Diffusion in a generalized (dense and mobile) model of a lattice gas

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Following a recent theory of diffusion in a lattice gas, we present a generalization of the local mean-field approach to study diffusion in a dense system in which particles are mobile. Our model reduces in well-defined limits to the lattice gas and fluid models which we have proposed recently for an adsorbate diffusion on the surface of a metal.

I. INTRODUCTION

Description of a diffusion processes in dense and low dimensional systems attracts considerable attention in view of their fundamental importance for many branches of physics, chemistry, and biology, and their self-evident technological applications.[1] In spite of that, theory of diffusion processes in a low dimensional system, for example, in adsorbates, is incomplete, particularly when the density becomes sufficiently high for mutual particle interactions to be of importance. Experiments reveal the temperature and the density (coverage) dependence of the diffusion coefficient, which is difficult to account for by following conventional theories.[2] These theories employ usually lattice gas models of different complexity[3] or, rather infrequently, are based on concepts of modern fluid dynamics like memory functions or cellular automata.[4-6] The lattice gas model provides a convenient description of many equilibrium properties of dense low dimensional systems and of adsorbates, allows us to chart their phase diagrams, and is easily simulated numerically by means of the Monte Carlo techniques. Results obtained in this way are generally in a good agreement with the available experimental data.[3] The use of lattice gas models to describe dynamical processes is a much less successful endeavor. In a recent publication, we have shown how the properly tailored application of the local mean-field technique[7] can bring the lattice gas kinetics into very satisfactory agreement with results of Monte Carlo simulations for diffusion in dense interacting $d = 2$ systems.[8]

In spite of this, the kinetic lattice gas description has still some shortcomings, because it ignores the momentum distribution of the particles and, therefore, is ill suited to describe all phenomena related to the "flow" properties of the system. The diffusion process in a dense system comprise both hopping like and flow aspects of redistribution of particles and therefore, as we believe, a generalization of the conventional lattice gas description which takes care of the changes of particle momenta and goes away with instantaneous "jumps" of particle between (quasi-)equilibrium positions is necessary. In a sense the cellular automaton models of diffusion[6,9] are complementary to the lattice gas description. Indeed, in the cellular automata models, the primitive physical process responsible for the system behavior is the particle velocity change upon suitably defined collisions. These models suffer from other difficulties, often of a more fundamental nature, which are well documented in the abundant literature of the subject.[10]

In the present paper, we propose a model which, as we believe, bridges the gap between our lattice gas,[8] cellular automata,[6] and mesoscopic[5] models of diffusion. The basic ingredient of our model is generalized to the $2d$-dimensional μ-space master equation, which in well-defined limits reduces to the standard form of master equation[8] or to the Boltzmann-Lorentz kinetic equation, an essential element of the cellular automata analysis in Ref. 6. We show that our model provides a description of the diffusion processes in which fluidlike characters of the process, emphasized in Refs. 6 and 5 are combined with the hopping mechanism of Ref. 8. Using suitable generalization of the local mean-field analysis from Ref. 8, we derive an expression for the diffusion coefficient, which permits us to analyze its dependence on several parameters, like temperature, density, and a value of the coupling constant measuring the strength of mutual particle interactions. In view of our interest in physics of dense adsorbates, we couch our discussion in a way that permits us to use the available experimental data on surface diffusion as a guiding rule in the analysis of our results.

II. THE MODEL

Consider a d-dimensional, classical, many particle system dense enough so the mutual particle interactions cannot be neglected. We describe the state of such a system by a μ-space distribution function $F(\mathbf{r}, \mathbf{v}, t)$, where $\mathbf{r}$ and $\mathbf{v}$ denote the particle position and velocity, respectively. The customary normalization of $F(\mathbf{r}, \mathbf{v}, t)$ is $\int d\mathbf{r} d\mathbf{v} F(\mathbf{r}, \mathbf{v}, t) = N_{\text{tot}}$, where N_{tot} is the total number of particles in the system. This distribution function obey the generalized master equation in the μ space, which we postulate in accord with two fundamental requirements.

