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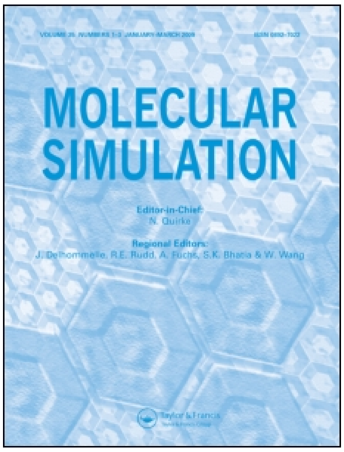

Molecular Simulation

Publication details, including instructions for authors and subscription information:
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Online publication date: 03 June 2010

To cite this Article Boodoosingh, Glenda and LÓpez, Gustavo(2002) 'An efficient algorithm in the grand canonical ensemble: constructing adsorption isotherms', Molecular Simulation, 28: 3, 273 — 285
To link to this Article: DOI: 10.1080/08927020290014376
URL: http://dx.doi.org/10.1080/08927020290014376

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Molecular Simulation, 2002, Vol. 28(3), pp. 273 – 285

AN EFFICIENT ALGORITHM IN THE GRAND CANONICAL ENSEMBLE: CONSTRUCTING ADSORPTION ISOTHERMS

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(Received September 2000; accepted February 2001)

A new computational method is presented that efficiently describes open thermodynamic systems within the grand canonical ensemble formalism. The method is based on the j-walking algorithm, which circumvent sampling difficulties by coupling random walkers in different thermodynamic states. By imposing detailed balance, a new acceptance probability is derived and applied to the construction of adsorption isotherms for atomic monolayers. The method converges much faster than the standard grand canonical Monte Carlo method and permits the construction of accurate adsorption isotherms and the identification of phase transitions occurring in the adsorbed material.

Keywords: Grand canonical ensemble; J-walking algorithm; Quasi-ergodicity; Adsorption isotherms; Statistical thermodynamics

INTRODUCTION

One of the most active areas of research related to surface science is the study of the equilibrium properties of adsorbed atoms and/or molecules on surfaces. This area of investigation plays a crucial role in the understanding of adhesives, catalyst, colloids, surface coating, thin films, and wetting phenomena. In particular, the wide variety of chemical and physical processes that adsorbates can undergo on surfaces has provided a constant source of challenge to scientist. A surge of progress in surface science experiments and theoretical methods has facilitated new highly detailed

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ISSN: 0892-7022 © 2002 Taylor & Francis Ltd DOI: 10.1080/08927020290014376

studies of adsorbed materials. In particular, the adsorption process of systems at coverage up to a monolayer has been extensively considered because of its two-dimensional nature. Experimental techniques such as temperature programmed desorption [1] (TPD) has been used to study the formation of monolayers.

In recent years, computer simulations have become a powerful tool in the description of many chemical and physical processes. In general, a proper thermodynamic ensemble is defined and various average quantities can be computed. These computational techniques have played an important role in the understanding of the gas–solid adsorption equilibrium. Many computational studies that considered this equilibrium are performed using the canonical ensemble [2, 3] or the isothermal–isobaric ensemble [4] because of their computational simplicity. However, in order to compute non-mechanical properties in these ensembles, special models have to be used. The most widely used method is the test particle model [5], which permit the computation of the configurational chemical potential as a function of density at a fixed temperature.

Another commonly used approach is based on implementing the standard Metropolis grand canonical Monte Carlo (SMGCMC) technique [6], where the chemical potential, volume, and temperature (μ, V, T) are fixed. The density of the systems is computed as an average value because particles are created and destroyed during the simulation. This ensemble has been used in the study of open systems [7] and in particular in the description of gas/solid adsorption equilibrium.

As in the case of computer simulations in the canonical ensemble, one of the main difficulties of the SMGCMC method is the poor convergence of thermodynamic averages. In the grand canonical ensemble, the poor sampling of the configuration-density hyperspace is extremely inefficient and hence large uncertainties in the computed average values are obtained. In particular, the creation of particles seems to be the bottleneck in these simulations. This problem has been termed quasiergodicity by several researchers [8]. In recent years, several attempts have been made in order to solve this computational difficulty. Remarkable success has been encounter by the so-called j-walking method [9], where the problem is solved by coupling the standard Monte Carlo procedure with a walker that sample the desired space in an efficient way. The method was originally developed and implemented in the canonical ensemble [9], but more recently it has been applied to the microcanonical [10] and the isothermal–isobaric [11, 12] ensembles. The method has been successfully applied [13–16] to study problems such as cluster phase transitions. More recently, Nadal and López

[17] applied the method to the construction of adsorption isotherms using the test particle method.

