A Thermodynamic Perturbation Method to Calculate Surface Forces in Confined-Fluid Systems

Sang Woo Han[†] and Joonkyung Jang[*]

School of Nano Science & Technology, Pusan National University, Busan 609-735, Korea. [*]E-mail: jkjang@pusan.ac.kr
[†]Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea
Received November 12, 2005

In studying phase behavior of confined fluids, a lattice gas model[1] is widely used. It has been successfully applied to the phase behavior of water trapped in a carbon nanotube.[2] We have used a similar model to study the capillary force due to a water meniscus that forms between an AFM tip and a surface.[3,4] In the Monte Carlo simulation of a confined fluid, it is often reasonable to fix the *chemical potential* μ (e.g. in phase equilibria) instead of the number of molecules N. It is then sensible to work with a grand-canonical (μVT) ensemble.[2-4] Figure 1 illustrates a grand-canonical Monte Carlo simulation of a liquid confined between two surfaces. The liquid sites, drawn as circles in the figure, mimic water molecules[3,4] at a relative humidity of 29%. The circular upper surface is modeled after a nanoscale AFM tip, and the flat lower surface corresponds to the surface probed by the tip. As the *inter-surface distance* h increases by one *lattice spacing* l [from A to B in Figure 1], the liquid profile changes (usually, the meniscus narrows in its waist). The force between two surfaces, F, is given by[5]

$$F(h) = -\left(\frac{\partial \Omega}{\partial h}\right)_{\mu,T} - p\left(\frac{\partial V}{\partial h}\right)_{\mu,T} \tag{1}$$

, where Ω and V are the *grand potential* and volume of the system, respectively, and p is the pressure of the bulk system with a chemical potential μ. The key quantity in the Monte Carlo calculation of equation (1) is the derivative of Ω with respect to h (the bulk pressure p can be easily calculated by using an analytic theory such as the density functional theory[3]). Within a lattice model in general, the derivative is given by the change in Ω as h increases by l. Therefore, in order to calculate the force, one needs $[\Omega(h + l) - \Omega(h)]$, where $\Omega(h + l)$ and $\Omega(h)$ are the grand potentials at inter-surface distances of $h + l$ and h, respectively.

Unfortunately, Ω is not a direct observable in a standard Monte Carlo simulation. Previously, we used a *thermodynamic integration* method that utilizes the following relation,[6]

$$\left.\frac{\partial(\beta\Omega)}{\partial\beta}\right|_{\mu,h} = E - \mu N \qquad (\beta^{-1} = k_B T), \tag{2}$$

where E and N are the energy and number of molecules, respectively. In order to calculate Ω, we numerically integrated equation (2) as follows. Starting from $\beta = 0$ (infinite T where Ω is known exactly), we ran simulations

for at least 10 intermediate β values. At each β value, we evaluated the right-hand side of equation (2) by using a standard Monte Carlo method. Obviously, running simulations at intermediate temperatures is the computational bottleneck in the force calculation. There is another thermodynamic integration method that involves an integration with respect to μ,[3,4] but its computational load is nearly identical to that required for the above integration with respect to β.

Here we propose a thermodynamic perturbation method to calculate the change in the grand potential. Let us write the difference in the grand potential as

$$\Omega(h + l) - \Omega(h) = -k_B T \ln[Z(h)/Z(h + l)] \tag{3}$$

, where $Z(h)$ and $Z(h + l)$ are the partition functions of the systems with inter-surface distances of h and $h + l$,
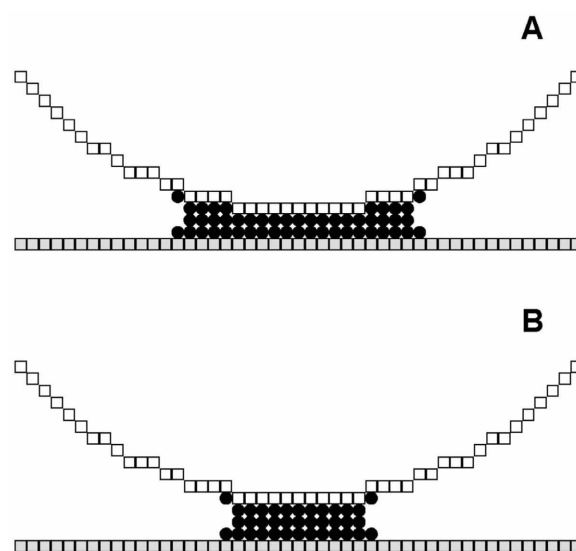

Figure 1. Profile of a liquid confined between two solid surfaces. The upper- and lower- surface sites are drawn as open and filled squares, respectively. The liquid sites (defined as the lattice sites with an average occupancy above 1/2) are represented as filled circles. These figures represent 2-dimensional cross sections of water menisci condensed between an AFM tip and a flat surface under an ambient condition. A lattice gas model[2-4] has been used in this simulation. The liquid profile changes when the distance between two surfaces, h, increases from 3 [A] to 4 [B] lattice spacings, ls.

respectively. The formal expression of $Z(h)$ is

$$Z(h) = \sum_{c_1=0}^{1} \sum_{c_2=0}^{1} \cdots \sum_{c_B=0}^{1} \exp[-\beta H(c_1, c_2, \ldots c_B)] \quad (4)$$

, where B is the total number of lattice sites, and c_i ($i = 1, 2, \ldots, B$) is the occupation number (0 or 1) of the ith site. The *effective energy* H in equation (4) is defined as

$$H(c_1, c_2, \ldots c_B) = E(c_1, c_2, \ldots c_B) - \mu N(c_1, c_2, \ldots c_B) \quad (5)$$

