vec{R}(t_{m+k}) \rangle \right], \qquad (3)$$

where the averages on the right-hand side (RHS) are with respect to t_m. The time-dependent correlation functions in Eq. (3) depend only on the time differences. The extension to the spatially anisotropic cases is obvious. By denoting

$$C_C(t) \equiv \langle \delta\vec{R}(0) \cdot \delta\vec{R}(t) \rangle, \qquad (4)$$

we obtain the expansion

$$D_{\text{c.m.}} = \frac{1}{4N\tau_0} \left[C_C(0) + 2 \sum_{k=1}^\infty C_C(k\tau_0) \right]. \qquad (5)$$

The first term $C_C(0) = \langle |\vec{R}(\tau_0) - \vec{R}(0)|^2 \rangle$ gives the average mean-square displacement of $\vec{R}$ for a time interval of length τ_0. The following terms in the expansion measure the memory of additional displacements with respect to the initial displacement. If the c.m. motion follows Markovian random-walk statistics, then the leading term $C_C(0)$ is the only contribution to $D_{\text{c.m.}}$. For interacting cases, however, this is not generally true, which leads to a finite value for the correlation functions $C_C(k\tau_0)$ for $k \neq 0$. In general, the analytic evaluation of these functions is prohibitively difficult. However, the main point here is that since these functions are expected to decay rapidly over microscopic time scales, the expansion of Eq. (5) converges rapidly when evaluated *numerically*. In fact, it is expected from Eq. (5) that the hydrodynamic regime in which the c.m. mean-square displace-

ment varies linearly with time is only reached after the correlation expansion has converged. We have verified this through extensive numerical studies as detailed below. Details of the convergence will be discussed in the context of results in Sec. III.

B. Tracer diffusion

We next outline the corresponding memory expansion for the tracer diffusion coefficient D_T. Within the Kubo-Green formalism, D_T comes from Eq. (1) with the single-particle flux $\vec{J}(t) = \vec{v}_i(t)$ and constant A. An alternate way to express tracer diffusion is to use the well-known Einstein relation, which in the isotropic 2D case defines D_T as[4]

$$D_T = \lim_{t \to \infty} \frac{1}{4t} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle. \tag{6}$$

The tracer diffusion coefficient is therefore proportional to the slope of the mean-square displacement of a tagged particle i in the hydrodynamic limit, and describes its motion in the presence of other particles $j \neq i$. For this single-particle quantity, a description similar to Eq. (5) with $N = 1$ can be written. The thermodynamic factor ξ no longer plays a role and one considers correlation terms

$$C_T(t) \equiv \langle \delta \vec{R}_i(0) \cdot \delta \vec{R}_i(t) \rangle, \tag{7}$$

where $\delta \vec{R}_i(t_m)$ is the change in the position of a single particle i between two consecutive observations at times t_m and t_{m-1}. Then we obtain the expression[11]

$$D_T = \frac{1}{4\tau_0} \left[C_T(0) + 2 \sum_{k=1}^{\infty} C_T(k\tau_0) \right]. \tag{8}$$

Similarity between Eqs. (5) and (8) is evident. Thus the main ideas of the correlation terms $C_C(k\tau_0)$ discussed in Sec. II A are valid also for the present terms $C_T(k\tau_0)$ in a tracer diffusion process.

C. Choice of time scales

The parameter τ_0 in numerical calculations of Eqs. (5) and (8) is arbitrary and its practical choice is dictated by the optimization of the computational speed. An overly small choice of τ_0 leads to an excessively large number of computational steps with redundant information, while a large value beyond the characteristic decay times of $C_C(t)$ and $C_T(t)$ also leads to waste of computational efforts. Further, it is important to note that each displacement step $\delta \vec{R}(t_m)$ of the c.m. in general results from the motion of different adparticles, so that the memory effects of collective diffusion are often weaker than those of tracer diffusion where strong correlations exist between the successive displacement steps of the tagged particle $\delta \vec{R}_i(t_m)$.[11,12] As we demonstrate below, the expansion method is an extremely powerful tool for the numerical evaluation of D_C in strongly interacting systems. This is because unlike the conventional methods,[4] using Eq. (5), there is no need to go deep into the hydrodynamic regime to extract the diffusion coefficient. Instead, the long-time correlation functions provide only weak corrections to the memory expansion. Indeed, our studies indicate that the

present method reduces the computational cost of calculating the collective diffusion coefficient by about two orders of magnitude. For tracer diffusion, however, such a large speedup is not achieved in practice. This is because at finite coverages, the calculation of D_T through the average mean-square displacement is relatively easy, unless one has true long-range correlation effects. Another advantage is the generality of the present approach and its applicability to both discrete lattice-gas models and particles with continuous interaction potentials. In the former case, the motion is described in terms of stochastic jumps between neighboring sites and often studied via MC simulations, while the continuous systems obey Newtonian dynamics with no readily identifiable "jump" steps.

