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LETTER TO THE EDITOR

Collective diffusion of lattice gases in disordered lattices in the absence of a single-particle diffusion coefficient

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Abstract. Collective diffusion of particles is studied in a three-dimensional lattice-gas model with site-energy disorder. The distribution of the site energies is exponential, and the diffusion coefficient of independent particles may vanish. It is demonstrated by numerical simulations that a coefficient of collective diffusion exists. An estimate of the diffusion coefficient for smaller particle concentrations suggests a power-law dependence on concentration, consistent with the simulations. An effective-medium calculation of the coefficient of collective diffusion gives good agreement with the data at smaller particle concentrations and rough agreement at larger concentrations.

The comprehension of diffusion of many particles in disordered systems is an important task and has many applications, e.g. for transport in amorphous substances. It is also a challenging theoretical problem in view of the correlations which arise from the exclusion of double occupancy of sites [1, 2]. These correlation effects are particularly pronounced in disordered systems. Consequently, the diffusion of many particles in disordered systems is not yet well understood [3]. In contrast, the major aspects of the diffusion of independent particles in disordered systems are understood [4–6]. Disordered systems may exhibit the interesting phenomenon of anomalous diffusion, for instance subdiffusive behaviour of the mean-square displacement of particles. In this note we investigate a disordered system with random site energies with an exponential distribution of the energies. If thermal activation of the particles is required for diffusion, the well known consequences of this model are anomalous diffusion of independent particles and dispersive transport at lower temperatures. We will demonstrate that in this situation collective diffusion still exists although the diffusion coefficient of independent particles vanishes.

The underlying idea is quite simple. Particles are present in the system at a given average concentration. In equilibrium, the particles will saturate the sites with lower energies; these sites are responsible for the anomalous effects in the independent-particle diffusivity. If then a density variation of small amplitude is created in the system, the density disturbance will decay diffusively. This will be confirmed by numerical simulations below, and the coefficient of collective diffusion will be estimated at various particle concentrations. It is more difficult to derive theoretically the coefficient of collective diffusion for this situation. We will first present an estimate of the coefficient of collective diffusion, which applies to smaller particle concentrations. For larger concentrations we can only give some qualitative arguments for the observed behaviour. We then perform an effective-medium

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calculation where we use symmetrized mean-field single-particle transition rates. This approximation gives good agreement at lower particle concentrations and fair agreement at larger concentrations.

The model that we study in this letter is the random site-energy model, with the distribution of site energies

$$P(E) = \frac{1}{\sigma}\exp\left(\frac{E}{\sigma}\right) \qquad E \leqslant 0\,. \tag{1}$$

The parameter σ determines the width of the distribution. We assume that the transition rates to neighbouring sites are solely determined by the site energies (site symmetry of the rates) and are given by an Arrhenius law,

$$\Gamma(E_i) = \Gamma_0 \exp(E_i/k_B T) \qquad E_i \leqslant 0\,. \tag{2}$$

Here E_i is the energy of site i, which is chosen from the distribution (1). In the computer simulations Γ_0 will be taken to be unity and the energy will be measured in units of $k_B T$. From (1) and (2) follows a power-law distribution of the transition rates,

$$W(\Gamma) = \frac{\alpha}{\Gamma_0}\left(\frac{\Gamma}{\Gamma_0}\right)^{\alpha-1} \tag{3}$$

with the parameter $\alpha = k_B T/\sigma$. The diffusion coefficient of independent particles in the random site-energy model is given, in arbitrary dimensions, by the inverse of the inverse first moment of the transition rates, if it exists [4]. An immediate consequence of (3) is that this diffusion coefficient vanishes for $\alpha \leqslant 1$. For $\alpha < 1$, the mean-square displacement of the particles shows subdiffusive behaviour with [5, 7]

$$\langle r^2(t)\rangle \sim t^{2/d_w} \tag{4}$$

and the random-walk exponent

$$d_w = \begin{cases} 1 + \dfrac{1}{\alpha} & d = 1 \\ \dfrac{2}{\alpha} & d \geqslant 2\,. \end{cases} \tag{5}$$

We have verified this behaviour by some numerical simulations.

If particles with a concentration c are filled into the system, they occupy the sites in equilibrium according to Fermi–Dirac statistics. That is, the occupation probability of a site with energy E is given by

$$f(E) = \frac{1}{1 + \exp[\beta(E-\mu)]} \tag{6}$$

where $\beta = 1/k_B T$ and μ is the chemical potential. The chemical potential is determined for given c from the implicit relation

$$c = \int_{-\infty}^{0} \mathrm{d}E\, P(E) f(E)\,. \tag{7}$$

To study collective diffusion, we prepare the system in a way that represents, on a hydrodynamic scale, a constant density plus a cosine profile in the x direction,

$$c(x) = \bar{c} + \delta c \cos(kx) \tag{8}$$

where $k = 2\pi/\lambda$ and λ is the wavelength of the density disturbance. We use a three-dimensional simple-cubic lattice and randomly assign energies to the sites, taken from the exponential distribution (1). We then put particles on the yz planes with occupation