In the present study, we have focused in extending the j-walking procedure to the grand canonical ensemble. The method is termed the j-walking gran canonical Monte Carlo (JWGCMC) method. The method generates a non-Boltzmann distribution, which is obtained by imposing detailed balance. The method is used to compute accurate adsorption isotherms for an atomic monolayer.

METHOD

In any standard Monte Carlo method [18], a random walker is defined in order to sample certain mathematical space with an acceptance probability p, given by

$$p = \min[1, a(q_f, q_i)] \tag{1}$$

where q_f and q_i represent the final and initial states, respectively, and $a(q_f, q_i)$ is obtained by imposing detailed balance such that

$$a(q_f, q_i) = \frac{T(q_i|q_f)\rho(q_f)}{T(q_f|q_i)\rho(q_i)} \tag{2}$$

In this equation $T(q_i|q_f)$ is the sampling distribution, which in the standard Metropolis method is generated from a uniform deviate and $\rho(q_s)$ is the distribution function in state s. In the grand canonical ensemble the distribution function is given by [19]

$$\rho(q) = \frac{(V^N/N!)z^N e^{-\beta U(q)}}{\Xi(\mu, V, T)} \tag{3}$$

Here V is the volume, N is the number of particles, $U(q)$ is the configurational energy, $\Xi(\mu, V, T)$ is the grand canonical partition function, and z is the activity which is given by

$$z = \frac{e^{\beta\mu}}{\Lambda^3} \tag{4}$$

where μ is the chemical potential and Λ is the thermal de Broglie wavelength

$$\Lambda^2 = \frac{h^2}{2\pi m k_B T} \tag{5}$$

In general, the SMGCMC method has three types of moves: particle displacement, particle creation and particle destruction. The particle displacement follows the usual $\exp(-\beta\Delta U)$ acceptance probability obtained from random displacements of particles. In the particle creation moves, Eq. (3) is substituted into Eq. (2) with the final state having $N+1$ particles and the initial state with N particles,

$$a(q_f, q_i) = \exp[-\beta\delta C] \tag{6}$$

where δC in the variation in the creation function given by

$$\delta C = \Delta U - \frac{1}{\beta}\ln\left[\frac{Vz}{(N+1)}\right] \tag{7}$$

The quantity ΔU is the variation in configurational energy between the final and initial states.

On the other hand, for particle destruction it is obtained that

$$a(q_f, q_i) = \exp[-\beta\delta D] \tag{8}$$

where δD is the variation in the destruction function

$$\delta D = \Delta U - \frac{1}{\beta}\ln\left(\frac{z}{NV}\right) \tag{9}$$

The implementation of the j-walking method to the grand canonical ensemble involves the definition of a new probability sampling distribution. This new function is obtained when $T(q_f, q_i)$ is set to

$$T(q_f, q_i) = \frac{V^{N_J}}{N_J!} z_{\beta_J}^{N_J} e^{-\beta U(q_i)} \tag{10}$$

Here, N_J is the number of particles at β_J, and z_J is the activity when $N = N_J$. The distribution function for the final state is

$$\rho(q_f) = \frac{(V^{N_J}/N_J!) z_{\beta}^{N_J} e^{-\beta U(q_f)}}{\Xi(\mu, V, T)} \tag{11}$$

such that when detailed balance is applied

$$a(q_f, q_i) = \exp[-\beta A] \tag{12}$$

where A is given by

$$A = -\frac{1}{\beta}\ln z_{\beta}^{\Delta N} z_{\beta_J}^{\Delta N} \exp\left[\frac{(\beta_J - \beta)}{\beta}\Delta U\right] \tag{13}$$

Here ΔN is the difference in the number of particles between the J state and the initial state. Details of the implementation of the method are presented in the next section.

