

Constant-Pressure Monte Carlo Simulations for Lattice Models.

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Abstract. - Computer simulations of lattice systems have not been performed under constant pressure conditions since a volume change move involving the addition or removal of a whole lattice layer has a low acceptance probability. We propose a new method to improve the efficiency of the volume change move and thus allow for the simulation of lattice systems in the isothermal-isobaric ensemble. The method is shown to predict properties for lattice polymer systems in two and three dimensions in excellent agreement with thermodynamic integration results.

Lattice models are widely used in statistical mechanics, both in the development of theories and for simulations. Examples include the Ising model used for the study of phase transitions and critical phenomena [1] and the lattice homopolymer model in widespread use in polymer physics [2, 3]. For partly filled lattice models pressure is a relevant state variable for describing thermodynamic properties. For fully filled lattice systems with monomeric solvent, a homomorphic partly filled analog can be defined by considering the solvent as vacancies or holes. Pressure in the latter case is equivalent to the solvent's osmotic pressure in the former.

For simulations of continuous-space models, calculation of the pressure is typically performed by using the virial theorem [4] or by performing a constant-pressure simulation during which the simulation cell volume is occasionally changed against an external pressure reservoir [5]. Neither of these methods is applicable to lattice models because use of the virial theorem requires intermolecular potentials that are continuously differentiable with respect to distance, and changing the volume of a lattice by a full lattice spacing is a major perturbation with a very small probability of acceptance. This second difficulty becomes

more pronounced for polymeric systems because of chain connectivity. As a consequence, the determination of pressure for lattice polymers is possible only by using indirect techniques [6-10]. Recently, Nies and Cifra [11] have proposed a method in which the volume change move is implemented in a fashion where the lattice expansion/contraction is achieved at the scale of a single lattice site. While this method has been shown to work for lattice chains, nevertheless, this procedure results in a lattice polymer system which is confined between two walls one of which has «jagged» edges.

In the present work, we consider volume changes involving addition or removal of a whole lattice layer. The efficiency of the move is enhanced through the use of the Configurational Bias Monte Carlo (CBMC) procedure, which samples favorable chain configurations in a preferential manner [12]. We first describe the CBMC technique as applied to the simulation of chain systems under constant temperature and pressure conditions. The limitations of the method in terms of the density and chain length range that can be practically simulated are then discussed.

It is important that any proposed scheme satisfies detailed balance. We consider a system of ideal, non-interacting lattice monomers to illustrate the proposed algorithm. Consider a lattice of L (> 1) layers each of m sites on which we place N monomers. The probability of a layer containing n particles is

$$\varphi(n, L; N) = \binom{N}{n} \times \left[\frac{1}{L} \right]^n \left[\frac{L-1}{L} \right]^{N-n}. \quad (1)$$

Since we are dealing with systems in the NPT ensemble, the probability of a system having L lattice layers is

$$\mathcal{P}_B(L) = \frac{\exp[-\beta P mL] \times Q(N, mL)}{\sum_L \exp[-\beta P mL] \times Q(N, mL)}, \quad (2)$$

where the canonical partition function for the system of N monomers on L layers is $Q(N, mL) = (mL)^N / N!$, β is the inverse temperature and P the pressure. To construct a scheme that satisfies detailed balance and samples the correct limiting distribution, the probability of adding a lattice layer to a system comprised of L layers and moving n monomers into this newly formed layer should exactly equal the reverse move of eliminating this $(L+1)$ -th layer and redistributing the n monomers over the rest of the lattice,

$$\begin{aligned} \mathcal{P}_B(L) \times \mathcal{P}_{\text{trial}}(L \rightarrow \{L+1, n\}) \times \mathcal{P}_{\text{accept}}^f = \\ = \mathcal{P}_B(L+1) \times \mathcal{P}_{\text{trial}}(\{L+1, n\} \rightarrow L) \times \mathcal{P}_{\text{accept}}^r \times \varphi(n, L+1; N), \end{aligned} \quad (3)$$

where the f and the r denote the forward and reverse trial moves, while the subscript «accept» denotes the acceptance probability. We now construct the following scheme: the lattice size is increased or decreased by one layer with equal probability. The trial probability of going from a system comprised of L layers to one consisting of $(L+1)$ layers, with the extra layer having exactly n molecules is chosen to be $\varphi(n, L+1; N)$ from eq. (1), while the reverse move occurs with a probability of unity. Using eq. (2) for $\mathcal{P}_B(L)$ and $\mathcal{P}_B(L+1)$, respectively, yields

$$\frac{\mathcal{P}_{\text{accept}}^f}{\mathcal{P}_{\text{accept}}^r} = \exp[-\beta P m] \left[\frac{L+1}{L} \right]^N. \quad (4)$$

This derivation shows that, for the case of monomers, the use of the *a priori* probability of

finding n monomers in a layer (eq. (1)) allows us to construct a scheme that satisfies detailed balance. The implementation of this scheme to interacting systems is similar in principle in that we select the number of monomers to be moved based on this ideal distribution, and any energetic factors are naturally absorbed into the Boltzmann factor.