The first one is that this equation reduces to the well known master equation for a lattice gas (in the continuum limit) when the velocity degrees of freedom of particles are "averaged out." This means that in some limit, discussed below, the diffusion process described by our model has to reduce to that discussed in Ref. 8. The second requirement is that in the opposite limit, when fluid properties of the system are of greater importance than the hoppinglike ones embodied in master equation of Ref. 8, we recover the fluidlike description provided either by mesoscopic model of Ref. 5 or by the cellular automaton model.[6] This in turn implies that the master equation in the μ space must bear a similarity with the Boltzmann-Lorentz kinetic equation, an essential ingredient of the model in Ref. 6. The third condition imposed on our model is that it must take into account mutual interactions between particles in such a way as to make the applications of the local mean-field model discussed in Ref. 8 possible.

The master equation, which fulfills above conditions reads:

$$\partial_t F(\mathbf{r}, \mathbf{v}, t) = -\mathbf{v} \cdot \nabla F(\mathbf{r}, \mathbf{v}, t) + \widehat{W}\{F\} \ . \tag{1}$$

The crucial step in our analysis is the construction of the operator $\widehat{W}\{F\}$. In Ref. 8, the operator analogous to $\widehat{W}$ was build containing the local values of the effective field, felt by the lattice gas particle undergoing the transition from one lattice site to another. This local field was subsequently treated as a stochastic (quenched) variable, distribution of which was calculated using a generalization of the procedure proposed in Ref. 7. We adopt here the same point of view modified in two ways. First, we consider a continuum description of the diffusion process (i.e., an appropriate long wavelengths limit of the lattice version). Second, we consider the full μ-space distribution as a cell variable. The cells are constructed by splitting the configuration space into a (quasi-) lattice with a spacing a and letting a particle in each configuration space cell explore the entire momentum (or velocity) space.

The operator $\widehat{W}$ acting on the phase space function $F(\mathbf{r}, \mathbf{v}, t)$ can be written down explicitly in the following form:

$$\widehat{W}F(\mathbf{r}, \mathbf{v}, t) = \phi_B(\mathbf{v}) \int d\mathbf{v}' \sum_{\mathbf{a}} \Gamma(\mathbf{r} + \mathbf{a}, t) F(\mathbf{r} + \mathbf{a}, \mathbf{v}', t)$$

$$-z\Gamma(\mathbf{r})F(\mathbf{r}, v, t) \ , \tag{2}$$

where $\phi_B(\mathbf{v})$ is the Maxwell-Boltzmann distribution function. The sum in Eq. (2) runs over all z nearest neighbors of the particle located at a site $\mathbf{r}$. The coefficients Γ are the transition rates for particle short range "jumps" between the sites $\mathbf{r}$ and $\mathbf{r} + \mathbf{a}$. Equation (2) resembles closely the generalization of the Boltzmann-Lorentz collision operator.[11] Indeed, replacing Γ's by averaged values and replacing $\phi_B(\mathbf{v}) \int d\mathbf{v}'$ by the integral operator averaging velocities over the surface of a unit sphere in the velocity space, we obtain the Boltzmann-Lorentz operator. Cellular automaton version of this collision operator was important in the construction of the model in Ref. 6.

In a general case, the operator $\widehat{W}$ is nonlinear due to the F dependence of the transition rates Γ. The local mean-field method assumes that Γ's are defined as space dependent functions and the local adsorbate state dependence for them is introduced by the procedure described below. Strictly speaking, the definition of $\widehat{W}$ given above should be considered only in its long wavelength limit. The most convenient way of writing it is to go over to the Fourier space representation. We can write then the Master operator as

$$(\widehat{W}F)_{\mathbf{q}} = -z \sum_{\mathbf{q}'} \int d\mathbf{v}' \Gamma_{\mathbf{q}-\mathbf{q}'} \Bigg[\delta(\mathbf{v} - \mathbf{v}')$$

$$- \frac{z + S_{\mathbf{q}}}{z} \phi_B(\mathbf{v}) \Bigg] F_{\mathbf{q}'}(\mathbf{v}', t) \ , \tag{3}$$

where z is the coordination number and $S_{\mathbf{q}}$ is the static structure factor $S_{\mathbf{q}} = \sum_{\mathbf{a}} \exp(i\mathbf{q} \cdot \mathbf{a}) - z$. The construction presented above satisfies the fundamental requirements imposed above Eq. (1). In the following section, we shall analyze its predictions.