D. Connection to the dynamical mean-field theory

When the memory effects are disregarded by neglecting terms $C_C(k\tau_0)$ for $k \neq 0$ and using a very small time step τ_0, the present scheme can be compared with previous analytical results.[12,13] To this end we consider a lattice-gas model with Monte Carlo dynamics such that during one Monte Carlo step (MCS) each particle attempts to jump to a neighboring site. Then with the choice of $\tau_0 = \tau/N$, where τ corresponds to one MCS, the leading random walk term $C_C(0)$ in Eq. (5) takes on the value $\Gamma(\theta) N \tau_0 a^2$, where $\Gamma(\theta)$ is the single-particle jump rate defined as the average number of jumps of a particle observed in the period τ. The quantity θ is the coverage and a is the jump length between neighboring sites. Keeping only the leading term, Eq. (5) then leads to the expression

$$D_C = \xi \Gamma(\theta) a^2 / 4 \tag{9}$$

for the collective diffusion coefficient. This is precisely the same form as the phenomenological result proposed by Reed and Ehrlich.[14] This result has been derived recently as a dynamical mean-field approximation (DMF) in the Mori formalism.[12,13] In this sense, the leading term $C_C(0) = \langle |\vec{R}(\tau_0) - \vec{R}(0)|^2 \rangle$ in Eq. (5) can be viewed as a generalized DMF theory.

For tracer diffusion, one finds in a similar way that $C_T(0)$ takes on the value $\Gamma(\theta) \tau_0 a^2$, thus leading to an expression

$$D_T = \Gamma(\theta) a^2 / 4 \tag{10}$$

for the tracer diffusion coefficient. This result is identical to the DMF prediction for D_T,[12] when memory effects are neglected altogether.

Note that here the separation of the contributions to $D_{\text{c.m.}}$ and D_T from a "random walk" or "mean field" term and memory effect corrections [that are not present in Eqs. (9) and (10)] depend implicitly on the choice of the basic time scale τ_0. It is only for special cases such as in the lattice-gas model that one has a natural time scale in terms of the inverse of the single-particle attempt frequency. For continuous systems studied by MD simulations, there is no obvious choice of τ_0.
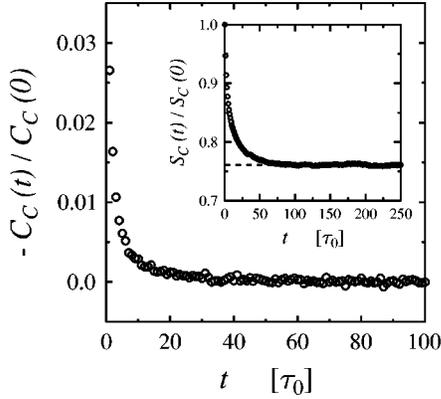
FIG. 1. The correlation function $C_C(t)$ in a lattice-gas model of the O/W(110) system at $\theta = 0.45$ and $T = 0.833 T_c$. The time interval $\tau_0 = 1$ MCS. The vertical scale has been expanded to show the decay. The convergence of $D_{c.m.}$ via $S_C(t) = C_C(0) + 2\sum_{k=1}^{k_{max}} C_C(k\tau_0)$ with $t = k_{max}\tau_0$ is shown in the inset. The asymptotic value of $S_C(t)$, as determined by the Kubo-Green method at long times [Eq. (2)], is denoted by a dashed line.

III. RESULTS

We have applied the present formalism to evaluate D_C and D_T in various strongly interacting model systems: the O/W(110) adsorption system, chainlike molecules adsorbed on smooth substrates, and a model of interacting atoms adsorbed on a substrate with regularly spaced steps and terraces. In addition to Monte Carlo studies of these three model systems, we have considered a simple model of diffusion of interacting particles in a periodic potential through molecular dynamics simulations.

