

Constant pressure simulations of lattice gas models

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(Received 27 August 1996; accepted 30 October 1996)

A method for constant pressure Monte Carlo simulations in lattice gas models is described. The simulation box is placed between two hard walls with fluctuating distance, and periodic boundary conditions are applied in the perpendicular directions. Continuous volume fluctuations in the bounded direction are made possible by introducing a generalized volume, which interpolates between the discrete values that correspond to the given lattice. This is achieved by using a surface potential variable which makes the lattice surface layer next to the hard wall gradually less accessible to particle occupation. The method is applied to the equation of state of noninteracting lattice gas models, where exact results are available for comparison, and also to less trivial models of interacting point-particles and athermal lattice chains, for which the quasichemical approximation (QCA) provides reliable results to compare with. For the chain simulations the method can be used in conjunction with the configuration biased Monte Carlo procedure in order to enhance its performance. However, since the Monte Carlo moves can be chosen to fit any desired kinetic model, our method can be used not only to generate constant pressure equilibrium ensembles, but also in the context of dynamic Monte Carlo studies. The center of mass diffusion in dense systems of athermal chains is investigated as an example. In all our static applications the method performs very well in comparison with exact or with QCA results, provided that the system size is large enough in the bounded direction. For small systems finite size effects are observed and analyzed, suggesting potential applications in the study of confined systems. © 1997 American Institute of Physics. [S0021-9606(97)50406-5]

I. INTRODUCTION

Lattice gas (LG) models are widely used in theoretical studies of complex condensed phase systems such as fluid mixtures, alloys, polymer solutions and polymer melts. Monte Carlo (MC) simulations have greatly contributed to the theoretical understanding of static and dynamic properties of such models.¹ Provided one focuses on qualitative generic issues, which are not sensitive to the microscopic local structure and dynamics, lattice MC simulations can often replace the more realistic molecular dynamics (MD) and MC calculations of continuous models. One obvious advantage of lattice models is the extended range of accessible time scales. For example, Baschnagel and Binder² have estimated the accessible time in their bond fluctuation LG model for the glass transition in polymeric systems to be in the range 10^{-12} – 10^{-5} s. This should be compared with the time window shorter than $\sim 10^{-9}$ s currently accessible for MD and MC simulations of continuous systems.

In various applications, e.g., in investigations of the equation of state or possible phase changes it is required to compute the pressure of a simulated system, or to execute a constant pressure simulation. The glass transition studies of Ref. 2 are an example. While these studies demonstrate that a glass transitionlike behavior exists in a model simulated at constant volume, one expects both intuitively and with the

background of free volume models,³ that the behavior at constant pressure may change significantly when the system volume changes upon cooling. Similarly, when simulating transport properties as a function of temperature, a constant pressure simulation is usually more relevant to experimental work than the usual constant volume simulations.

In simulations of continuous systems the pressure can be computed from the virial theorem. This procedure cannot be carried out in LG simulations when the potential as a function of position is not differentiable. Alternative methods were proposed and tested successfully.^{4–8} In particular, Dickmann⁸ has shown that the pressure can be computed by simulating a system between two hard walls in, say, the x -direction. The walls are located at $x=0$ and $x/a=L+1$ (a is the lattice constant), so the lattice is made of L layers denoted by l ($l=1, \dots, L$). An additional external positive energy ϵ_s is imposed uniformly on the surface layer $l=L$, so that as $\epsilon_s \rightarrow \infty$ all particles are driven away from the layer. The equilibrium fractional population on the surface layer, $f(\epsilon_s) = \langle n_s \rangle / S$, where $\langle n_s \rangle$ is the average number of particles and S the number of sites in the surface layer, is monitored. The pressure can then be obtained from the relation

$$pv = \int_0^\infty d\epsilon_s f(\epsilon_s), \quad (1)$$

where $v = a^3$ is the volume per site. Putting $\lambda = \exp(-\beta\epsilon_s)$ with $\beta = (k_B T)^{-1}$ leads to the dimensionless form of Eq. (1),

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$$\beta p v = \int_0^1 \frac{d\lambda}{\lambda} f(\epsilon_s). \quad (2)$$

The advantage of this elegant result over the previous methods⁴⁻⁷ based on insertion algorithms is that it can be applied with equal ease to simple systems as well as to lattice models of macromolecular systems.

