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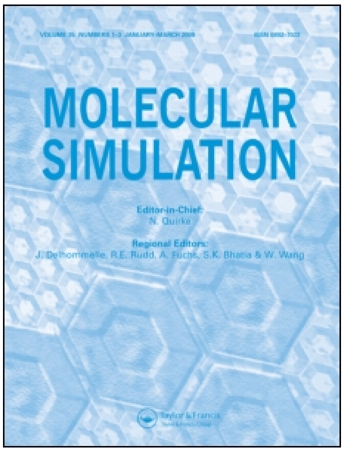

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M. J. Bojan[a]; V. A. Bakaev[a]; W. A. Steele[a]
[a] Department of Chemistry, The Pennsylvania State University, University Park, PA

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SMART MONTE CARLO ALGORITHM FOR THE ADSORPTION OF MOLECULES AT A SURFACE

M. J. BOJAN, V. A. BAKAEV and W. A. STEELE*

Department of Chemistry, The Pennsylvania State University,
152 Davey Laboratory, University Park, PA 16802

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A modified grand canonical ensemble Monte Carlo (GCMC) technique has been developed to simulate adsorption isotherms for molecules on or near a surface. The speed and accuracy of the simulation is increased by using a non-uniform distribution function, related to the force field exerted by the surface and the current configuration, to generate coordinates for the creation of new particles in the simulation. With this method, isotherms are generated more efficiently than with current techniques in which the creation step relies on a uniform distribution to generate the coordinates of a new molecule. This is shown by comparing the calculation of an isotherm for a simple molecule adsorbed on a graphite substrate from a traditional GCMC simulation with that calculated using this new technique.

Keywords: Modified GCMC; adsorption; surface

1. INTRODUCTION

The physical adsorption of vapors on solid surfaces is a topic of great practical and fundamental significance since many modern processes for purification and separation of gas mixtures rely on this technique for their success. Thus, this field has been the subject of intense interest for many decades. The use of computer simulations to supplement experimental studies is a relatively recent development which has proven to be of great utility in quantifying the relationship between observable quantities and molecular behavior in these systems.

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*Corresponding author.

Although the adsorption isotherms of water vapor on chemically unreactive solids is especially interesting, it has been the subject of only a few simulation studies [1–4]. Simulators have encountered difficulties when studying water systems because of the complexity of the intermolecular interactions of the water molecule. These complexities are such that the generation of acceptable configurations becomes highly improbable, necessitating long computer runs to achieve reliable results. Techniques to overcome some of these problems exist for simulations of the bulk fluid [5–7], but comparable methods for a nonuniform fluid in contact with a surface have not been developed. The purpose of this work is to develop an approach to simulate the adsorption isotherm of water (or other simple nonlinear molecules) in contact with a rigid inert surface using biased sampling techniques that give increased efficiency of the algorithm.

One of the best methods for doing this is the grand canonical ensemble Monte Carlo (GCMC) technique [5, 8]. In this simulation, the chemical potential μ, Volume V and temperature T are fixed, and three kinds of trial moves are performed; creation, deletion and displacement. The adsorption isotherm (number of molecules adsorbed as a function of μ) is among the results obtained in the course of the simulation.

A technique commonly used in GCMC is the method of Norman and Filinov [9]. In this method, the three different trial moves are performed with equal probability: for displacement, a molecule is shifted using the Metropolis method [5, 8]. For deletion, a randomly chosen particle is destroyed and creation is done by placing a new particle at a randomly chosen (and uniformly distributed) position in the fluid.

For a non-spherical molecule (such as water), the creation step must be done in two stages: the coordinates of the center of mass of the molecule must be chosen and then the orientation must be specified. To increase the efficiency of the Monte Carlo simulation, both aspects of the creation process, coordinate selection and orientation, should be addressed. For uniform fluids, methods have been developed for choosing the orientation of a newly created particle [10]. These methods will be useful in the case of non uniform (*i.e.*, adsorbed) fluids as well. However, despite the fact that biased sampling techniques have been developed to address a number of difficulties related to the center of mass coordinate selection in uniform systems [5–7], none of these techniques address the problems encountered in the simulation of fluids interacting with a solid. In this work, we have developed an algorithm to find a favorable center of mass location for insertion of new molecules in an existing configuration of the adsorbate-adsorbent system. To do this, we exploit a unique property of the fluid-substrate system, *i.e.*, its non-uniform nature.