A. Model system O/W(110)

We first study diffusion in a lattice-gas model of oxygen atoms on a W(110) surface with Monte Carlo dynamics. The oxygen-oxygen interaction Hamiltonian contains pair interactions and also a contribution from three-body interactions that are important at large coverages. Details of the model system and parameters can be found in Ref. 15. We concentrate on the behavior of the diffusion coefficients at a fixed coverage of $\theta = 0.45$, when crossing over from a high-temperature disordered phase down to a low-temperature $p(2\times1)$ phase in the model. In the numerical calculation of the expansion in Eqs. (5) and (8), τ_0 was set equal to 1–4 Monte Carlo time steps (MCS), which was sufficiently large for our purposes.

In our studies for this model system, we find that the correlation functions $C_C(t)$ for collective diffusion for $t \neq 0$ are predominantly negative, i.e., the leading positive term $C_C(0)$ gives an upper bound for the collective diffusion coefficient. This is illustrated in Fig. 1. The inset of Fig. 1 in turn illustrates the convergence of the memory expansion in Eq. (5) for the jump mobility $D_{c.m.}$. We note that the precise value of where the expansion has converged to the hydrodynamic long-time limit is somewhat difficult to assess. Nevertheless, we can observe from Fig. 1 that the expansion coincides with the value obtained by the Kubo-Green method at long times, and furthermore that the expansion converges to an accuracy of 1% in about 50–100 terms. The
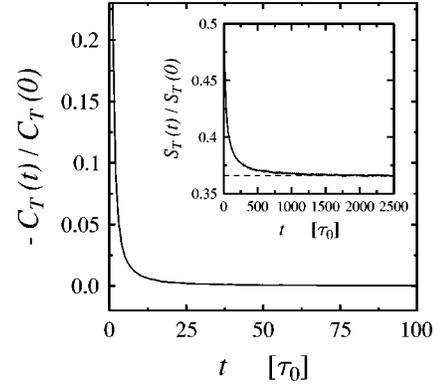

FIG. 2. The correlation function $C_T(t)$ in the O/W(110) model system at $\theta = 0.45$ and $T = 0.833 T_c$, where T_c is the critical temperature of the order-disorder transition at this coverage (Ref. 15). The time interval $\tau_0 = 4$ MCS. The convergence of D_T via $S_T(t) = C_T(0) + 2\sum_{k=1}^{k_{max}} C_T(k\tau_0)$ with $t = k_{max}\tau_0$ is shown in the inset. The asymptotic value of $S_T(t)$, as determined by Eq. (6) at long times, is denoted by a dashed line.

corresponding time scale of about 100 MCS is in agreement with the onset of the hydrodynamic regime for collective diffusion, as determined by the Kubo-Green method for the mean-square displacement of the c.m.

The rapid decay of the memory expansion is characteristic for collective diffusion, where memory effects have been shown to be rather weak.[12,15,16] The situation is very different in tracer diffusion, where successive displacements of a single particle are strongly correlated.[12,15,16] This phenomenon is most pronounced in ordered phases such as the $p(2 \times 1)$ phase in the present study. Illustrative results are given in Fig. 2. We first note that the correlation functions $C_T(t)$ are again predominantly negative for $t \neq 0$. Unlike the case of collective diffusion, however, the correlation functions do not decay very rapidly but require relatively long time scales to die out. In this regard, the decay of $C_T(t)$ in Fig. 2 is slightly misleading since one might conclude that the memory effects are negligible after about $75\tau_0$. A more detailed consideration based on the inset of Fig. 2 reveals, however, that a true convergence of the tracer diffusion coefficient D_T via Eq. (8) requires a time scale of about $1500\tau_0$ (with $\tau_0 = 4$ MCS), the accuracy of 1% being achieved in about 600 terms. Thus, although the correlation functions $C_T(t)$ at intermediate times are already very small, they are not negligible and they do contribute to the expansion up to the onset of the hydrodynamic limit. In this case, the onset has a value as large as about $1500\tau_0$,[17] implying the importance of dynamical correlation effects in a tracer diffusion process in ordered phases.