Constant pressure simulations are performed by taking the volume as a dynamical variable. For continuous systems, the methodology of constant pressure (NPT ensemble) MC simulation has been described by Wood⁹ and by McDonald,¹⁰ while the corresponding dynamical equations of motion were derived by Andersen.¹¹ In lattice systems a volume changing move constitutes a large perturbation with a prohibitively low acceptance probability, particularly in simulations involving chain molecules. Mackie *et al.*,^{12,13} have overcome this problem by using the methodology of configurational bias Monte Carlo (CBMC) procedure¹⁴ while performing volume changing steps involving the addition or removal of a whole lattice layer. This method has the advantage of efficiency (with limitations discussed by the authors) in creating a constant pressure ensemble. However, by its very nature of performing large unphysical steps it cannot be used in estimating relative time scales of dynamical processes such as diffusion. Another method advanced by Nies and Cifra¹⁵ uses a different methodology. The system is confined between two hard walls along one direction (periodic boundary conditions are imposed in the perpendicular directions), and the volume change is executed by building/destroying the wall site by site, using the Boltzmann factor $\exp(-\beta p V)$ to decide on the acceptance of such a move. Apart from producing a system interacting with a ragged wall, this method is hampered by long equilibration times in particular when dealing with chain molecules.

The methods reviewed above were tested successfully by comparing the simulated equation of state behavior to theoretical results for exactly solvable models as well as for systems where the quasichemical approximation (QCA Ref. 16) is known to perform well. In the present paper we propose an alternative method that appears to be as efficient as the CBMC method of Mackie *et al.*^{12,13} for calculating equilibrium properties, but which can also be used in the context of dynamical MC simulations. The proposed method involves volume changes via the motion of a planar wall ("piston"), which provides the boundary to the system in the x -direction. In order to achieve volume fluctuations on acceptable time scales, we subdivide the removal or addition of a layer next to the wall into an arbitrary number of steps. This is done by assigning a repulsive potential ϵ_s to this surface layer, which varies stochastically between zero and a value $\epsilon_s^{\max} \gg k_B T$. As ϵ_s increases particles get removed from the surface layer, making it possible for the wall to move inward, thus reducing the volume of the system by one layer. The opposite process of expansion involves the reverse gradual decrease in ϵ_s . The method is naturally formulated in terms of a generalized volume, which is equal to the actual volume each time a layer is completely added or removed, and interpolates between these values according to the cho-

sen steps in the potential ϵ_s . The energy of the system can be written explicitly in terms of this generalized volume, thus making it possible to execute reversible and consistent MC steps. For the constant pressure simulation of chain molecules the method can be combined with the CMBC procedure¹⁴ at the equilibration stage, while the fact that the wall remains smooth at all times and that the step size of its motion can be made as small as needed, makes it possible also to carry out physically meaningful *dynamical* MC simulations at constant pressure.

Details of the method and an outline of the algorithm are given in the next section. As a performance check of our method we discuss a comparison of simulation results to exact predictions for a simple noninteracting lattice gas. In Sec. III we provide some simulation results for less trivial models; a simple lattice gas with nearest neighbour (nn) interactions, and a system of athermal lattice chains. These results are compared with predictions made using the QCA, an approximation known to work well for such systems. Finally, in Sec. IV we demonstrate the applicability of this method to dynamical MC simulations by showing preliminary results for diffusion in a system of athermal lattice chains. Further applications to transport are deferred to a later publication.

II. THE SIMULATION METHOD

In order to describe the implementation of our method in detail, consider a three-dimensional simple cubic lattice of spacing a and a volume per site $v = a^3$, which is confined along the x -axis between impenetrable walls at $x/a = 0$ and $x/a = L + 1$. In the directions perpendicular to x the system size is aL_{\perp} , and periodic boundary conditions are imposed. The total number of sites is therefore $M = SL$ with $S = L_{\perp}^2$. Sites can be occupied by particles or chain beads, which may interact with each other and move on the lattice in specified ways. Multiple occupation of sites is excluded.