Because of the attractive solid-adsorbate interaction, molecules prefer to be near the surface of an adsorbent. Thus the density close to the surface is high, decreasing as the distance from the surface increases. When applying techniques developed for uniform fluids to non-uniform systems, volume elements in the simulation cell are sampled with equal probability [5] even though it is probable that molecules will adsorb preferentially near the surface. Here, we will use knowledge of the interaction to find the preferred locations of the molecules as a function of distance from the surface. Thus, we can preferentially sample the regions which are most probable. In developing this method, we have used a simple model (one site, Lennard-Jones potential) for the adsorbate, but the technique can be extended easily to more complex model adsorbates. Using this idea, we have developed an algorithm in the GCMC simulation which can be used to increase the acceptance rate of created particles and which can be extended to increase the efficiency and speed of a simulation of non-spherical molecules in contact with a surface.

2. TECHNIQUE

In the scheme developed here, we change only the creation step in the GCMC algorithm [5]. As with the other steps, the transition probabilities (matrix elements) π_{ji} from state i to state j, must satisfy the equation for microscopic reversibility:

$$\pi_{ji}\mathcal{P}_i = \pi_{ij}\mathcal{P}_j \tag{1}$$

where $\mathcal{P}_i$, $\mathcal{P}_j$ are the probabilities of the i'th and j'th configurations in the grand canonical ensemble. If the i'th configuration contains N particles, then in the creation step, the j'th configuration contains $N+1$ particles and [5]

$$\frac{\mathcal{P}_j}{\mathcal{P}_i} = \frac{Z}{N+1}\exp\left(\frac{-\Delta U}{kT}\right)d\mathbf{r} \tag{2}$$

Here Z is the activity of the particles ($= \exp(\mu/kT)/\Lambda^3$), $\Delta U = U_j - U_i$ is the change in energy that results from adding an extra particle to the i'th configuration and $d\mathbf{r}$ is a volume element that determines the position of the newly created particle. The transition matrices can be factorized as $\pi_{ji} = T_{ji}A_{ji}$ where T_{ji} is the probability of a trial transition from i to j and A_{ji} is the probability that a trial move will be accepted [5]. The fulfillment of microscopic reversibility is guaranteed when

$$A_{ji} = \min\{1, q\};\ A_{ij} = \min\{1, 1/q\};\ q = \frac{T_{ij}\mathcal{P}_j}{T_{ji}\mathcal{P}_i} \tag{3}$$

since in this notation Eq. (1) takes the form $A_{ji} = A_{ij}q$.

In the unbiased technique [5],

$$T_{ji} = \frac{1}{(N+1)}\frac{d\mathbf{r}}{V};\ T_{ij} = \frac{1}{N+1} \tag{4}$$

where V is the volume of the simulation box. This means that all positions inside the simulation box are equally probable for insertion of a particle. Thus in Eq. (3),

$$q = \frac{ZV}{(N+1)}\exp\left(\frac{-\Delta U}{kT}\right) \tag{5}$$

The peculiarity of our algorithm is that we divide the total volume V into small and equal volume elements ΔV and first choose the k'th element with the probability density

$$\mathcal{P}(\mathbf{r}_k) = \frac{\exp[-U_{\mathrm{eff}}(\mathbf{r}_k)/kT]}{\sum_k \exp[-U_{\mathrm{eff}}(\mathbf{r}_k)/kT]} \tag{6}$$

where $\mathbf{r}_k$ gives the position of the center of the k'th volume element, U_{eff} is some effective energy for a particle in this volume. At this point, the position $d\mathbf{r}$ inside this volume element is chosen with equal probability. For this case

$$T_{ji} = \frac{1}{(N+1)}\frac{d\mathbf{r}}{\Delta V}\mathcal{P}(\mathbf{r}_k) \tag{7}$$

and

$$q = \frac{Z\Delta V}{(N+1)}\frac{\sum_k \exp[-U_{\mathrm{eff}}(\mathbf{r}_k)/kT]}{\exp\{[\Delta U - U_{\mathrm{eff}}(\mathbf{r}_k)]/kT\}} \tag{8}$$