Based on the data for the correlation functions at very short times, we found them not to be smooth but to contain certain fluctuations. This is demonstrated at short times in Fig. 1 for D_C. This scatter is not due to statistical fluctuations since the number of independent samples is about 10^8, and in studies with even better statistics the situation did not change. Instead, this *fine structure* is expected to arise from the coarse-grained description for adatom motion in the lattice-gas approach, thus suggesting that the related memory effects are very complex. Nevertheless, after some initial crossover period, the correlation function $C_C(t)$ shows an
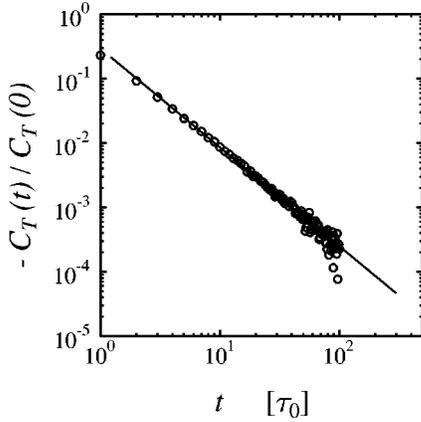
FIG. 3. The correlation function $C_T(t)$ of tracer diffusion (circles) in the O/W(110) model system at $\theta = 0.45$ and $T = 0.833 T_c$, up to the point where $C_T(t)$ starts to fluctuate near the zero level. Here $\tau_0 = 4$ MCS. The power-law decay with $x = 1.53 \pm 0.05$ in the intermediate time regime is shown with a solid line.

approximate power-law decay $C_C(t) \sim t^{-x}$ in intermediate time regimes, while at large times it levels off exponentially. For $D_{\text{c.m.}}$ at $\theta = 0.45$ in the ordered phase, we find an estimate of $x = 1.5 \pm 0.1$. For $C_T(t)$ in tracer diffusion, we observe a similar power-law decay with $x = 1.53 \pm 0.05$ as illustrated in Fig. 3.

We conclude this section by discussing the importance of memory effects. In Fig. 4, we show the results for $D_{\text{c.m.}}$ as an Arrhenius plot. The agreement between the present method and the direct MC data using the Kubo-Green method [Eq. (2)] is remarkably good. Also shown are the results for the DMF using Eq. (9), which includes all interaction effects through ξ but neglects dynamical correlation effects due to multiple jumps. It turns out that, although the DMF works rather well in the whole temperature region, it deviates from the expected behavior at very low temperatures. This differ-
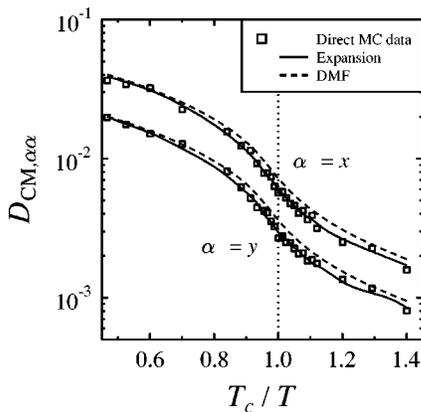

FIG. 4. Results for $D_{\text{c.m.}}$ as a typical Arrhenius plot in the O/W(110) model system at $\theta = 0.45$. The results of conventional MC simulations [via Eq. (2)] along the two principal directions (x,y) are shown by squares while the corresponding results of the present expansion method are presented by a full line. The DMF results are indicated by a dashed line. The critical temperature of the order-disorder phase transition is denoted by T_c. The error bars of the direct MC results are roughly of the size of the symbol, while the error bars of the other two quantities are much smaller.
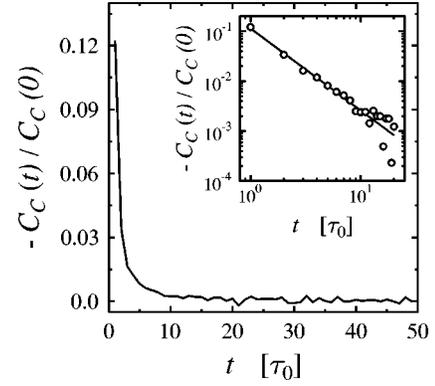

FIG. 5. Results for the center-of-mass displacement correlation functions $C_C(t)$ for $t = k\tau_0$ with $k \geq 1$ and $\tau_0 = 50$ MCS in the model polymer system, when there is an attractive interaction $J = -1$ between the chains, the number of segments in a chain is $N_{FB} = 6$, and the coverage is $\theta = 0.85$. (For details of the model and the parameters, see Ref. 8.) The power-law behavior $C_C(t) \sim t^{-x}$ with $x = 1.6 \pm 0.1$ (shown with a full line) is demonstrated in the inset.

ence is a measure of the memory effects in D_C. For tracer diffusion, the difference is even more pronounced.[12,16]

B. Model polymer system

Next we discuss the results for a model of flexible, chain-like molecules on smooth surfaces,[8] in which the memory effects turn out to be most pronounced of the model systems considered in this work. The chains are modeled by the two-dimensional fluctuating-bond model with mc dynamics,[18,19] in which each segment excludes four nearest and next-nearest neighbor sites on a square lattice. The exclusion induces a strong entropic repulsion between the molecules even if there are no direct interactions present. The repulsion strongly influences diffusion in this system, and has been studied in detail in Ref. 8. In this work, we concentrate on the case where there is a direct Lennard-Jones type of attraction between segments of different chains. Details on the model and parameters can be found in Ref. 8.