COMPUTATIONAL DETAILS

In order to test the method, the construction of adsorption isotherms for an atomic monolayer was undertaken. The monolayer was simulated as a two-dimensional system with periodic boundary conditions and the minimum image convention implemented. A total of 100 atoms were used, interacting through a pair-wise Lennard-Jones potential.

The JWGCMC method was implemented in the following manner. A very long run consisting of 5×10^7 warm up moves and 5×10^7 Monte Carlo moves was used to generate the initial j-walking configuration. The activity and temperature, in reduced units, used to generate this initial j-walking distribution were fixed to 0.18 and 1.0, respectively. At this thermodynamic state, the system is in a gas-like form but at relatively high density, hence the problem of quasi-ergodicity is minimized. This initial distribution was used to generate additional j-walking distributions at various temperatures and

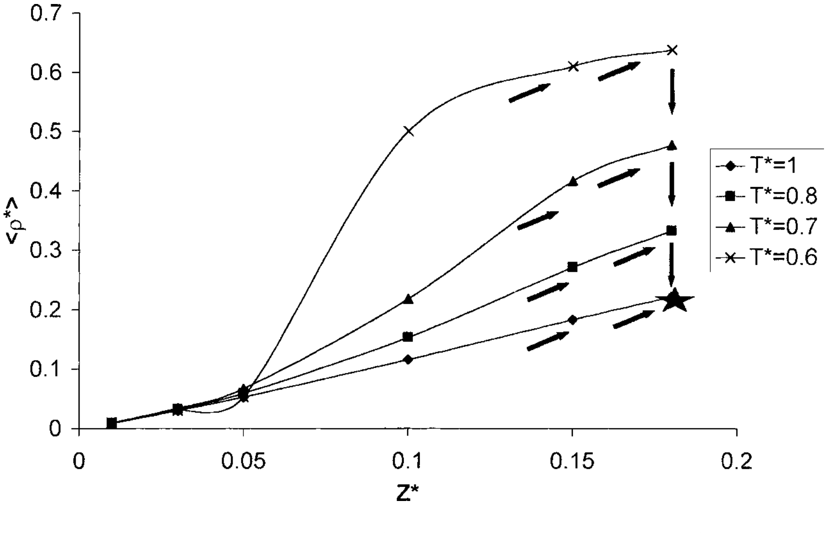

FIGURE 1 Schematic representation of adsorption isotherms with the procedure used for the generation of the j-walking distribution illustrated by arrows. The end of the arrows represents the thermodynamic state that in being used for the jumps. The black start represents the initial configuration used to initiate the generation of j-walking configuration. This state corresponds to $T^* = 1.0$ and $z^* = 0.18$.

activities. Specifically, two different procedures were used to generate these distributions: (i) $\beta = \beta_J$ and $z_J > z$ and (ii) $\beta < \beta_J$ and $z_J = z$. Figure 1 depicts the procedure used for the generation of the j-walking distributions. The arrows represent the direction where the jumps were attempted. For example, the initial j-walking distribution ($T^* = 1.0$, $z^* = 0.18$) was used to generate distributions at $T^* = 0.8$, $z^* = 0.18$ and $T^* = 1.0$, $z^* = 0.15$. Each additional j-walking distribution was generated when the acceptance ratio of jumps was less than 10%. Various schemes for the generation of the j-walking distributions were tested but the one described above was the most efficient. On each distribution, the positions of the atoms, internal energy, density of particles, and the virial energy were saved in external arrays every 1000 Monte Carlo steps. At temperatures where the j-walking configurations were not generated, the simulations were broken into 10 blocks with uncertainties calculated to one standard deviation. Each block consisted of 10^6 warm up moves and 10^6 moves where data was collected.

RESULTS AND DISCUSSION

Figure 2 shows the adsorption isotherms for the two-dimensional Lennard-Jones monolayer considered here. The isotherms were constructed by plotting the reduced density of the adsorbed layer as a function of the reduced activity. It can be observed that the isotherms show the usual type I form at high temperatures. Namely, as the activity of the gas increases, the amount of adsorbed material increases in an almost linear fashion, until the saturation value is reached, which is indicative of the formation of a full monolayer. At lower temperatures, the amount of adsorbed material increases very fast with small variations in the activity and the saturation value is reached at low values of activity. This is expected because at lower temperatures the desorption process become less efficient and hence the amount of adsorbed material increases considerably.