As mentioned before, a site energy $\epsilon_s \geq 0$ is uniformly assigned to all sites of the surface layer $x/a = L$, whereas sites in the bulk, $1 \leq x/a \leq L - 1$, have zero energy. The surface potential ϵ_s can take a set of values $\epsilon_s(k')$, $1 \leq k' \leq K$, and decreases in K steps from $\epsilon_s^{\max} = \epsilon_s(1) \gg k_B T$ to $\epsilon_s(K) = 0$ as k' increases from 1 to K . Volume fluctuations (in the x -direction only) occur in the following way: Whenever k' moves during the MC evolution down from its lowest value $k' = 1$, its value is set to $k' = K$ and the number of layers L is reduced by 1, $L \rightarrow L - 1$. Whenever k' is increased from its maximum value $k' = K$, its value is set to $k' = 1$ and the value of L is reset according to $L \rightarrow L + 1$. In this way we insure that actual moves of the wall, i.e., the formal elimination or addition of a surface layer is only done when the removed or added layer is empty. The constant K denotes the number of steps in which a surface layer is completely removed or added in this way. The actual form of the function $\epsilon_s(k')$ will be discussed later.

At this point it is convenient to introduce an integer variable k , $0 < k < \infty$, which is related to the length L in the x -direction by

$$k = (L-1)K + k'; \quad 1 \leq k' \leq K. \quad (3)$$

Once the constant K is chosen, the integer variable k uniquely determines both the number of layers L and the integer k' , which determines the surface energy via

$$L-1 = k \bmod K, \quad k' = k - (L-1)K. \quad (4)$$

Keeping in mind that by decreasing k' [i.e., increasing $\epsilon_s(k')$] particles get progressively repelled from the surface layer $x/a=L$, we may regard the quantity $\mathcal{V}/v = Sk/K$ as a generalized volume of our system. Correspondingly, we define the generalized number of layers (dimensionless length) by $\mathcal{L} = k/K$. \mathcal{V} and \mathcal{L} coincide with the actual volume V and the dimensionless length parameter L whenever $k' = K$.

Configurations of the whole system, including both the lattice gas particles and the generalized volume, are now specified by the set of occupation numbers of lattice sites, $\mathbf{n} = \{n_j\}$, together with the variable k . The partition function of this system takes the form

$$Z(N, T, p) = \sum_{\mathbf{n}}'' \sum_{k=k_{\min}(N)}^{\infty} \exp[-\beta \mathcal{H}(\mathbf{n}, k)], \quad (5)$$

$$\mathcal{H}(\mathbf{n}, k) = H(\mathbf{n}) + n_s \epsilon_s(k') + pvSk/K, \quad (6)$$

where $H(\mathbf{n})$ is the configurational energy due to interparticle interactions. n_s denotes the number of particles in the surface layer $x/a=L$ and the variable p is conjugate to the generalized volume and is hence regarded as the (generalized) pressure. The prime in the first summation in Eq. (5) denotes summation over particle configurations with a fixed total number of particles, $\sum_j n_j = N$, and $k_{\min}(N)$ corresponds to the smallest value of the generalized volume admitting N particles. It determines the minimum number of layers by the relation $L_{\min} = 1 + k_{\min}(N)$. Clearly, from Eqs. (5) and (6) we have the standard relations

$$\langle \mathcal{V} \rangle = -k_B T \frac{\partial \ln Z}{\partial p} \quad (7)$$

and

$$\langle \mathcal{V}^2 \rangle - \langle \mathcal{V} \rangle^2 = -k_B T \frac{\partial \langle \mathcal{V} \rangle}{\partial p} = (k_B T)^2 \frac{\partial^2 \ln Z}{\partial p^2}. \quad (8)$$

The existence of a well defined Hamiltonian, Eq. (6), makes it possible to evaluate the thermodynamic properties of our system using a MC simulation. Configurations $\{\mathbf{n}, k\}$ are sampled using the standard Metropolis algorithm, while the acceptance criterion is determined by the configuration energy $\mathcal{H}(\mathbf{n}, k)$.

Finally, consider the surface potential $\epsilon_s(k')$. A convenient choice of this function is

$$\epsilon_s(k') = -k_B T \ln \frac{k'}{K}, \quad (9)$$

which ensures that for a noninteracting system the average occupation of the surface layer changes linearly with k' . In the calculations presented in the following sections we have

used the form (9) for the surface potential, but other choices may be advantageous in certain cases. Note that the chosen value of K defines $\epsilon_s^{\max} = k_B T \ln K$.

A MC move consists of changing either \mathbf{n} or k . The ratio between the frequencies of attempted k -moves and attempted changes in \mathbf{n} is denoted by R . In addition, the choice of K determines how smoothly wall moves affect the system. The choice of these parameters is a technical issue which affects the efficiency, but not the results of the equilibrium simulations.