In the numerical calculation of the expansion in Eq. (5), we varied τ_0 between 1 and 100 MCS. Here, one MCS is defined as an attempt to move each monomer of every chain. The results for the different choices were found to be consistent with each other. We discuss here only the results for $\tau_0 = 50$ MCS for the collective diffusion coefficient D_C. In our studies, we again find that the correlation functions $C_C(t)$ for $t \neq 0$ are predominantly negative and that they show a power-law decay $C_C(t) \sim t^{-x}$ with $x = 1.6 \pm 0.1$ in intermediate time regimes (see the inset of Fig. 5), while at large times the memory terms level off exponentially. Concerning the decay of $C_C(t)$, we note that even in this case with the strongest memory effects we have studied, it initially decays very rapidly such that $|C_C(\tau_0)/C_C(0)| \approx 0.10$. The remaining terms $C_C(k\tau_0)$ with $k \geq 1$ also decay rapidly, as illustrated in Fig. 5. For a convergence of the correlation expansion in Eq. (5) to an accuracy of 1% for the jump mobility $D_{\text{c.m.}}$, about 40 terms were needed in this case.

In Fig. 6, we show a comparison of $D_{\text{c.m.}}$ as extracted from Eq. (2) through direct MC simulations with the data
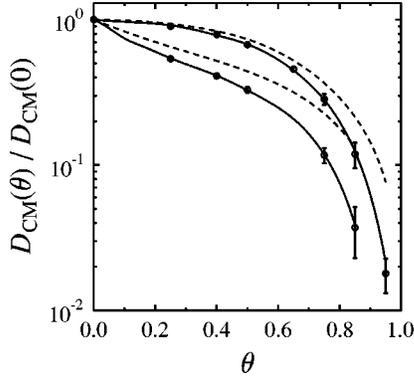
FIG. 6. Results for $D_{c.m.}(\theta)$ as a function of coverage θ for the model polymer system with the number of segments in a chain $N_{FB}=6$. The direct MC results are given by circles (with error bars), while the corresponding data for the expansion method based on Eq. (5) are shown by full lines (error bars about the thickness of the line). The DMF results are shown by dashed lines. The upper set of results is for a system with excluded volume interaction only ($J=0$), while the lower set is for attractive chains ($J=-1$) (Ref. 8).

obtained from the present method. For the latter, the number of successive terms included in the expansion of Eq. (5) varied from $k=5$ at low coverages to about $k=50$ at high coverages (with $\tau_0=50$ MCS). Dashed lines in Fig. 6 indicate the DMF results from Eq. (9).[12] The poor accuracy of the DMF description at high coverages illustrates the importance of memory effects in this complex system.

C. Lattice gas on a stepped substrate

As another demonstration of the usefulness of the memory expansion method, we consider collective diffusion of adatoms on an inert stepped substrate with submonolayer coverages. This case differs from the other model systems considered previously in that the average jump rate Γ is not the same for all lattice sites, but for each site it depends on the distance from the step edges.

The model for the adsorbate-substrate interaction includes an extra binding energy at step edges, an extra Schwöebel barrier for climbing over step edges, and enhanced diffusion along step edges, as described in Ref. 20. In previous works on stepped substrates, we have demonstrated that for the model with on-site exclusion only[20] and for a model with repulsive adsorbate-adsorbate interactions,[12] the DMF approximation works very well for collective diffusion. In the present study, we consider the computationally most challenging case, where the interactions between the adsorbates are attractive. In this case, for increasing total coverage the adsorption layer grows starting from a step edge and, consequently, mass transport across the step edge region with a high adsorbate concentration is very slow.