Finally, we consider the extension of this method to the polymeric system of interest. It is clear that some of the chains will be cut by the plane where the volume change move is implemented. We could, in principle, leave the conformations of all chains unchanged during the volume change, but this will result in a move with low probability of acceptance. We enhance this acceptance probability by regrowing the «cut» chains using the CBMC procedure accounting only for overlap. Briefly, the CBMC procedure [12] for growing chains involves checking the neighboring lattice sites of the current monomer's position for occupancy. One of the unoccupied sites is selected at random and the next chain segment is added at this position. The Rosenbluth weight [13] of that segment is then defined as $z_{\text{unoccupied}}/z$, where $z_{\text{unoccupied}}$ is the total number of unoccupied neighbors, while z is the lattice coordination number. Knowledge of the Rosenbluth weights of the initial and final conformations of the chains, which are products of the Rosenbluth weights of the individual segments, allows one to account for the bias involved in using the CBMC procedure as has been shown recently by Frenkel and coworkers (see also eq. (5)) [12].

The method used for performing volume changes on the lattice is shown schematically in fig. 1 for a square lattice. For a layer removal step we first select, with uniform probability, a plane of the lattice to be removed (shaded layer in the upper part of fig. 1). One of the two ends of chains with beads on this layer is selected with equal probability (dotted segment in the upper part of fig. 1). Beads are removed one at a time starting from the marked end and ending at the point at which a single uncut chain fragment remains. It is possible that this procedure would result in complete elimination of a full chain, if the other chain end also happens to lie on the layer being removed. In this case the complete chain is removed. The Rosenbluth weight [13] of the old configuration is calculated during this removal step ensuring that the last bead removed does not contribute to this factor. If a whole chain is cut, on the other hand, the last bead has a Rosenbluth weight corresponding to the fraction of unoccupied sites on the plane to be removed. The total Rosenbluth weight of the old

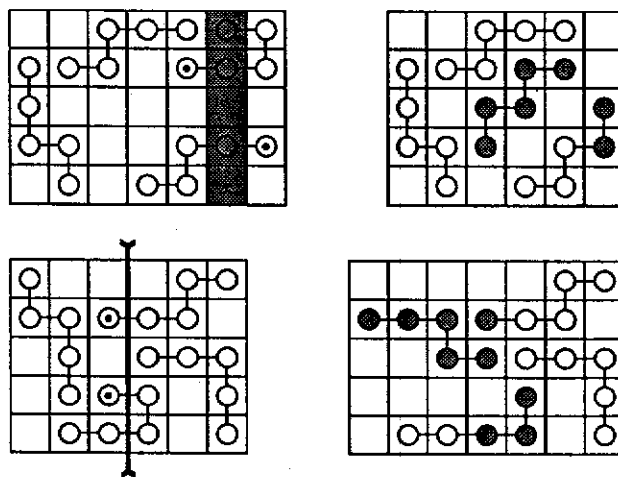


Fig. 1. — Schematic diagram of volume change steps, illustrated for the square lattice. The chain ends selected for removal are marked with a dot. Shaded segments have been grown using the Rosenbluth procedure.

configuration, W_{old} , is computed as the product of the Rosenbluth weights of the chains that have been partly or completely removed from the system. The selected layer is then removed, and the chains are regrown to their original dimensions with the requirement that the first bead added to a partially cut chain always cross over to the other side of the cut layer. If this requirement was not imposed, a chain could emerge in its regrown form without ever crossing the «cut» plane. If one now chooses to reverse this layer removal and restore the cut plane at the same point, this «regrown» chain will not be cut in this addition process and will, therefore, not have to be regrown. This violates detailed balance.