In the case where the concentration of adsorbed particles is so low that one can neglect the adsorbate – adsorbate energy in comparison to the solid-adsorbate energy, $\Delta U = U_{gs}(\mathbf{r})$ where $U_{gs}(\mathbf{r})$ is the gas-surface interaction potential [11]. If we chose $U_{\text{eff}}(\mathbf{r}_k) = U_{gs}(\mathbf{r}_k)$ and choose ΔV to be infinitesimal, then

$$q = \frac{Z}{(N+1)} \int \exp[-U_{gs}(\mathbf{r})] d\mathbf{r} = \frac{K_H Z}{(N+1)} \tag{9}$$

where the integral on the right hand side of the equation is the Henry's Law constant, K_H [11]. Since in this region, $K_H Z = \langle N \rangle$ where $\langle N \rangle$ is the average number of adsorbed particles on the surface, Eq. (9) reduces to

$$q = \frac{\langle N \rangle}{N+1} \tag{10}$$

Even when the concentration of particles over the surface is low, $\langle N \rangle$ can be large such that the right hand side of Eq. (10) is nearly 1. In other words, the acceptance rate in the creation step of the GCMC algorithm will be close to unity in the Henry's Law region of adsorption where the isotherm is linear in pressure.

As surface converge increases beyond the linear region of the isotherm, adsorbate – adsorbate interactions become increasingly more important and the assumption that $\Delta U = U_{gs}(\mathbf{r})$ is no longer valid. An effective potential must be defined that is the sum of the gas-surface interaction and the gas – gas interaction. If we consider the case of a homogeneous plane surface at $z = 0$, the gas-surface potential will depend only on z – the perpendicular distance from the surface, *i.e.*, $U_{gs}(\mathbf{r}) = U_{gs}(z)$. (Here and below x, y, and z are Cartesian coordinates.) Similarly, the density of the adsorbate will depend only on z, as will the effective potential, $U_{\text{eff}}(z)$ in Eqs. (6) and (8). For this study, U_{eff} was obtained as follows. For a given value of the pressure, a sequence of N configurations ($N \cong 10{,}000$) was generated by the conventional GCMC procedure and stored. Then 100 values of x and y were chosen at random. For each value (x, y), 80 values of z were chosen by dividing the simulation box into equal portions from top to bottom, and z would be the perpendicular distance from the surface at the center of each portion. At each point (x, y, z) and for each n-configuration, the value of the total energy of interaction of a probe atom at this point with all of the other atoms of the configuration and with the surface of the adsorbent $U^n_{\text{tot}}(x, y, z)$ was calculated. Then $U^n_{\text{tot}}(x, y, z)$ was averaged over all the configurations in the following manner:

$$\langle U_{\text{tot}}(x,y,z)\rangle = \frac{\sum_{n=1}^{N} U_{\text{tot}}^{n}(x,y,z)\exp[-U_{\text{tot}}^{n}(x,y,z)/kT]}{\sum_{n=1}^{N}\exp[-U_{\text{tot}}^{n}(x,y,z)/kT]} \qquad (11)$$

Finally the arithmetic mean over the 100 random values of $\langle U_{\text{tot}}(x,y,z)\rangle$ was taken over x and y to give $U_{\text{eff}}(z)$.

To simulate using this method, a Lennard-Jones (12–6) potential function was used to describe the molecule–molecule interaction. The potential parameters (well-depth ε_{gg}/k and size parameter σ_{gg}) used here correspond to Ne (33.9 K and 2.78 Å respectively). The potential for the interaction of a molecule with the graphite surface is the well-known summed 10–4 potential model of Steele [11]. The simulation cell was a box with x and y length equal to 27.8 Å, and periodic boundary conditions in these dimensions. The z-coordinate ranged from 0 (at the surface) to 23 Å; there is a reflecting wall at the upper boundary. The GCMC simulation technique of Norman and Filinov [9] was used and in a typical simulation, 10^6 steps were taken to reach equilibration, followed by 10^6 data gathering steps. During the simulation, the adsorption isotherm at 37 K (number of molecules $\langle N\rangle$ *versus* pressure P) was determined. In addition, the efficiency of the simulation was determined by calculating the percentage of attempted moves which were accepted.