In Fig. 7 we compare the approach to the hydrodynamic limit of the mean-square displacement of the center-of-mass motion [via Eq. (2)] and the convergence of the memory expansion for $D_{C,xx}$ [via Eq. (5)]. Here x direction is the direction perpendicular to and y the direction parallel to the steps. In both cases, the number of Monte Carlo steps needed to confirm the convergence is much smaller than that for the conventional mean-square displacement analysis. From both
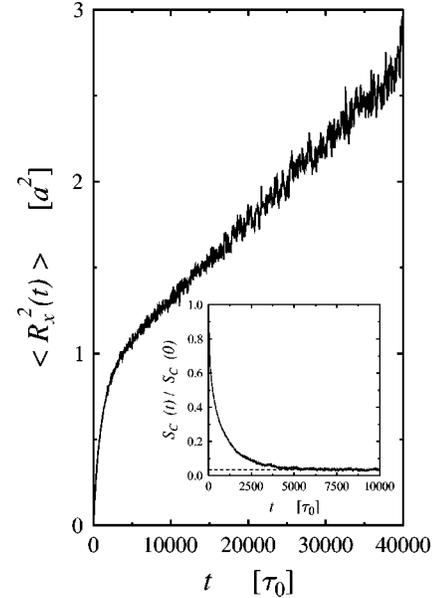

FIG. 7. The approach to the hydrodynamic limit of the mean-square displacement of the center of mass of the adlayer for diffusion perpendicular to the steps on a stepped substrate. The inset shows the convergence of the memory expansion for collective diffusion via $S_C(t)=C_C(0)+2\Sigma_{k=1}^{k_{max}}C_C(k\tau_0)$, where $t=k_{max}\tau_0$. In the inset, the asymptotic value of $S_C(t)$ as determined by the mean-square displacement analysis is denoted by a dashed line. Here $\tau_0=1$ MCS and a is the lattice constant. The adsorbate-substrate and adsorbate-adsorbate interaction parameters are related by $E_B/kT=E_S/kT=(E_0-E_2)/kT=2E_{NN}/kT=3$, where E_0 is the activation barrier in the terrace region, E_B is the extra binding at step edge, E_S is the Schwoebel barrier, E_2 is barrier for diffusion along step edge, and E_{NN} is the nearest-neighbor attraction; see Ref. 20. The terrace width is four lattice sites and the coverage is 1/2.

the figure and its inset we observe that the onset of the hydrodynamic limit is around 5000 MCS. The temperature dependence of D_C as extracted by the various methods shown in Fig. 8 demonstrates the accuracy of the expansion. For comparison, the DMF result is indicated by a dashed line.[21] Our data for the correlation functions $C_C(t)$ are consistent with a power-law decay with $x\approx1.5$. However, the transient
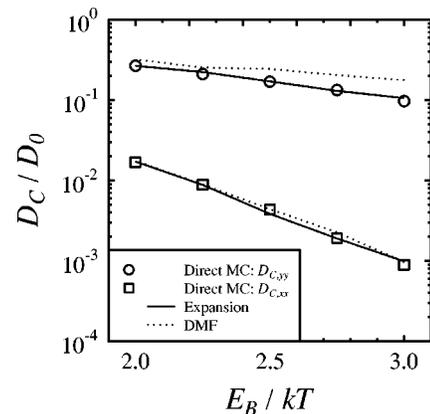

FIG. 8. The temperature dependence of collective diffusion on a stepped substrate. The relative magnitudes of the various energy parameters are the same as in the caption of Fig. 7, and D_0 is the diffusion coefficient in the zero-coverage limit.

period prior to the power-law behavior is rather long, and it is difficult to obtain enough statistics to actually extract a reliable exponent from the data.

Concerning the evaluation of the tracer diffusion tensor D_T using the expansion of Eq. (8), the main conclusions of the previous sections hold. In particular, D_T is relatively easy to evaluate by the conventional mean-square displacement analysis so that it is the evaluation of D_C where the memory expansion is most useful.

D. Diffusion in a periodic potential using molecular dynamics

To demonstrate that the present method works also in the case of a continuum model, we present results of a molecular dynamics simulation of the Langevin equation[7] describing the Brownian motion of an adatom in a two-dimensional adsorption potential $U(x,y)$. For $U(x,y)$, we have chosen the following 2D separable form:

$$U(x,y) = V_0 \left[\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) \right], \qquad (11)$$