As previously stated, the main difficulty of the SMGCMC method is the low ratio of acceptance for the creation of particles and hence the low values for the average density. Table I shows the values for the average density computed with and without the j-walking method at various temperatures and activities. It can be observed that at high temperatures the average density of the adsorbed layer is very similar in both methods. The reason for this is that at high temperatures the density of the adsorbed layer is relatively small and hence the SMGCMC method create the number of particles in equilibrium relatively fast. At temperatures of $T^* = 0.7$ and

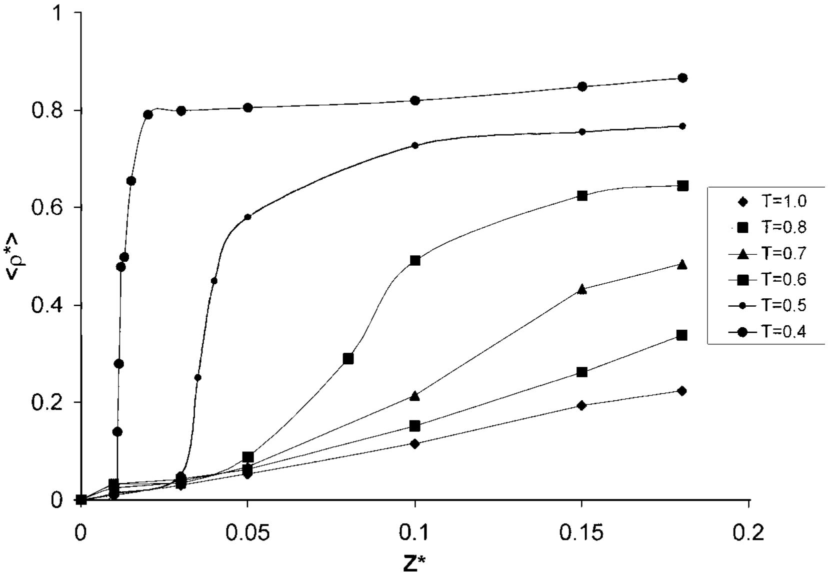

FIGURE 2 Adsorption isotherms for a two-dimension Lennard-Jones system generated using the j-walking grand canonical Monte Carlo method developed in this study. Error bars are within the size of the data point.

TABLE I Average densities computed using the grand canonical Monte Carlo with and without the j-walking method for various temperatures and activities. The numbers in parentheses indicate the statistical uncertainties in units of the last digit

T^*	Z^*	$\langle\rho^*\rangle$ (*SMGCMC*)	$\langle\rho^*\rangle$ (*JWGCMC*)
1.0	0.15	0.183(6)	0.195(2)
	0.10	0.116(4)	0.116(2)
	0.05	0.053(2)	0.053(1)
	0.03	0.030(1)	0.031(1)
0.8	0.18	0.332(7)	0.345(2)
	0.15	0.261(4)	0.272(2)
	0.10	0.151(5)	0.153(1)
	0.05	0.0620(3)	0.0604(3)
	0.030	0.0342(3)	0.033(3)
0.7	0.18	0.47(6)	0.482(2)
	0.15	0.41(4)	0.432(2)
	0.10	0.21(5)	0.214(1)
	0.05	0.067(4)	0.0670(1)
	0.03	0.034(6)	0.0341(1)
0.6	0.18	0.63(8)	0.645(3)
	0.15	0.61(9)	0.624(1)
	0.10	0.50(8)	0.590(2)
	0.05	0.053(4)	0.0680(3)
	0.03	0.030(3)	0.0390(1)

$T^* = 0.6$ a more pronounce difference between both method can be observed. Specifically, the average value for the density of the adsorbed material increases when the JWGCMC method is incorporated. In most cases, an increment of approximately 5% is observed. This result clearly suggest that the problem of quasi-ergodicity associated to the SMGCMC