It is instructive to examine the performance of our method for a simple noninteracting lattice gas (NILG), for which the partition function Eq. (5) can be evaluated exactly. For this system $H(\mathbf{n})=0$, and Eq. (5) becomes after some calculations

$$Z(N, T, p) = \sum_{L=L_{\min}}^{\infty} e^{-\pi S(L-1)} \sum_{n_s=0}^{\tilde{N}} \binom{S(L-1)}{N-n_s} \binom{S}{n_s} I(n_s), \quad (10)$$

where in the present case Z depends on temperature and pressure only through the variable $\pi = \beta p v$. In addition, we have introduced $\tilde{N} = \min(N, S)$ and

$$I(n) = \sum_{k'=1}^K \exp[-n\beta\epsilon_s(k')] \exp[-\pi S(k'/K)]. \quad (11)$$

From Eq. (10) the equation of state is obtained by calculating the generalized length $\langle \mathcal{L} \rangle = -(1/S) \partial \ln Z / \partial \pi$. In the thermodynamic limit it is straightforward to reproduce the well-known equation of state for a NILG

$$\pi = -\ln(1-c), \quad (12)$$

where $c = N/(S\langle \mathcal{L} \rangle)$. As a test case we carried out Monte Carlo simulations as described above for a NILG system, using parameters $K=10^3$ and $R=1$. Perfect agreement with Eq. (12) was found as long as $\langle \mathcal{L} \rangle$ was sufficiently large ($\langle \mathcal{L} \rangle \geq 20$). Additional tests of our simulation algorithm for situations with smaller $\langle \mathcal{L} \rangle$ were carried out by comparison with numerical calculations based on expression (10). Clearly, as $\langle \mathcal{L} \rangle$ becomes comparable with one lattice constant, $\langle \mathcal{L} \rangle \sim 1$, the results will notably be affected by the particular choice of the function $\epsilon_s(k')$. This range, however, is physically not relevant.

Before we proceed to describe some applications of our simulation method to more complex systems, let us remark here that the simple NILG model makes it possible to illustrate some distinct properties of few particle systems, which are expected to hold also under more general conditions. Similar to Eq. (10) we write the exact expression for the distribution function $P(\mathcal{L})$ for length fluctuations at constant pressure. Deviations from a Gaussian distribution are readily obtained as $\langle \mathcal{L} \rangle \leq 20$. In that case it turns out that $P(\mathcal{L})$ becomes asymmetric and develops a tail towards larger \mathcal{L} . This asymmetry gets enhanced by reducing the system size in the lateral direction. We find that large asymmetries in $P(\mathcal{L})$ are associated with a shift of $\langle \mathcal{L} \rangle$ towards values which are larger than in the corresponding bulk limit [Eq. (12)], indicating that the equation of state is modified for

small confined systems. This latter theme has attracted some attention in recent years,¹⁸ and we point out that such issues are accessible also by the constant pressure algorithm presented here.

III. EQUILIBRIUM SIMULATIONS OF INTERACTING PARTICLES AND ATHERMAL CHAINS

In this section we describe results on simple model systems that do not admit exact solutions, but are known to be described fairly well by simple approximate methods. In particular we compare the simulated equation of state behaviour with results obtained using Guggenheim's quasichemical approximation (QCA).¹⁶ The systems considered are (a) single particles with repulsive nearest neighbor (nn) interactions and (b) systems of athermal chains. As previous work has shown, the QCA renders a very good approximation for the equation of state of these systems. Therefore this investigation provides a further, more stringent test of our simulation method.

The quasichemical approximation for a system of n_c chemical species is based on the assumption that the system configurations can be enumerated and their energy evaluated, as a function of the number of particles of species α , $\{N_\alpha\}$, and of the number of nearest neighbor pairs, $\{N_{\alpha\beta}\}$. The Gibbs free energy $G = E(\{N_\alpha\}, \{N_{\alpha\beta}\}) - k_B T \ln \Omega(\{N_\alpha\}, \{N_{\alpha\beta}\}) + pV(\{N_\alpha\})$ is then minimized with respect to $\{N_{\alpha\beta}\}$ and to the number of vacancies N_0 , for given p , T , and $\{N_\alpha\}$. This leads to the following set of equations:

$$\frac{\bar{\phi}_\alpha}{1 + \bar{\phi}_0} = \chi_{\alpha\alpha} + \sum_{\beta, \beta \neq \alpha} \chi_{\alpha\beta}, \quad (13)$$