where a is the lattice constant. The single-particle diffusion barrier Δ for this potential equals $2V_0$ and the frequency of the translational mode is $\omega_0 = (2\pi/a)\sqrt{V_0/m}$,[22] where m is the mass of the adatom. The adatom's coupling to the substrate exitations is characterized by a constant friction coefficient η in the Langevin equation. We have made calculations in the case of rather high friction $\eta/\omega_0 \approx 9$,[22] which means that diffusion takes place as a motion from one surface potential minimum to the adjacent one, without significant recrossing events or longer jumps.[22] In the high friction limit, an exact analytic solution for the single-particle diffusion coefficient can be found for a separable potential of the type in Eq. (11).[23] Here we focus on studies at a finite density of adatoms and thus define the surface coverage θ in this model as the number of adatoms divided by the number of surface potential minima. The interaction potential between adatoms was of the usual Lennard-Jones type, where the distance of the potential minimum was chosen to be the lattice constant a and the strength of the potential was chosen to be $\epsilon/k_B T = 1.25$. Here we show results from calculations where the temperature and the coverage were fixed at values of $\Delta/k_B T = 3$ and $\theta = 0.3$. With these parameters we used $\tau_0 = 100$ integration time steps, which is one-third of the time that adatoms on the average spend in each potential well. This ensures that we measure correlation of diffusive behavior and not just the correlation of vibrational motion in the surface potential well.

In Fig. 9 we show the convergence of the tracer diffusion expansion [Eq. (8)] to the hydrodynamic long-time limit determined by Eq. (6) (see the inset). The convergence of D_T is quite rapid in this case, the onset of the hydrodynamical regime being around $300\tau_0$. As far as the intermediate time behavior is concerned, in Fig. 10 we show that even in this continuous system there is a power-law decay $C_T \sim t^{-x}$ after a short initial time regime. In this case, the decay is characterized by an exponent $x = 1.6 \pm 0.2$.

The MD results allow us to comment on two interesting points. First, there is an initial time regime up to about $3\tau_0$ where the particles on average have not yet performed a diffusion jump to their nearest-neighbor sites. This regime
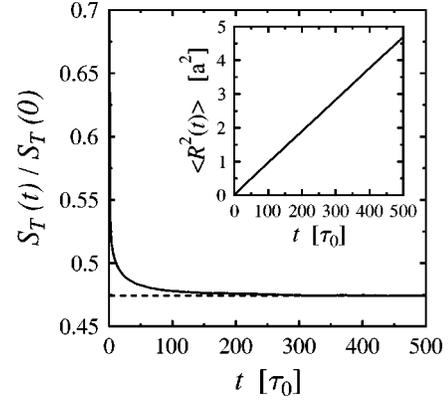
FIG. 9. The convergence of the memory expansion for tracer diffusion via $S_T(t) = C_T(0) + 2\sum_{k=1}^{k_{max}} C_T(k\tau_0)$ with $t = k_{max}\tau_0$ in the model system via MD simulations. The dashed line indicates the corresponding long-time limit as determined by the mean-square displacement of an adatom, which in turn is shown in the inset. Here the coverage $\theta = 0.3$ and the temperature is chosen as $\Delta/k_B T = 3$. The time scale τ_0 corresponds to 100 integration time steps.

arises from correlations due to vibrational motion in the potential well, and is obviously not present in the MC simulation data. This is followed by a crossover to an intermediate regime starting after a few jumps where power-law behavior is evident. This power-law decay characterizes memory effects in diffusive motion. Second, the decay exponent $x = 1.6 \pm 0.2$ we find here is comparable with those found in our MC studies. However, we have not carried out systematic MD work over wide ranges of T and θ to see if the decay exponent depends on the thermodynamic conditions. Thus the question of universality in the power-law decay remains to be addressed.

IV. SUMMARY AND DISCUSSION

To summarize, we have in this work presented a memory function expansion for the evaluation of transport coefficients of strongly interacting systems. We have applied this formalism to study diffusion in a variety of systems with vastly different dynamics. The first three systems are based
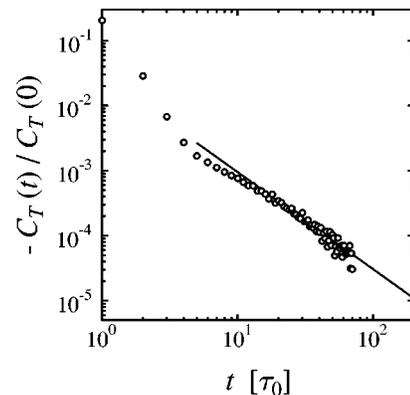
FIG. 10. Results for the decay of $C_T(t)$ at intermediate times in the model system studied through MD simulations. The parameters are the same as in the caption of Fig. 9. The straight line describes power-law behavior with $x = 1.6 \pm 0.2$, the fit being made between $20\tau_0 - 70\tau_0$.

on the lattice-gas approximation with stochastic dynamics, and studied with Monte Carlo simulation methods. The last model system consists of particles interacting with a Lennard-Jones potential moving in the presence of a periodic continuum potential and coupled to a heat bath. This system is described by Langevin dynamics and studied by appropriate extension of standard molecular dynamics simulations for deterministic systems.