3. RESULTS

Using the method described above, probability density distribution functions were obtained for each point on an isotherm at 37 K at or above the monolayer ($\sim$67 atoms). These results are shown in Figure 1. Below 0.72 atm where coverages were less than a monolayer, the probability density which is a function of the gas-surface interaction only was used:

$$\mathcal{P}(z_k) = \exp[-U_{gs}(z_k)/kT] \qquad (12)$$

This probability density (which has a single peak at 3.1 Å) is the solid curve in Figure 1 which is off scale. This is an indication that the effective potential is strong in the monolayer region but at distances greater than 8 Å from the surface, it is virtually negligible. As coverage increases beyond the monolayer, the effective potential close to the surface (for $z < 5$ Å) is large and positive, resulting in a probability density in that region which is small,

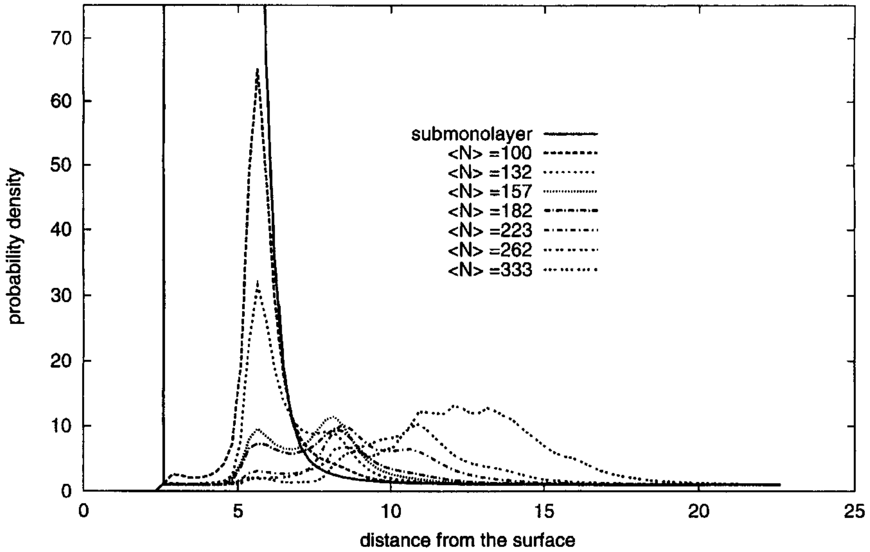

FIGURE 1 The effective probability density functions (Eq. (6)) are shown as a function of the distance from the surface (z in Å). The curve for the submonolayer coverage (solid line – Eq. (12)) is off scale.

while in the volumes far from the surface (beyond 5 Å) the effective potential becomes non-negligible, and its effect extends further from the surface as coverage continues to rise.

The isotherm results for simulations done at and below the monolayer coverage for both the unbiased and biased techniques are shown in Figure 2. Because the gas-surface potential was used to generate the probability distribution function, (the solid line in Fig. 1), this simulation was biased such that there is a high probability of creating a particle in the region between 2.8 and 4 Å, while the chances of creating a particle in the simulation cell above 4 Å are nearly zero. Because of this, the simulation results are identical to the ones obtained from the unbiased GCMC in the submonolayer region only. Since it is virtually impossible to create a particle in the simulation volume above 4 Å, the coverage levels off at the monolayer value, and never increases beyond that for any pressure. (See Fig. 2 inset.) In the region where the thermodynamic properties are reproduced, the efficiency of the simulation is significantly increased, *i.e.*, the acceptance rate (the percent of accepted trial insertions) for creation (and deletion) of particles is an order of magnitude greater than the acceptance rate for creation