$$\chi_{\alpha\alpha} \chi_{\beta\beta} = e^{\beta \Delta \epsilon_{\alpha\beta}} \chi_{\alpha\beta}^2, \quad (14)$$

$$\pi \equiv \frac{pv}{k_B T} = - \left[(1-z) \ln \bar{\phi}_0 + \frac{z}{2} \ln(1 + \bar{\phi}_0) + \frac{z}{2} \ln \chi_{00} + \left(\frac{z}{2} - 1 \right) \ln \frac{M}{N_q} \right], \quad (15)$$

with

$$\chi_{\alpha\beta} = \frac{N_{\alpha\beta}}{N_q + N_0}; \quad \bar{\phi}_\alpha = \frac{q_\alpha N_\alpha}{N_q}, \quad (16)$$

$$N_q = \sum_{\alpha=1}^{n_c} q_\alpha N_\alpha; \quad q_\alpha = \frac{r_\alpha(z-2)+2}{z}; \quad (q_0=1), \quad (17)$$

$$\Delta \epsilon_{\alpha\beta} = \epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta}, \quad (18)$$

where r_α is the number of beads in a chain of type α , $\epsilon_{\alpha\beta}$ is the nn interaction energy between nonbonded beads of types α and β , M is the total number of lattice sites and z is the lattice coordination number. The subscript 0 corresponds to the vacancy "species" and $\epsilon_{0\alpha}$ is taken to be zero. For a system of N identical single particles interacting with a nn

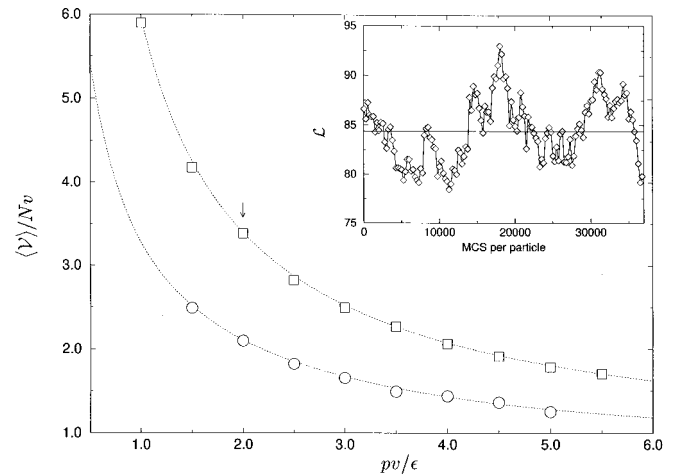


FIG. 1. The specific volume $\langle M \rangle / N = \langle \mathcal{V} \rangle / (Nv)$ plotted against the reduced pressure pv/ϵ for two systems of single particles with repulsive nn interaction ϵ . Squares, simulation results for 400 particles and $k_B T/\epsilon=5.0$. Circles, simulation results for 250 particles and $k_B T/\epsilon=2.0$. Dotted lines, QCA results for the same systems. In these simulations $S=16$, $K=200$ and $R=1$. The inset shows the "evolution" of the generalized length \mathcal{L} along the MC "trajectory" for the 400 particle system in the macroscopic state defined by $k_B T/\epsilon=5.0$ and $pv/\epsilon=2.0$ (the point marked by an arrow in the main figure). The horizontal line in the inset denotes the corresponding average $\langle \mathcal{L} \rangle$.

energy ϵ , Eqs. (13) and (14) are solved numerically for $\chi_{\alpha\beta}$ in terms of N and $M = N + N_0$. Equation (15), in which the rhs is only expressed in terms of z , N , and M , is the desired equation of state. This procedure yields the QCA line in Fig. 1. For a system of N identical homogenous athermal r -mers ($\Delta \epsilon_{\alpha\beta} = 0$) Eqs. (13) and (14) can be solved analytically, yielding the equation of state

$$-\pi = \ln(1-c) - \frac{z}{2} \ln \left(1 - \frac{2(r-1)}{zr} c \right), \quad (19)$$

where $c = Nr/M$. The QCA lines in Fig. 2 are obtained from Eq. (19) with $z=6$.

