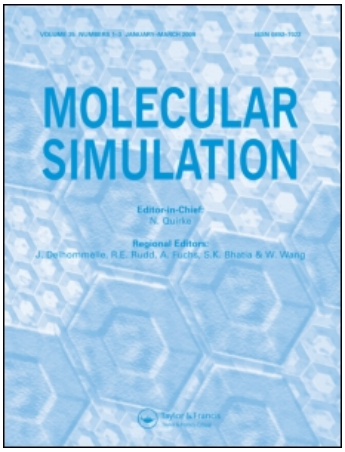

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Jan Forsman[a]; Clifford E. Woodward[b]
[a] Physical Chemistry 2, Chemical Center, Lund, Sweden [b] School of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra, Australia

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IMPROVING THE EFFICIENCY OF A NEW INFINITE ORDER PERTURBATION METHOD TO SIMULATE SURFACE FORCES

JAN FORSMAN[a] and CLIFFORD E. WOODWARD[b]

[a]*Physical Chemistry 2, Chemical Center, P.O. Box 124, S-221 00 Lund, Sweden;* [b]*School of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Canberra ACT 2600, Australia*

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Svensson and Woodward [1] have recently developed an infinite order thermodynamic perturbation technique, utilizing free energy differences, with which surface forces and free energies may be simulated without particle insertions. In this Note, we investigate another free energy difference method, in which we employ an isotension ensemble version of the variance minimization scheme, introduced by Bennet [2] for canonical systems. It is shown that this method provides a substantially improved efficiency, as compared with the simple thermodynamic perturbation technique. The applicability is also increased, since fluids with hard cores may be treated without restrictions.

Keywords: Monte Carlo simulations; surface forces

1 INTRODUCTION

The physics of fluids confined in narrow geometries is of considerable interest and confined fluids have been extensively investigated using computer simulations. A common constraint in such studies, is the constancy of the fluid chemical potential, ensuring equilibrium with a bulk reservoir. Simulation methods designed to accommodate this type of constraint include Grand Canonical [3] and Gibbs Ensemble [4] Monte Carlo. These employ particle deletions and insertions during the course of the simulation in order to maintain the chemical potential. Their implementation can become problematic however, when the fluid density is high and this is exacerbated

significantly if the fluid is polymeric. Recently, Svensson and Woodward [1] introduced a new simulation technique for confined fluids at constant chemical potential. The method, which employs the so-called Isotension Ensemble [5] (IE), requires the calculation of the free energy difference between two known states of the system. It has been successfully applied to studies of the force and free energy of interaction between surfaces confining both simple and polymeric fluids [1, 5–8]. The free energy difference method (FEDM), employed in those studies, utilized a simple thermodynamic perturbation scheme to estimate the change in the free energy of the fluid as the separation between the confining walls was changed in a stepwise manner. As with virtually all FEDM's, the technique requires that the states, whose free energy difference is to be estimated, are not very different and that there is significant overlap between their important regions of configurations space. For surface interaction studies, this means that one is restricted to making only small stepwise increments in the surface separation.

In this Note was explore an alternative FEDM based on a scheme introduced by Bennet [2]. Here a weight function is introduced, chosen so as to minimize the variance in the estimated free energy difference. We hoped that this method would prove more efficient than the thermodynamic perturbation method. For surface interaction studies, in particular, this could allow for larger stepwise increments in the surface separations. As we shall see below, this proved to be the case. Furthermore, Bennet's method also solves a difficulty encountered by the thermodynamic perturbation scheme when it is applied to surface interactions across fluids with repulsive cores. The improvements one obtains will of course depend on the particular problem under study. For simplicity, we have chosen to investigate a truncated and shifted Lennard-Jones liquid, confined between two Lennard-Jones walls.