, where we wrote the energy $E(c_1, c_2, \ldots c_B)$ and number $N(c_1, c_2, \ldots c_B)$ as functions of the occupation number of each site. $E(c_1, c_2, \ldots c_B)$ is typically given as a sum of intermolecular and molecule-surface interactions both taken to be of a nearest-neighbor type. Now suppose the total number of lattice sites at an inter-surface distance of $h + l$ is $B'(> B)$. Note

$$Z(h) = 2^{(B-B')}$$

$$\times \sum_{c_1=0}^{1} \sum_{c_2=0}^{1} \cdots \sum_{c_B=0}^{1} \cdots \sum_{c_{B'}=0}^{1} \exp[-\beta H(c_1, c_2, \ldots c_{B'})] . \quad (6)$$

Using the above equation, we can write the ratio of partition functions in equation (3) as

$$\frac{Z(h)}{Z(h+l)} = \frac{2^{(B-B')}}{Z(h+l)} \sum_{c_1=0}^{1} \sum_{c_2=0}^{1} \cdots \sum_{c_{B'}=0}^{1} e^{\beta \Delta H}$$

$$\times \exp[-\beta H(c_1, c_2, \ldots c_{B'})] = 2^{(B-B')} \langle e^{\beta \Delta H} \rangle_{\mu, h+l, T} \quad (7)$$

, where $\Delta H = H(c_1, c_2, \ldots c_B, \ldots, c_{B'}) - H(c_1, c_2, \ldots c_B)$, and $\langle \ldots \rangle_{\mu, h+l, T}$ means the ensemble average for a fixed chemical potential μ, an inter-surface distance $h + l$, and temperature T. Using equation (7), we can write equation (3) as

$$\Omega(h + l) - \Omega(h) =$$

$$k_B T [(B - B') \ln 2 + \ln(\langle \exp[\Delta H / k_B T] \rangle_{\mu, h+l, T})] . \quad (8)$$

The above equation expresses the difference in the grand potential as an ensemble average of exponentiated ΔH.

In principle, equation (8) can be evaluated by running a simulation at a single thermodynamic state. An accurate evaluation of equation (8) however will require sampling a range of ΔH much broader than obtained in a standard Monte Carlo method. There are advanced Monte Carlo techniques designed to meet such a requirement. Overlapping distribution method and umbrella sampling[7] would be examples. Another numerical difficulty arises when typical ΔH values are large, causing a divergence in $\langle \exp[\Delta H / k_B T] \rangle_{\mu, h+l, T}$. To make ΔH smaller in magnitude, one could introduce an intermediate geometry as follows. Let us consider the case where the inter-surface distance h
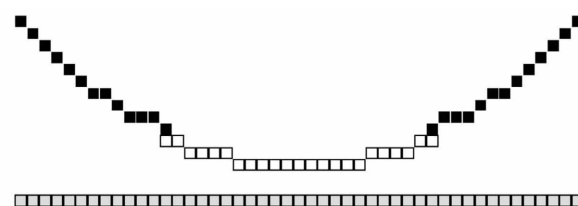

Figure 2. An intermediate geometry of Figure 1A ($h=3l$) and Figure 1B ($h=4l$). As in Figure 1, gray-filled squares represent the lower surface sites. Open and black-filled squares correspond to the tip-surface sites at $h=4l$ and $h=3l$, respectively. The liquid profile for this geometry (not shown) is expected to be in the middle of the two profiles shown in Figure 1.

varies from $3l$ to $4l$ (as in Figure 1). One can think of this transition in the geometry as a two-step process by inserting an intermediate geometry shown in Figure 2. In this choice of an intermediate geometry (one can think of various other geometries different from Figure 2), the half of the upper surface sites are identical to the upper surface sites at $h = 3l$ (Figure 1A), and the rest of the upper surface sites corresponds to the upper surface sites at $h = 4l$ (Figure 1B). The transition from Figure 1A to Figure 1B can be divided into the transitions from Figure 1A to Figure 2 and from Figure 2 to Figure 1B. Equation (8) can be applied to each step, and the net change in Ω is given by the sum of Ω change in each step. In this way, one can vary the system geometry gradually, and ΔH values in simulation will be smaller. The decrease in the magnitude of ΔH will be helpful in preventing the divergence of exponential function in equation (8). This scheme, combined with the advanced Monte Carlo techniques, is expected to be less time-consuming than thermodynamic integration methods (which typically require 10 additional simulations for a given thermodynamic state). In summary, equation (8) will provide an efficient computational method compared to the previous Monte Carlo methods using a thermodynamic integration.

References

1. Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956; Chap. 7.
2. Maibaum, L.; Chandler, D. *J. Phys. Chem. B* **2003**, *107*, 1189.
3. Jang, J.; Schatz, G. C.; Ratner, M. A. *J. Chem. Phys.* **2004**, *120*, 1157.
4. Jang, J.; Schatz, G. C.; Ratner, M. A. *Phys. Rev. Lett.* **2003**, *90*, 156104.
5. Evans, R.; Marini Bettolo Marconi, U. *J. Chem. Phys.* **1987**, *86*, 7138.
6. Peterson, B. K.; Gubbins, K. E. *Mol. Phys.* **1987**, *62*, 215.
7. Frenkel, D.; Smit, B. *Understanding Molecular Simulation*; Academic Press: San Diego, 2002; Chap. 7.