In Fig. 1 we show a comparison between our simulations and the corresponding results of the QCA approximation for a system of simple point-particles with repulsive nn interactions ϵ on a simple cubic lattice. Shown is the specific volume, $\langle M \rangle / N = \langle \mathcal{V} \rangle / (Nv)$ as a function of the dimensionless pressure, pv/ϵ , for two systems with different temperatures and numbers of particles. The experience from the NILG simulations directs us to use a system that is strongly extended in the x -direction (along which the system is bounded by the moving wall). In the present simulations we took $S=16$, which implies that $L = M/S$ varies in the range 30–200. The inset to Fig. 1 shows the fluctuations in the generalized length \mathcal{L} along the MC trajectory for the point marked by an arrow in the main figure ($N=400$, $k_B T/\epsilon=5.0$, $pv/\epsilon=2.0$). In these simulations we have used $K=200$ and $R=1$, however the results are not sensitive to this choice within relatively broad limits. In the cases displayed, the agreement between the simulation results and the QCA predictions is excellent. Preliminary results for temperatures lower than the critical temperature for the order–disorder

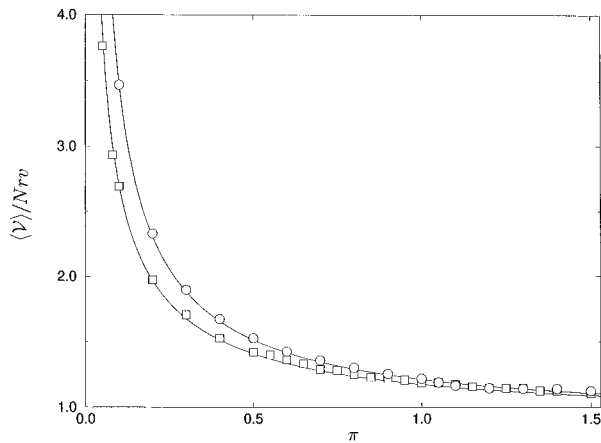


FIG. 2. MC simulation results for the specific volume (per bead), $\langle V \rangle / Nr v = \langle \mathcal{V} \rangle / Nr v$, in a system of 500 noninteracting linearly connected chains made of 5 beads (circles) and a system of 400 similar chains with 13 beads (squares), plotted against the reduced pressure $\pi = pv / k_B T$. The full lines are the corresponding QCA results, Eq. (19). In these calculations we chose $S=100$, $K=100$, $R=500$ for $r=5$ and $R=800$ for $r=13$ in the equilibrium stage (during which the CBMC procedure was used), while $R=50$ resp. $R=80$ during the rest of the equilibrium MC "trajectory" (in which end-jump, kink-jump, and crankshaft moves were used).

transition in our system ($k_B T_c / \epsilon \approx 1.23$ in the QCA while the exact value is ≈ 1.13) indicate a discrepancy of $\sim 10\%$ between the simulation results and the QCA, part of it, however, may be related to the slow convergence to equilibrium of the ordered phase.

Next consider athermal chains. Figure 2 shows the volume vs pressure behavior of a system of noninteracting lattice chains made of linearly connected beads with site exclusion. The systems simulated contain 500 chains with $r=5$ (2500 beads in total) and 400 chains with $r=13$ (5200 beads). We have chosen a simulation box of size $L_{\perp}=10$ (i.e., $S=100$). After the preparation of the system with the desired number of chains, we have equilibrated it using the CBMC procedure for changing the chain configuration. The wall evolution was carried out with $K=100$ and $R=500$ for $r=5$ and $R=800$ for $r=13$ (i.e., 500 resp. 800 attempts to change the energy of the surface layer were made for each attempt to change a chain configuration by the CBMC procedure).¹⁹ In principle we could use the same procedure to generate all the needed equilibrium configurations. However, in some cases, once equilibrium was reached, we have switched to using small configurational changes (see Sec. IV) and correspondingly smaller values of R .

As before, the equilibrium behavior of this system, as shown in Fig. 2, is very well reproduced by the QCA. This remarkable agreement provides an additional demonstration of the success of this approximation for systems of this type, while at the same time it shows the validity of our numerical procedure for simulating lattice chains at constant pressure. In addition, since the elementary steps of our volume fluctuations are always small (individual beads are pushed out of, or reintroduced into the surface layer), our procedure can be used also in the context of dynamic MC calculations, as we show next.

IV. DYNAMIC MC CALCULATIONS

This section provides some preliminary results which demonstrate the potential usefulness of our method in the context of dynamic MC calculations. Concerning the dynamic interpretation of MC simulations, it suffices to emphasize that we are dealing with a dynamical model, similar to what is implied by any phenomenological master equation. The process studied therefore depends on the nature of the MC steps allowed, and such a study can yield information about *relative* transport coefficients at different temperatures, pressures, chain lengths, etc.