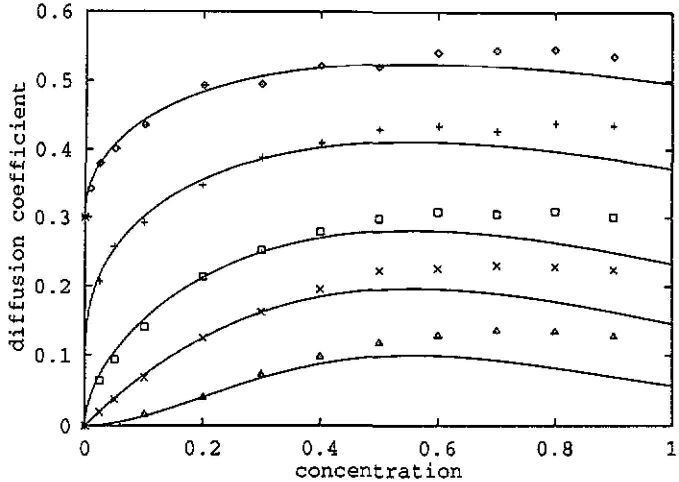

Figure 1. Coefficient of collective diffusion as a function of particle concentration. Symbols, numerical data; curves, results of the effective-medium theory. Results are given for the parameters $\alpha = 1.43(\Diamond)$, $1.0(+)$, $0.667(\square)$, $0.5(\times)$, and $0.333(\Delta)$.

probabilities according to (8). For equilibration we let particles jump in the y and z directions before beginning with the investigation of the decay of the cosine profile.

The dynamics of the system is the usual lattice-gas dynamics and it is performed with the transition rates that are specified in (1) and (2). We use the vectorized computer code that was developed in [8]. If the decay of the density profile is governed by the diffusion equation, the amplitude δc decays as $\exp(-D_{\mathrm{coll}}k^2t)$ and one can extract a coefficient of collective diffusion. We observe an exponential decay on the time-scale resolved by our method and hence we can deduce diffusion coefficients from our data. Only in the case of small α and c do we get deviations from the exponential decay. The results are presented in figure 1 for various particle concentrations and several values of the parameter α. For small concentrations, the diffusion coefficient approaches the correct value for $\alpha > 1$, and it seems to approach 0 for $\alpha \leqslant 1$, consistent with theory. The diffusion coefficient increases strongly with c, for $\alpha < 1$, and reaches a roughly constant value at larger concentrations.

We now try to understand qualitatively the behaviour of the coefficient of collective diffusion in the model with an exponential distribution of site energies. The essential point is that sites with lower energy are saturated by particles that do not participate in the diffusion process. We assume that at smaller particle concentrations diffusion is effected by single particles which visit sites with energies E larger than a characteristic cut-off energy E^*. To estimate the cut-off energy E^* we postulate that for a given concentration c all sites with energies $E < E^*$ are filled,

$$\int_{-\infty}^{E^*} \mathrm{d}E \frac{1}{\sigma} \exp\left(\frac{E}{\sigma}\right) = c\,. \tag{9}$$

This means that we neglect the thermal broadening of the site occupation probabilities in the determination of E^*. The cut-off energy E^* is then given by

$$E^* = \sigma \ln(c)\,. \tag{10}$$

Since only a small fraction of the particles will promote diffusion, we can identify the coefficient of collective diffusion with the diffusion coefficient of independent particles,

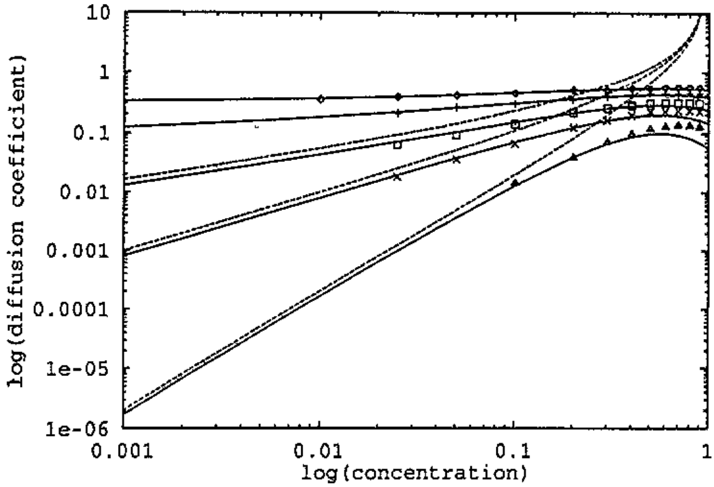

Figure 2. Coefficient of collective diffusion as a function of particle concentration in double-logarithmic representation. Symbols, numerical data; broken curves, estimate of (12); full curves, effective-medium theory. The parameter values are the same as in figure 1.