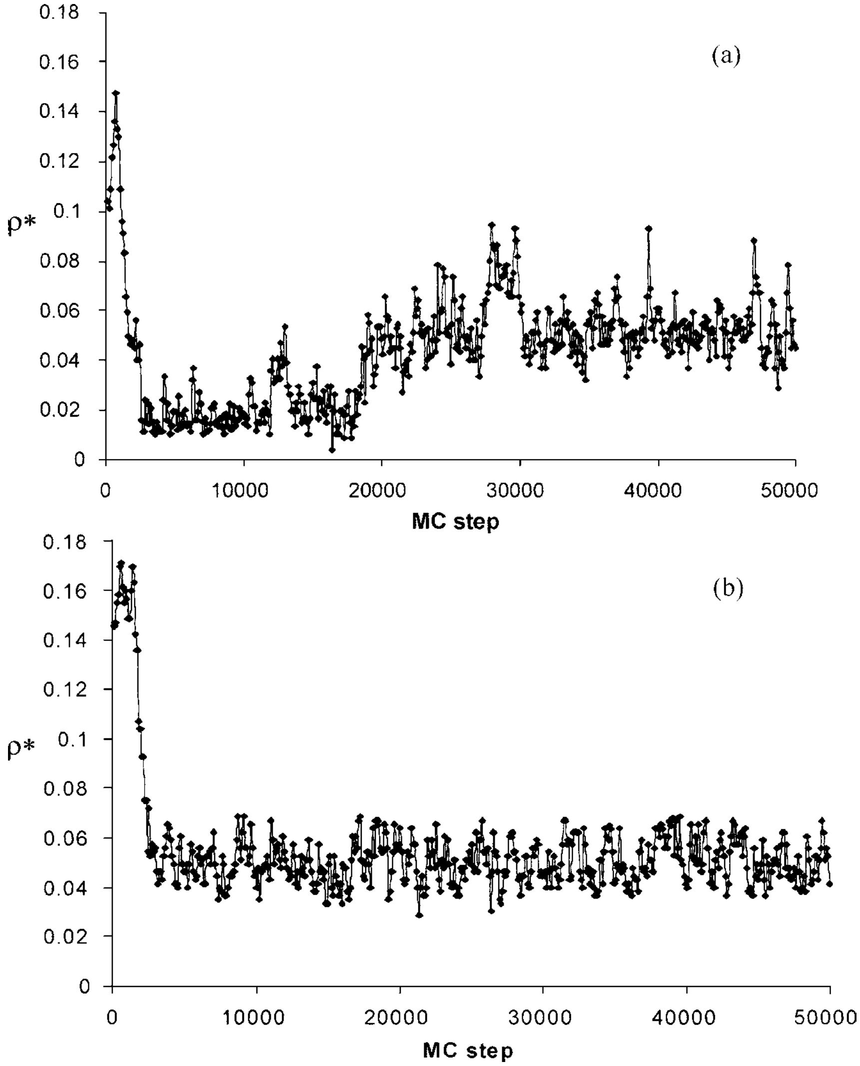

FIGURE 3 Instantaneous value for the reduced density as a function of Monte Carlo step using (a) the standard Metropolis Monte Carlo method, and (b) the j-walking grand canonical Monte Carlo method.

method, which is manifested by a small number of particle creation, can be overcome with this new technique. Also, Table I shows that the uncertainties are considerable reduced when the JWGCMC method is