In all the cases studied, the memory function expansions in Eqs. (5) and (8) converge at a point that corresponds to the onset of the hydrodynamic regime. Thus we expect the memory expansion to be applicable in studies of mass transport where a diffusive regime exists; i.e., in cases where the mean-square displacement is linear in time at long times. In contrast to the conventional method of evaluating the transport coefficient, which focuses on the long-time limit as illustrated in Eq. (2), the memory expansion formalism presented here builds up the transport coefficient as a sum of the different time contributions to an appropriately defined time-dependent correlation function. For this sum, the predominant contributions actually come from the short-time regime, while the long-time regime close to the onset of the hydrodynamic limit only provides a weak correction. The evaluation of the short-time contributions allows the extra benefit of self-averaging not possible in the long-time limit. Thus numerically, the present approach is far superior to the conventional methods. In all the cases studied here, the expansion method gives results that are not only in full agreement with the conventional methods but have also smaller error bars. Yet the computational cost for the present method was just about 10% of that used in evaluating Eq. (2) for collective diffusion through the long-time limit. We estimate that, as far as collective diffusion is concerned, the total saving in computing time to reach a comparable accuracy is roughly two orders of magnitude. For the single-particle tracer diffusion, the speedup is not as significant.

Besides the numerical efficiency, the various terms in the memory expansion have actual simple physical interpretations. The leading term corresponds to a generalized mean field result. For a special choice of the time scale, this can be simply related to the average single-particle jump rate as shown in Eqs. (9) and (10). These simple results in terms of single-particle jump rates have been widely applied to interpret experimental data for collective and tracer diffusion coefficients. Our results here show that the memory effects are very strong for complex systems with strong short-range order such as the long chain polymers or simple molecular systems with attractive interactions at low temperatures such as the O/W(110) system. For quantitative and sometimes even for qualitative purposes, the further terms in the memory expansion have to be included. These terms also can be directly compared with experimental measurements. To date, most of the microscopic studies of surface diffusion through STM measurements, for example, have only focused on the average jump rate. Further experimental studies of the memory effects in the expansion would not only provide more accurate values for the diffusion coefficient but also increase our understanding of the collective dynamics of interacting systems. Finally, the general approach presented here also allows a precise theoretical analysis for systems at relatively elevated temperatures where the paths of diffusive motion are extremely complicated and not just dictated by nearest-neighbor jumps over the saddle-point barrier.

For the decay of memory effects, we find an approximate power-law decay for the correlation function $C(t) \sim t^{-x}$ for all the systems studied at intermediate times when each individual particle has a chance to execute a few jumps on the average. Eventually, the correlation function $C(t)$ decays exponentially in the long-time limit. The origin of the power-law behavior is currently unclear. The MC studies for the three lattice-gas systems yield an estimate of decay exponent $x = 1.5 \pm 0.2$ for both tracer and collective diffusion. The MD studies for the continuum system yield a value of $x \approx 1.6$, comparable to the value found in the lattice-gas systems with stochastic dynamics. This rather universal behavior observed in all systems shows that this intermediate regime power-law behavior is most likely not the result of any specific dynamics, but holds for any system at low temperatures where the diffusive motion occurs via thermally activated jumps. Further studies of the origin of the power-law behavior and the related exponents are in progress.

Our final comment concerns applying the present approach to other transport coefficients such as shear and longitudinal viscosities and conductivity.[9] In view of Eq. (5), it is clear that the memory expansion can be written for any transport coefficient that can be expressed in terms of the mean-square displacement of some measurable dynamical variable. In the case of collective diffusion, this dynamical variable is simply the position of the center-of-mass. For shear viscosity, on the other hand, the appropriate dynamical variable can be expressed in terms of positions and velocities of flowing particles, and for thermal conductivity, this variable depends on the positions and total energies of the particles.[9] The hydrodynamic transport coefficient in question can then be expanded as formulated here in a series of terms, which describe the dynamical correlations (memory effects) characteristic for the given transport coefficient. Simulation studies to test these ideas are currently in progress.

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