III. LOCAL MEAN-FIELD APPROXIMATION

The local mean-field concepts[7,8] rely on replacing the many body master equation by the effective single particle one in which the transition rates are functionally dependent on a single-site effective field that is randomly distributed. The effective master equation has to obey the H theorem, thus for each realization of the local field distribution, the density differs from its global mean value ρ_0 by a factor $\propto \Gamma^{-1}$:

$$\rho(h) = \Gamma^{-1}(h) \frac{\rho_0}{\int dh f(h) \Gamma^{-1}(h)} \ , \tag{4}$$

where $\Gamma(h)$ is the effective transition rate, which depends on the value of the local field h, and $f(h)$ is the field distribution. The main point is now how one gets the field distribution $f(h)$. The explicit mean-field procedure for the construction of $f(h)$ was provided in our earlier work Ref. 8 following the procedure proposed in Ref. 7. We adopt here the same construction in view of its considerable success in bringing the results of the lattice gas model into a remarkable agreement with the results of the Monte Carlo simulations.

We assume from now on that the values of the transition rate coefficients in Eq. (1) are random functionals of the local fields. To proceed with an analysis of this equation, we use the pedestrian form of the Chapman-Enskog procedure. In order to do this, we use the time Fourier transform to rewrite Eq. (1) as

$$(\omega - \mathbf{q} \cdot \mathbf{v} + iz\Gamma_\mathbf{q}) F_\mathbf{q}(\mathbf{v}, \omega) = i[S_\mathbf{q} + z]\phi_B(\mathbf{v})\Gamma_\mathbf{q}\rho_\mathbf{q}(\omega) ,$$
$$(5)$$

where $\rho_\mathbf{q}(\omega) = \int d\mathbf{v} F_\mathbf{q}(\mathbf{v}, \omega)$. Integrating both sides of Eq. (5) over velocities and introducing the current $\mathbf{j}_\mathbf{q}(\omega) = \int d\mathbf{v} \mathbf{v} F_\mathbf{q}(\mathbf{v}, \omega)$, we obtain

$$(\omega - iS_\mathbf{q}\Gamma_\mathbf{q})\rho_\mathbf{q}(\omega) = \mathbf{q} \cdot \mathbf{j}_\mathbf{q}(\omega) . \qquad (6)$$

Equation (6) is the continuity equation in our model. Multiplying now Eq. (5) by a velocity and then integrating over the velocities, we obtain the second equation in the hierarchy that relates the particle current and density to the kinetic stress tensor:

$$(\omega + i\Gamma_\mathbf{q})\mathbf{j}_\mathbf{q}(\omega) = \mathbf{q} \cdot \int d\mathbf{v} \mathbf{v} \otimes \mathbf{v} F_\mathbf{q}(\mathbf{v}, \omega) . \qquad (7)$$

In the above, we have used well known properties of the Boltzmann distribution function.

To close the hierarchy, we use the lowest order Chapman-Enskog-like approximation, namely, we set $F_\mathbf{q}(\mathbf{v}, \omega) = \phi_B(\mathbf{v})\rho_\mathbf{q}(\omega)$. We obtain the relation valid for each realization of the local fields distribution:

$$(\omega - iS_\mathbf{q}\Gamma_\mathbf{q})(\omega + iz\Gamma_\mathbf{q})\rho_\mathbf{q} = \frac{\mathbf{q}^2}{m\beta}\rho_\mathbf{q} , \qquad (8)$$

where m is the adsorbate particle mass and $\beta = 1/k_B T$.

The standard assumption that for diffusive modes we expect $\omega \propto \mathbf{q}^2$ together with the small wave vector behavior of $S_\mathbf{q} \propto -q^2 a^2$ gives, with an accuracy up to q^2,

$$i\omega\rho_\mathbf{q} = \mathbf{q}^2 \left\{ \Gamma_\mathbf{q} a^2 + \frac{1}{m\beta z\Gamma_\mathbf{q}}\rho_\mathbf{q} \right\} . \qquad (9)$$

Equation (9) is the "quenched" diffusion equation. To obtain the diffusion coefficient from it we note that the diffusion equation for the density averaged over the distribution of local fields reads

$$i\omega\langle\rho_\mathbf{q}\rangle = \mathbf{q}^2 D\langle\rho_\mathbf{q}\rangle , \qquad (10)$$

where the angular brackets denote the field average $\langle A \rangle = \int dh f(h)A(h)$. Comparing now the right hand sides of Eqs. (9) and (10), we obtain the following expression for the diffusion coefficient:

$$D = \lim_{\omega \to 0, \mathbf{q} \to 0} \frac{1}{\mathbf{q}^2\langle\rho_\mathbf{q}\rangle} \left\langle \mathbf{q}^2 \left\{ \Gamma_\mathbf{q} a^2 + \frac{1}{m\beta z\Gamma_\mathbf{q}} \right\} \rho_\mathbf{q} \right\rangle . \qquad (11)$$