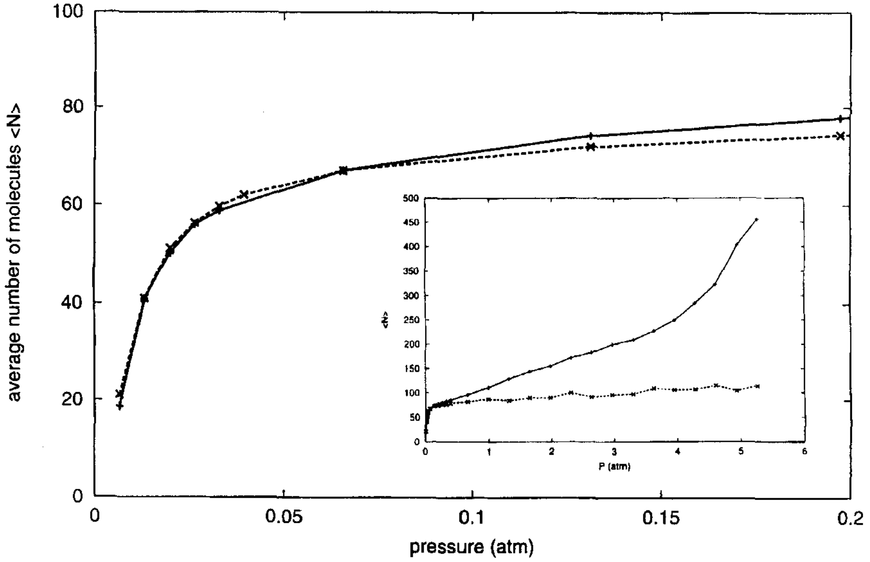

FIGURE 2 Isotherm for Ne adsorbed on graphite at 37 K. The solid line is the isotherm is obtained from an unbiased simulation. The dotted line is the isotherm obtained using the gas-surface potential as U_{eff} in Eqs. (6), (8) and (12). The submonolayer region where the two calculations are in agreement is emphasized, while the complete isotherms are shown in the inset.

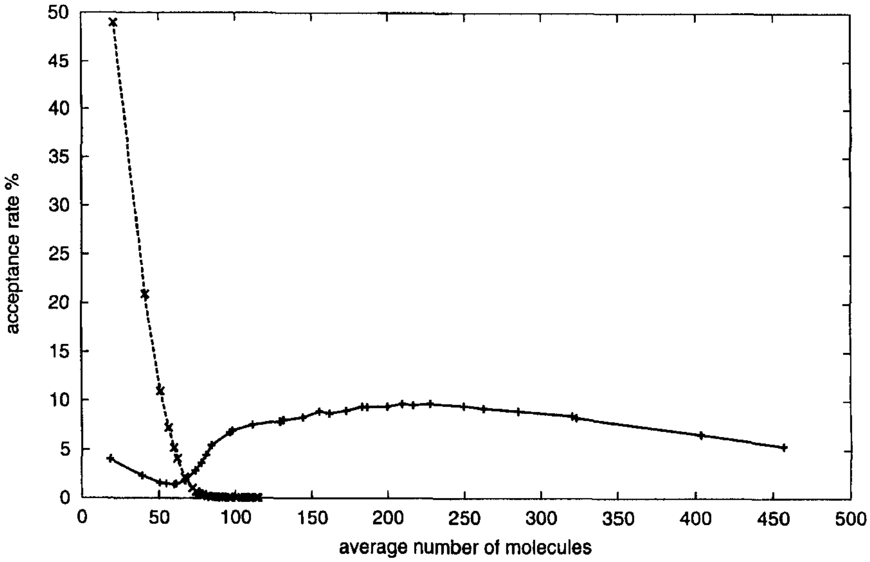

FIGURE 3 The efficiency of the biased simulation in the submonolayer region (broken line) is compared to the efficiency of the unbiased simulation (solid line).

in the unbiased simulation, Figure 3. The acceptance rate for creation of particles at the monolayer coverage remains unchanged compared to the acceptance rate in the unbiased simulation, and as expected, the efficiency decreases to zero beyond the monolayer region where the thermodynamic properties are no longer reproduced. Therefore, the potential distribution used to bias the simulation in the submonolayer region can be used to increase the speed and efficiency of a simulation as long as the coverage remains below a monolayer.

To simulate the isotherm in the multilayer region, the effective potentials and the distribution functions derived from them (shown in Fig. 1) can be used in the biased GCMC algorithm to improve the efficiency. Figure 4 shows the results obtained, along with the isotherm calculated initially with the unbiased technique, and one can see that they are identical. However, using the effective potential distribution functions, the efficiency of the simulation is two times greater compared to that of the unbiased method for most coverages, Figure 5. As the total coverage increases beyond about 3 layers, the increase in efficiency in the biased simulation is only a few percent over the traditional method. This can be attributed to the fact that the distribution functions for these higher coverages are broader, *i.e.*, they are similar to the uniform distribution used in the regular GCMC simulations,