Chains that have been completely removed from the system are inserted at random positions, with the first bead inserted at a randomly selected empty position and assigned a Rosenbluth weight equal to the fraction of unoccupied sites on the whole lattice. The Rosenbluth weight of other added chains is calculated in the usual way, and the total Rosenbluth weight of the new configuration, W_{new} , computed as the product of the Rosenbluth weights of the chains that have been partly or completely regrown. The move is accepted with probability

$$\mathcal{P}_{\text{acc}} = \min \left[1, \frac{W_{\text{new}}}{W_{\text{old}}} \exp \left[-\beta \Delta U + N \ln \frac{V + \Delta V}{V} - \beta P \Delta V \right] \right], \quad (5)$$

where ΔU is the change in the internal energy of the system in the volume change, N is the number of chains in the system and V is the system volume. The lattice expansion step proceeds as shown in the lower half of fig. 1. A plane between two layers of the lattice is selected with uniform probability. The polymer chains that are cut by this plane are marked, and one of the two ends is selected with equal probability. Beads of the marked chains are then removed with a procedure analogous to that used in the layer removal step. In this case it is not possible to eliminate a chain completely since the beads at the ends of any chain lie in a layer to be preserved. To satisfy the detailed-balance condition, therefore, it is necessary to select a number of chains (say n) at random to insert with one end located in the new layer. This is performed following the probability distribution of eq. (1) where N is the number of chains in the system. The chains selected (which could also be among the ones being cut by the plane of insertion) are then removed from the system and the Rosenbluth weight of the old configuration calculated. The Rosenbluth weight for the last bead of any completely removed chain is equal to the fraction of unoccupied lattice sites in the total system. A new lattice layer is then added at the insertion plane. All cut chains are regrown so that the first bead is always placed in the newly added layer, and then the rest of the beads are regrown following the Rosenbluth procedure. The first regrown bead does not contribute to the Rosenbluth weight, except for the case of completely regrown chains where it is assigned to the fraction of unoccupied lattice positions in this layer. The step is accepted following eq. (5).

We have applied this method to homopolymers on square and cubic lattices. Periodic boundary conditions are implemented in all directions, and each lattice site is, at most, singly occupied. Each nearest-neighbor contact is assigned a favorable energy of interaction, $-\varepsilon$, where $\varepsilon > 0$. Temperature is defined as $T^* = -1/\beta\varepsilon$, where β is the thermodynamic temperature.

The first set of calculations were performed in two dimensions [14-16]. Results are given in fig. 2. We begin by considering the case of athermal monomers ($\varepsilon = 0$) for which exact results can be obtained from exact enumeration [17]. We find quantitative agreement of our results for this system at all densities attempted. For the longest chain length considered ($l = 40$) at both the athermal limit and close to the θ temperature, there is good agreement between our calculations and previous results for densities of up to ca. 0.6. Higher densities are accessible for shorter chain lengths.

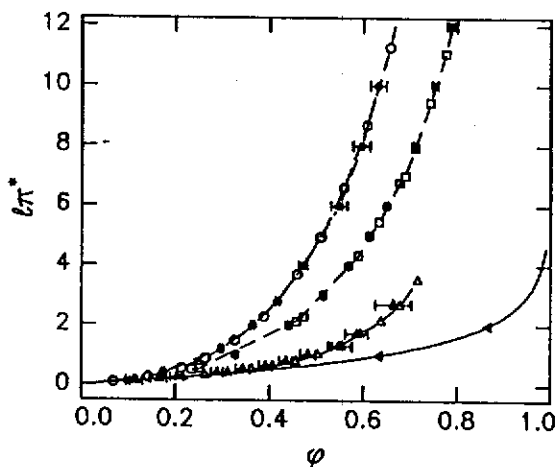


Fig. 2. - $\ln \pi^*$ vs. volume fraction ϕ for two-dimensional systems. From right to left: $l = 1$, athermal, $l = 40$, $T^* = 1.85$, $l = 20$ and 40 , athermal. Lines are drawn for visual clarity, except for $l = 1$ for which they represent the exact result. Filled symbols are from the present work, open symbols are literature values [6, 16, 17].

A few implementation issues need to be stressed here. First, no systematic system size dependence was found in the cases where the box size in each spatial direction was at least twice the unperturbed radius of gyration of the chains in the melt state. Second, the limitations of the maximum densities simulated by this algorithm are intimately related to the chain lengths of the molecules through the following factors. As the lengths of the chains are increased, it is clear that system sizes have to be increased to ensure that a chain will not interact with its periodic image. Consequently, more lattice sites are added (or removed) during a volume change move. In addition, the number of segments to be regrown on each cut chain, on average, increases with chain length. A combination of these two factors provides us with the real limitations of this algorithm as we consider longer chain lengths. In fact it was found that the acceptance probability of a volume change move decreased faster