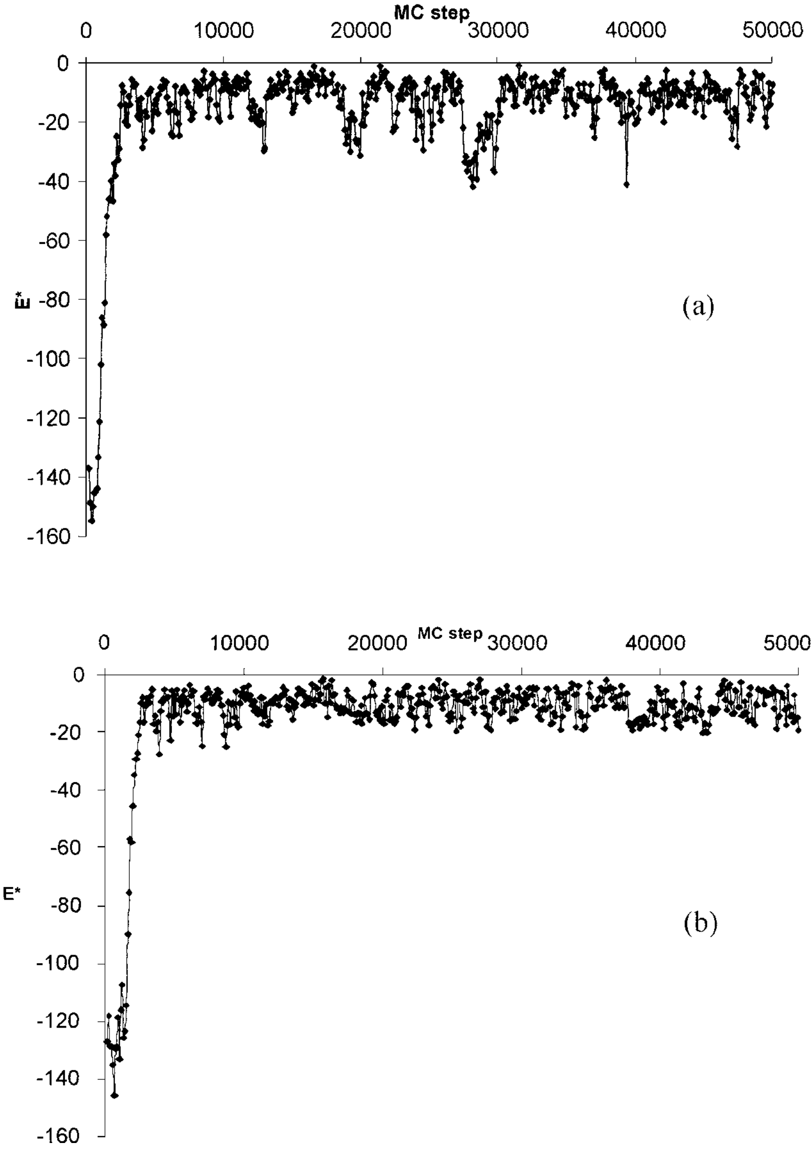

FIGURE 4 Same as Figure 3 but the quantity being monitored is the instantaneous internal energy.

implemented, in particular at lower temperatures and higher activities. In order for both methods to be equivalent, longer runs are needed when the SMGCMC method is used.

Two thermodynamic properties have been plotted as a function of Monte Carlo steps for both the SMGCMC and JWGCMC techniques. These plots are constructed in order to compare the fluctuation in the instantaneous value of the properties when these techniques were applied. Figures 3 and 4 show the fluctuation in density and internal energy as a function of the number of Monte Carlo steps, respectively, using both methods. It can be observed from Figure 3 that the fluctuation in density is much less during a JWGCMC simulation than in the SMGCMC. The JWGCMC method reaches the equilibrium value at approximately 5000 steps, whereas for the SMGCMC method requires approximately 30000 steps. A similar result is observed in Figure 4 where the internal energy is plotted as a function of Monte Carlo steps. In this case, the equilibrium value is reached by both methods at approximately 5000 Monte Carlo steps, but the fluctuations in the SMGCMC are larger than in the JWGCMC technique. The results of these two figures clearly indicate that the JWGCMC method give smaller uncertainties in the average thermodynamic quantities and convergence is reached much faster than the standard method.