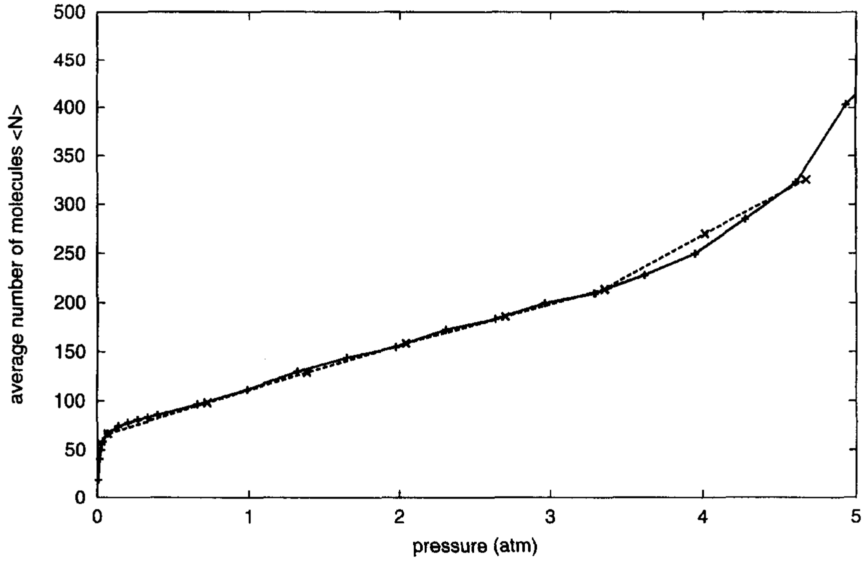

FIGURE 4 Isotherms simulated using the probability density distributions shown in Figure 1 are given by the dotted lines. The solid line gives the results of the unbiased simulation.

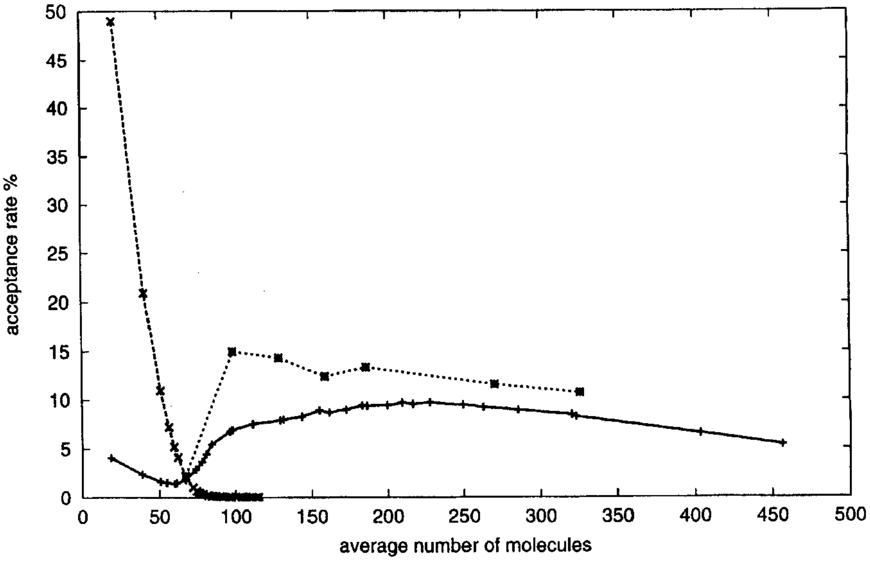

FIGURE 5 The efficiency of the simulation performed using the effective potentials (dotted line) is compared to the efficiency of the unbiased simulation (solid line) and that of biased simulation in the submonolayer region (broken line).

and therefore do not significantly increase the probability of creation or deletion.

4. CONCLUSIONS

We have shown that the effective potential biasing technique improves the efficiency of the creation and deletion steps in GCMC for coverages below ~2 layers by as much as an order of magnitude, except for the region where the coverage is close to one monolayer. The most significant increase in efficiency came when the probability density distribution function was very narrow, (*i.e.*, in the first and second layers).

To further improve the method, the efficiency of creating a particle in the monolayer region needs to be addressed separately. A two-dimensional analog to the cavity biased method of Mezei would be a good choice since the adsorbed fluid molecules in the monolayer form a two-dimensional dense fluid. At higher coverages (above two layers), it will be necessary to find a sharper probability density distribution if one hopes to further increase the efficiency of the simulations in that region.

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