In the present study we have calculated the self-diffusion coefficient in a system of noninteracting simple chain molecules, made of simply connected beads whose motion on our cubic lattice takes place via end-jump, kink-jump, and crankshaft moves.^{20,21} The constant volume dynamics of such models has been studied before, for relatively short chains, and the results are in close agreement with predictions based on Rouse theory.^{22,23} In performing these calculations we have equilibrated the system first using the CBMC procedure ($\sim 10^5$ such steps per chain were used at this stage), then restricted the MC steps to "elementary" (end, kink, and crankshaft moves) and evolved the system for additional $\sim 10^6$ steps per bead. The wall attempt rate was $R=500$ for $r=5$ and $R=800$ for $r=13$ in the equilibrium stage and $R=50$ resp. $R=80$ in the following equilibrium "trajectory." The difference in the values of R is taken because it compares the wall rate to the frequency of a CBMC step in the former case, and to the frequency of a small elementary move in the latter. The diffusion coefficient was obtained from the mean-square displacement, which, after an initial transient should be given by $D = \langle \mathbf{R}^2 \rangle / 6t$, where \mathbf{R} is the chain center of mass distance at "time" t from its position at time 0, t being the number of MC attempts per bead. It should be pointed out that due to the reflecting boundaries imposed on the system in the x -direction, care has to be taken to make the system long enough in this direction. Alternatively (and more efficiently) one can extract the diffusion coefficient from $(Y^2 + Z^2) / 4t$, using the displacements in the perpendicular directions only where periodic boundary conditions are imposed.

The results shown in Fig. 3 were obtained using the latter procedure. In this figure we have plotted the center of mass diffusion constant D as a function of pressure for the two systems studied. (The data are normalized so that $D=1$ corresponds to the diffusion of a freely moving single particle on the lattice.) Taken as a function of pressure, D is roughly proportional to an Arrhenius-type term $\exp(-p\tilde{v} / k_B T)$, with $\tilde{v} \approx 23v$. Note that for $\pi \geq 1$ the two curves display a small oscillatory component superimposed onto a smoothly decaying function. This appears to be a consequence of small structures in the equation of state, known already from the calculations for the noninteracting lattice gas in cases, where $\langle \mathcal{L} \rangle$ becomes of the order of a few lattice constants.

Next we show that when ignoring these structures, a relatively simple relationship exists between D and the free volume $V_0 = (\langle M \rangle - rN)v$. This can be seen in Fig. 4, where

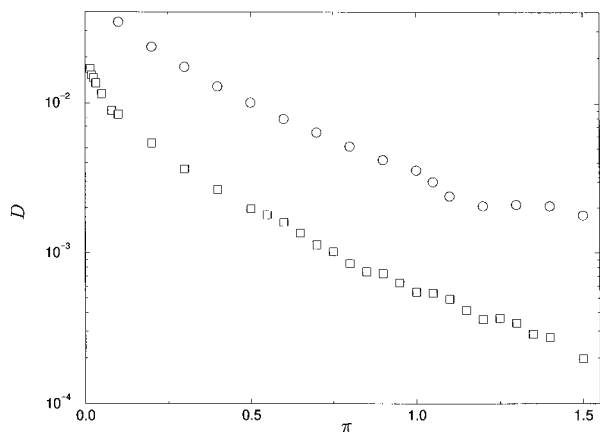


FIG. 3. The center of mass self-diffusion coefficient [calculated from $D = (\langle Y^2 \rangle + \langle Z^2 \rangle) / (4t)$, where t is the number of attempted MC steps per particle] for the systems described in Fig. 2, plotted against the reduced pressure $\pi = pv/k_B T$. Circles and squares correspond to the systems with 500 beads with 5 beads and 400 chains with 13 beads, respectively. The values for D are normalized, so that $D=1$ corresponds to the diffusion of a freely moving single particle on the lattice. These results were obtained from the equilibrium MC "trajectory" which has generated the data of Fig. 2.