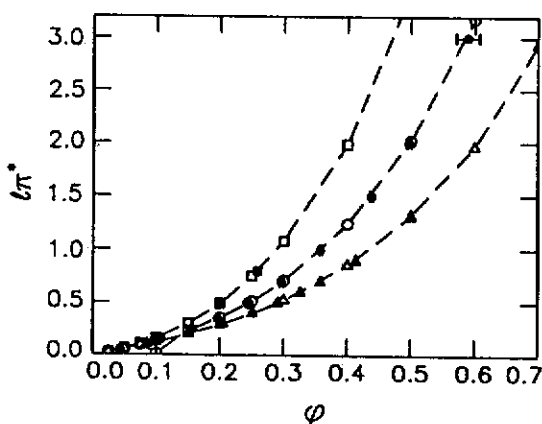


Fig. 3. - $\ln \pi^*$ vs. volume fraction ϕ for three-dimensional athermal systems. From right to left: $l = 5$, 10 and 20 . Filled symbols are from the present work, open symbols are literature values [19] and lines are drawn through the points for visual clarity.

than exponentially with increasing density, thus stressing the sampling problems encountered with increasing density. Enrichment procedures [18] would help alleviate these concerns and we shall consider these improvements in future work.

We have also considered athermal systems on a cubic lattice (three dimensions), and again find excellent agreement of the calculated values of the density with past findings (fig. 3) [19]. The density and chain length range accessible is narrower than for the two-dimensional systems. For example, a polymer system comprised of chains of length 10, placed initially on a $10 \times 10 \times 10$ lattice, can be simulated with ease to a density, ϕ , of 0.6. This maximum accessible density, however, drops to ca. 0.3 if one considers a lattice of size $20 \times 20 \times 20$ reiterating the current limitations of the proposed algorithm.

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REFERENCES

- [1] LANDAU L. D. and LIFSHITZ E. M., *Statistical Physics* (Pergamon Press) 1980.
- [2] FLORY P. J., *Principles of Polymer Chemistry* (Cornell University Press, Ithaca) 1953.
- [3] KREMER K. and BINDER K., *Chem. Phys. Rep.*, 7 (1988) 259.
- [4] See, for example: HUANG K., *Statistical Mechanics* (Wiley, New York, N.Y.) 1987.
- [5] WOOD W. W., *J. Chem. Phys.*, 48 (1968) 415.
- [6] DICKMAN R. and HALL C. K., *J. Chem. Phys.*, 85 (1986) 3023.
- [7] OKAMOTO H., *J. Chem. Phys.*, 64 (1975) 2686; OKAMOTO H. and BELLEMANS A., *J. Phys. Soc. Jpn.*, 47 (1979) 955.
- [8] MEIROVITCH H., *J. Chem. Phys.*, 97 (1992) 5803.
- [9] DICKMAN R. and HALL C. K., *J. Chem. Phys.*, 89 (1988) 3168.
- [10] DEUTSCH H.-P. and DICKMAN R., *J. Chem. Phys.*, 93 (1990) 8993.
- [11] NIES E. and CIFRA P., Poster presented at *Polymer Theory Conference in Mainz, October, 1993*, unpublished results.
- [12] FRENKEL D., MOOIJ G. C. A. M. and SMIT B., *J. Phys. Condens. Matter*, 3 (1991) 3053.
- [13] ROSENBLUTH M. N. and ROSENBLUTH A. W., *J. Chem. Phys.*, 23 (1955) 356.
- [14] HONNELL K. and HALL C. K., *J. Chem. Phys.*, 95 (1991) 4481.
- [15] DICKMAN R., *J. Chem. Phys.*, 91 (1989) 454.
- [16] DICKMAN R., *J. Chem. Phys.*, 96 (1992) 1516.
- [17] HILL T. L., *Statistical Mechanics* (McGraw-Hill, New York, N.Y.) 1956.
- [18] MOOIJ G. C. A. M. and FRENKEL D., *Mol. Phys.*, 74 (1991) 41.
- [19] HERTANTO A. and DICKMAN R., *J. Chem. Phys.*, 89 (1988) 7577.

Two-Dimensional Melting Approached via Finite-Size Scaling of Bond-Orientational Order.

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Statistical Mechanics of Continuous Random Networks: a Model Glass Transition.

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Singular Shape of a Fluid Drop in an Electric or Magnetic Field.

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An Atom Trap Relying on Optical Pumping.

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Virtual-Mode Excitations in Thin Metallic Films.

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A Microscopic Theory of the f.c.c.-b.c.c. Interface.

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Ward Identities in Canonical Formalism for a System with Singular Higher-Order Lagrangian.

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Instabilities in MBE Growth.

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Effects of Polaronic States in the Multiband Hubbard Model.

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