Note that in Eq. (11) we have treated the short range local interactions between adatoms as causing the fluctuations of the local fields on which the transition rates Γ depend. We note in passing that if the model described by Eq. (1) were supplemented with a nonrandom term akin to that used in a Vlasov plasma and describing weak long range adatom-adatom interactions $U_\mathbf{q}$, then these interactions would modify our results by changing the sound velocity of the system, $c = \sqrt{1/m\beta}$, in such a way that it would contain both the temperature and the potential energy contributions to it: $c = \sqrt{(1 + \beta\rho_0 U_0)/m\beta}$.

Final simplification, following Ref. 8, is obtained by assuming that $\rho_\mathbf{q} = \delta(\mathbf{q})\rho = \rho_0\Gamma^{-1}/\langle\Gamma^{-1}\rangle$, viz. (4). We obtain then the final expression for the diffusion coefficient averaged over the local field fluctuations:

$$D = \frac{a^2}{\langle\Gamma^{-1}\rangle} + \frac{c^2\langle\Gamma^{-2}\rangle}{\langle\Gamma^{-1}\rangle}$$
$$= D_\text{hopping} \left(1 + \frac{c^2}{a^2}\langle\Gamma^{-2}\rangle\right) , \qquad (12)$$

where D_hopping is the value of the diffusion coefficient following the simple kinetic lattice gas model discussed in Ref. 8.

The above equation combines two contributions to the diffusion process: the one which is due to fluidlike properties of the system and that which is due to its lattice gas properties. It is the inverse averaged transition rate dependence of this coefficient that makes a comparison with the Monte Carlo data in our recent work[8] so effective.

Equation (12) can be compared with the expressions for the diffusion coefficient obtained in Refs. 6 and 5. Both of these models, meant to be valid for dense fluidlike adsorbates, express the diffusion coefficient in terms of the ratio of the sound velocity squared to a single particle friction coefficient determined by the scattering of an adatom off the host lattice excitations—its surface and bulk phonons. This coefficient becomes identical to the second term in Eq. (12), provided we identify the friction coefficient with the appropriate ratio of averages involving the inverses of Γ.

IV. NUMERICAL RESULTS

We find it convenient to rewrite the diffusion coefficient D given in Eq. (12) as a sum of the hoppinglike term D_hopping and the fluidlike contribution to it. To see how these terms compare numerically for real systems, we choose the parametrization of the transition rates Γ analogous to that used in Ref. 8. Let V be the on-site potential and let J be the coupling constant measuring mutual short range repulsive interactions between the lattice gas particles. Following Ref. 8, we write the transition rates as $\Gamma(h) = \nu_0 \exp(-\beta V) \exp(-\beta h)$. The same algebra as in Ref. 8 gives

$$D = D_0\{\exp[-\rho_0 z(e^{\beta J} - 1)]$$
$$+ AT \exp[\rho_0 z e^{\beta J}(e^{\beta J} - 1)] \exp[2\beta V]\} , \qquad (13)$$

where $A = k_B/(m z \nu_0 a^2)$ and ν_0 is the overall rate factor setting a universal inverse time unit of our model. $D_0 = \nu_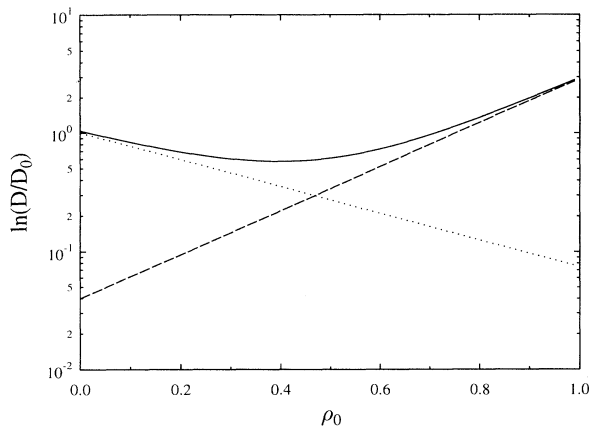0 a^2 \exp(-\beta V)$ is the diffusion coefficient for the