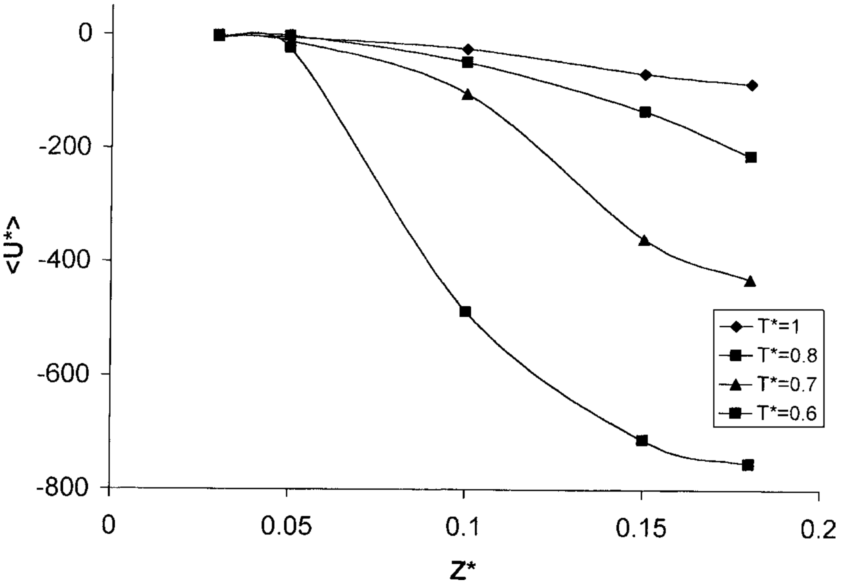

FIGURE 5 Average internal energy as a function of reduced activity at various temperatures.

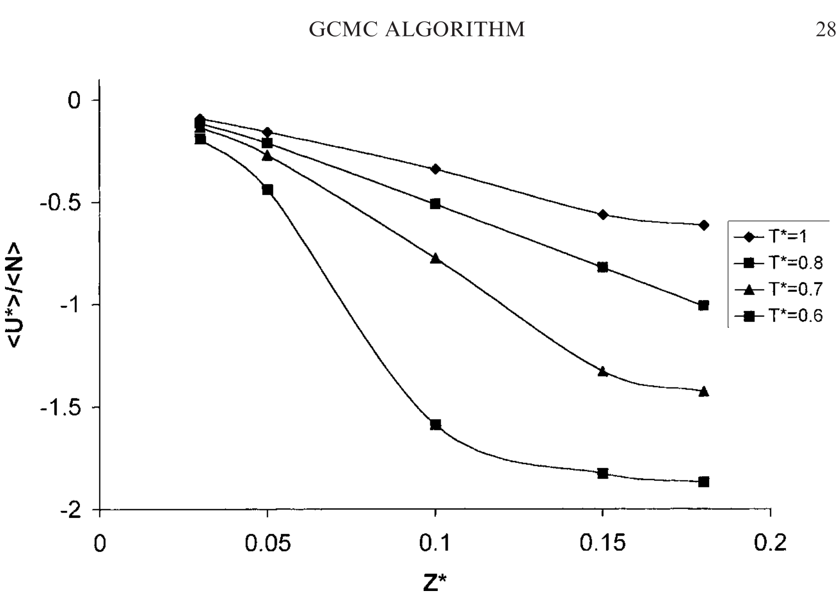

FIGURE 6 Average internal energy per average number of particles as a function of reduced chemical activity for various temperatures.

Figure 5 shows the variation in the average internal energy as a function of activity at various temperatures. It can be observed from Figure 5 that as the activity increases $\langle U^* \rangle$ decreases for a given value of T^*. This is expected because as z^* increases the number of particles adsorbed increases and hence the total internal energy decreases. In addition, it is observed that as the temperature decreases, $\langle U^* \rangle$ decreases for a fixed value of activity. This result is also expected because as the temperature decreases the amount of adsorbed material increases considerably and hence $\langle U^* \rangle$ decreases. It is interesting to notice that at low values of z^* the internal energy is almost unchanged. However, at $T^* = 0.6$ a considerable decrease in internal energy is observed. This result suggests that at this temperature the adsorbed material changes to a solid-like phase, which will have a lower energy than a liquid adsorbed phase. Therefore, it can be concluded that a phase transition occurs at approximately $T^* = 0.6$. Figure 6 shows a similar plot but the value for the average internal energy per particle is graphed as a function of the activity. The same behavior as in Figure 5 is observed, which confirm the possibility of a solid–liquid transition.

CONCLUSION

In the present study the equilibrium between an adsorbed layer and bulk gas was studied using a new algorithm in the grand canonical ensemble. The algorithm was obtained by applying the j-walking formalism to the gran canonical Monte Carlo procedure. The poor convergence in the average value of the density and internal energy are circumvented with this method and very precise adsorption isotherms were constructed. At present, the method is being applied to the construction of isotherms for material adsorbed on structured surfaces and to the formation of multilayers. Also, the method is being extended such that quantum effects are included through path integral formalisms.

Acknowledgement

NASA Space grant program and EPSCoR/NSF supported this work. G.E.L. is a Camille and Henry Dreyfus teacher-scholar.

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