$D_{\mathrm{coll}}^{-1} \approx D^{-1}$ and

$$D^{-1} = \int_{E^*}^{0} \mathrm{d}E\, P(E)\Gamma^{-1}(E)\,. \tag{11}$$

The integral is performed using (1) and (2) and the result is

$$D = \frac{\Gamma_0(\alpha^{-1} - 1)}{c^{(1-\alpha^{-1})} - 1}\,. \tag{12}$$

For small c we have approximately

$$D_{\mathrm{coll}} \approx \Gamma_0(\alpha^{-1} - 1)c^{(\alpha^{-1}-1)} \tag{13}$$

that is, a power-law dependence on the concentration. In figure 2 we have plotted the results of (12) in a doubly logarithmic presentation, together with the simulation data. The estimate is consistent with the data, although more numerical data are needed to really confirm, for instance, the power-law dependence of (13). The result is that (12) diverges in the limit $c \to 1$, where the underlying ideas of the estimate do not apply.

At larger particle concentrations, a majority of the sites is occupied and we cannot invoke the picture of diffusion of a few particles in a more or less complete lattice. We tentatively assume that we can identify an effective activation energy E^{**} solely from the distribution of the site energies, without considering any effects of the occupancy of sites. The idea behind this assumption is that collective diffusion is independent of particle concentration in the lattice gas with uniform transition rates. We hence assume that E^{**} is determined from

$$\int_{-\infty}^{E^{**}} \mathrm{d}E \frac{1}{\sigma} \exp\left(\frac{E}{\sigma}\right) = \nu \tag{14}$$

with a fixed fraction of states ν. The resulting activation energy is

$$E^{**} = \sigma \ln(\nu)\,. \tag{15}$$

If the result is used in the Arrhenius expression for the transition rate, we have

$$\Gamma^{**} = (\nu)^{1/\alpha}\,. \tag{16}$$

If we identify D_{coll} with Γ^{**}, we observe rough agreement with the data for particle concentrations in the plateau region when we choose $\nu = \frac{1}{2}$. However, there are deviations of up to 20 percent which demonstrate the roughness of the argument.

We now give an effective-medium theory (EMT) for the collective diffusivity for our problem. To use the formalism of EMT, the many-particle problem has to be reduced to a one-particle problem. In a recent letter [9] mean-field one-particle transition rates were introduced by a factorization of the two-particle correlations and the diffusion coefficient was evaluated by first-passage time methods. While this formulation is appropriate for the one-dimensional case, the application of the EMT requires symmetric transition rates. Symmetrized one-particle rates have already been introduced by Gartner and Pitis [2], and we will use their formulation subsequently. The symmetrized transition rates are obtained by multiplying Γ_i with the Fermi–Dirac occupation factors

$$W_{i,j} = \Gamma_j f_j(1 - f_i) = W_{j,i}\,. \tag{17}$$

We use the EMT in the single-bond approximation which was developed by Webman [10]. The self-consistency condition established by him reads in the static limit

$$\left\{ \frac{\overline{W} - W}{(d-1)\overline{W} + W} \right\} = 0 \tag{18}$$

where $\{\quad\}$ indicates the average over the disorder, i.e. over the distribution of the rates W. $\overline{W}$ is the effective transition rate which has to be determined from (18) and W is the symmetric single-bond transition rate. To ensure proper normalization, the resulting diffusivity has to be divided by the mean value

$$\{a^2\} = \{f(1-f)\}\,. \tag{19}$$

The EMT result in $d = 1$ is $\overline{W}^{-1} = \{W^{-1}\}$ and $D = \overline{W}/\{a^2\}$, in agreement with the results in [2, 9], which were obtained by different methods. We evaluate (18) in $d = 3$ by implementing the disorder average as a numerical integral and by varying $\overline{W}$ until the equation is satisfied. The resulting EMT diffusion coefficient is presented in figure 1. One recognizes rather good agreement with the simulations at smaller particle concentrations. Note that the EMT result also agrees with the estimate of the diffusion coefficient at small concentrations. At larger particle concentrations, there are differences between the EMT result and the simulation data, but the general behaviour is still satisfactory.

A possible source of the discrepancy between the EMT result and the numerical simulations at larger concentrations is the possibility that the simulations may not detect the asymptotic decay of the density disturbance. If the density disturbance initially decays faster, a larger diffusion coefficient would be observed in the simulations. Such problems did arise at smaller c, but not at larger c. Gartner and Pitis [2] emphasize that the mean-field approximation, that is the reduction of the many-particle problem to a single-particle problem, gives an upper limit for the diffusion coefficient. Here we observe larger values than the theoretical result. However, in our derivations two approximations are made, namely the mean-field approximation combined with the effective-medium approximation. Further, when one of the sites in the symmetric rate equation (17) already has a very low energy, the transition rate becomes very small. This may lead to an underestimate of the diffusion coefficient by the EMT.

In conclusion we have demonstrated that collective diffusion can exist in a situation where no coefficient of independent-particle diffusion exists. The effect is due to the saturation of the sites with low energies by particles. The particles participating in the diffusion process have to circumvent the immobile particles, apparently in dimension $d \geqslant 2$

they can achieve this. A paper that will present the EMT results in more detail and for other distibutions of site energies and dimensions is in preparation [11].

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