2 THEORY

Consider a system in which a fluid is confined between two parallel surfaces, separated by a distance h. In the IE, the area of the walls, S, are equal, but undergo fluctuations which are stabilized by the average of the component of the pressure tensor acting parallel to the walls, denoted as P. The configurational partition function, Q, for this ensemble is,

$$Q(h) = \frac{h}{N!}\int_0^\infty dS \exp[-\beta PSh] \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp[-\beta U] \qquad (1)$$

where N is the number of particles and, β^{-1} is the thermal energy. U is the interaction part of the Hamiltonian, which is a function of the configuration of the particles $\{\mathbf{r}_1 \ldots \mathbf{r}_N\}$. It consists of a sum of the fluid and wall-fluid interaction energies, In this study we use potential parameters which are similar to those used by Lane and Spurling [9] to model argon atoms interacting with solid carbon dioxide walls. Defining the z-axis to be perpendicular to the walls, wall-fluid potential is given by

$$w(z) = 2\pi\rho_w \sigma_w^3 \varepsilon_w \left[\frac{1}{45}\left(\frac{\sigma_w}{z}\right)^9 + \lambda\left[\frac{1}{45}\left(\frac{\sigma_w}{z}\right)^9 - \frac{1}{3}\left(\frac{\sigma_w}{z}\right)^3\right)\right]\right] \tag{2}$$

We used, $\varepsilon/k_B = 153$ K, where k_B is Boltzmann's constant, $\sigma_w = 3.73$ Å, and $\rho_w \sigma_w = 1.0$. The total potential acting on a fluid particle is given by the sum, $w(z) + w(h - z)$.

The interaction between the fluid particles is modelled by a truncated and shifted Lennard-Jones potential,

$$\phi(r) = \begin{cases} \phi_{LJ}(r) - \phi_{LJ}(r_c) & r < r_c \\ 0 & r > r_c \end{cases} \tag{3}$$

where r is the interparticle distance and ϕ_{LJ} is the Lennard-Jones potential,

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{4}$$

We chose, $\varepsilon/k_B = 119.76$ K, $\sigma = 3.405$ Å, and $r_c = 2.5\sigma$.

The configurational part of the chemical potential, μ, is related to the partition function according to,

$$Q(h) = \exp[-\beta\mu N] \tag{5}$$

Suppose the system is initially at some separation h_0, with pressure P_0. Changing the separation between the walls, to h_1, while maintaining equilibrium with a bulk reservoir, requires a change in the average parallel pressure from P_0 to some other value P_1, such that Q (or equivalently μ) remains constant. By setting the ratio $Q(h_1)/Q(h_0)$ to unity, a simple thermodynamic perturbation expression for the pressure change can be obtained [1]. It can be written in the following way,

$$\frac{Q(h_1)}{Q(h_0)} = \left(\frac{h_1}{h_0}\right)^{N+1} \int_0^\infty dS f(S, h_0) e(S, h_1, h_0) \exp[-\beta(P_1 h_1 - P_0 h_0) S] \quad (6)$$

where $f(S, h_0)$ is the area probability density at the separation h_0. We also have,

$$e(S, h_1, h_0) = \frac{\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp[-\beta(U_1 - U_0)] \exp[-\beta U_0]}{\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp[-\beta U_0]} \quad (7)$$

The function $e(S, h_1, h_0)$ is a ratio of Canonical Ensemble partition functions at a particular value of S. It is evaluated as an average in the h_0 ensemble, as the form of Eq. (7) suggests. For a particular configuration sampled in the h_0 system, U_1 is obtained by evaluating the energy after scaling the z coordinates of all particles by the factor h_1/h_0. The practical details of the implementation of this FEDM scheme are described in ref. [1]. The precision of the free energy difference estimate will decrease with increasing $|h_1 - h_0|$.

As we pointed out by Bennet [2], perturbation schemes of the type described above are not optimal for obtaining free energy differences. In Bennet's scheme the ratio of the partition functions is first expressed as,

$$\frac{Q(h_1)}{Q(h_0)} = \frac{\langle W \exp[-\beta U_1] \rangle_{h_0}}{\langle W \exp[-\beta U_0] \rangle_{h_1}} \quad (8)$$