the scaled diffusion constant D is plotted vs the relative free volume $v_f = V_0 / \langle M \rangle v = (1 - c) / c$, with $c = rN / \langle M \rangle$ denoting the concentration of sites occupied by a polymer bead. First we note that as v_f becomes small, D depends linearly on v_f within a certain range, $D \propto v_f - v_f^*$, see the dashed straight lines in the inset of Fig. 4. Evidently, the quantity $v_f^* = v_f^*(r)$ increases with increasing chain length r : $v_f^*(r) = 0.05, 0.12, 0.15$ for $r=5, 13, 20$, respectively. (In Fig. 4 we also included some data for $r=20$ in addition to the chain

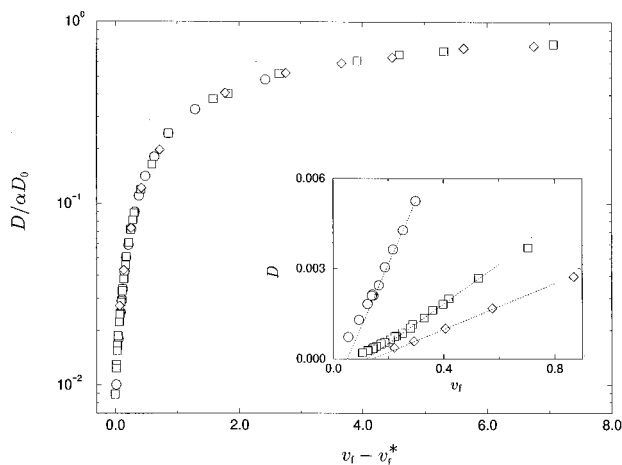


FIG. 4. The self-diffusion coefficient D for chains with 5 beads (circles), 13 beads (squares), and 20 beads (diamonds), in the inset plotted as a function of the specific free volume, $v_f = (1 - c) / c$, and in the main figure as a scaled function of $v_f - v_f^*$ [see Eq. (20)], where $v_f^*(r)$ is given by the intersection points of the dotted lines in the inset with the x -axis; $v_f^*(r) = 0.05, 0.12, 0.15$ for $r=5, 13, 20$, respectively. The values for the diffusion coefficient in the limit $v_f \rightarrow \infty$ are $D_0(r) = 6.03 \times 10^{-2}, 2.24 \times 10^{-2}, 1.37 \times 10^{-2}$ in units of $D_0(1)$, and α was found to be $\alpha(r) = 1.2, 1.02, 1.00$ for $r=5, 13, 20$, respectively.

lengths considered before.) This behavior of D is reminiscent of a recent investigation by de la Batie *et al.*²⁴ and Kolinski *et al.*²⁵ who reported a tendency of the diffusion constant to vanish at a finite volume fraction in a model of athermal chains, indicating the appearance of a liquid-glass-type transition. Our data confirm the existence of a "critical" free volume v_f^* in dense systems. As v_f approaches v_f^* , however, our data for the diffusion constant fall above those straight lines and seem to extrapolate to zero only in the limit $v_f \rightarrow 0$.

Moreover, we observe from Fig. 4 that data for the diffusion constant $D(v_f, r)$ for different chain lengths $r \geq 5$ fall onto a single curve when we use the representation

$$\frac{D(v_f, r)}{\alpha(r) D_0(r)} = f(v_f - v_f^*). \quad (20)$$

Here $D_0(r)$ denotes the diffusion constant at infinite dilution. For the factor $\alpha(r)$ we find $\alpha(r) \approx 1.2, 1.02, 1.00$ for $r=5, 13, 20$, respectively, suggesting that $\alpha(r)$ can be replaced by unity for larger chains.

Given this dependence of D on the free volume, its apparent exponential dependence on the pressure mentioned above is seen to reflect the dependence of the free volume on the pressure in this system. As seen from Eq. (20) this approximate exponential dependence is expected to be valid only in a limited range of pressures.

V. CONCLUSIONS

We have described a new method for constant pressure simulations in lattice gas systems and have demonstrated its usefulness. Given the importance of lattice models for fluids, polymer solutions and melts, glasses and alloys, the ability to carry out constant pressure simulations in such models increases their range of applicability. Several applications to problems of the glass transitions or to the temperature dependence of transport coefficients in polymer solutions and in glasses that were hampered before by the restriction of constant volume are now open for renewed studies.

ACKNOWLEDGMENTS

This research was supported in part by the Israel National Science Foundation and by the Lion Foundation. A.N. thanks the Alexander-von-Humboldt-Stiftung for supporting his stay in Germany under the Humboldt Research Award Program, and the Physics Department at the University of Konstanz for their hospitality.

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