where the function W is an arbitrary weight function and the angle brackets represent the ensemble averages in each of the two systems. For a finite number of statistically independent configurations, generated from simulations, the weight function is chosen so as to minimize the error of the estimate for the free energy difference. It is assumed that the number of sampled configurations is large enough so that the fluctuation in the estimated free energy is Gaussian. Assuming an equal number of statistically independent configurations are sampled at each separation, the optimal weight function leads to the following expression in the IE,

$$\frac{Q(h_1)}{Q(h_0)} = \frac{\int_0^\infty dS \int d\varepsilon f(S, h_0) \rho_0(\varepsilon, S) \mathcal{F}(H_0 - H_1 + C)}{\int_0^\infty dS \int d\varepsilon f(S, h_1) \rho_1(\varepsilon, S) \mathcal{F}(H_1 - H_0 + C)} \quad (9)$$

where

$$C = \ln[Q(h_0)/Q(h_1)] \quad (10)$$

The function $f(S,h)$ is the area probability density, as defined above. $\mathscr{F}$ is the Fermi function, $\mathscr{F}(x) = 1/(1+\exp(x))$ and $H_i = U_i + P_i S h_i - (N+1)\ln h_i$. The function $\rho_0(\varepsilon,S)$ is the conditional probability density that the h_0 system has an area S with an energy difference $\varepsilon = U_1 - U_0$. Here U_1 is obtained by scaling of particle co-ordinates, as described above. $\rho_1(\varepsilon, S)$ is analogously defined after an interchange of indicies 0 and 1.

The adaptation of Bennet's method to the problem of maintaining chemical potential in planar systems necessitates a self consistent solution of Eq. (9). This is because P_1 is not known *a priori*. An estimate, denoted by $P_1^{(0)}$, could be obtained from the simulation in the h_0 system and Eq. (6). More simply one could just choose $P_1^{(0)} = P_0$. In any case, the simulation at separation h_1 will generally be performed at this incorrect value for the pressure tensor. However, the area probability density $f(S,h_1)$ at pressure P_1 can be obtained by using the following perturbation formula,

$$f(S,h_1) = \frac{f^{(0)}(S,h_1)\exp\left[-\beta(P_1 - P_1^{(0)})hS\right]}{\int_0^\infty dS f^{(0)}(S,h_1)\exp\left[-\beta(P_1 - P_1^{(0)})hS\right]} \tag{11}$$

where $f^{(0)}(S,h_1)$ is the area probability density generated at the incorrect pressure. Using this expression, and setting the ratio $Q(h_1)/Q(h_0)$ to unity in Eq. (9), leads to the following equation for the pressure P_1.

$$\frac{\int_0^\infty dS \int d\varepsilon f(S,h_0)\rho_0(\varepsilon,S)\mathscr{F}(H_0 - H_1)}{\int_0^\infty dS \int d\varepsilon f(S,h_1)\rho_1(\varepsilon,S)\mathscr{F}(H_1 - H_0)} = 1 \tag{12}$$

The functions $f(S,h)$ and $\rho(\varepsilon,S)$ are obtained in tabulated form from the simulations after which P_1 is obtained by iteratively solving Eq. (12).

3 RESULTS

The model fluid we use in this study is able to undergo a liquid/gas phase transition. At a temperature of 100 K and a separation of $h = 20$ Å gas and liquid phases will coexist when the average parallel pressure tensor is about 18.7 bars [8]. We investigated the change in this pressure as the separation was decreased to 12 Å while the chemical potential was kept constant. Note that the liquid is the stable phase at the shorter separations. From 20 Å, h was reduced in a stepwise fashion. After reaching 12 Å the steps were then reversed in order to check for any hysteresis and obtain an indication of the accuracy of the results. The production simulations, at each separation,

consisted of 75000 passes (moves/particle). Area fluctuations and virtual h displacements were performed once every third pass. Where possible, the starting configuration for equilibrations came from the simulation at the preceding separation. Equilibrations were one tenth as long as the production runs. The original perturbation method, Eq. (6), and Bennet's method, Eq. (12), were compared. In Figure 1 we display the pressure curves, for various step lengths, δh. Using Eq. (6) and a very small step length, $\delta h = 0.1$Å, we found no noticeable hysteresis. Increasing the step length to 0.25 Å in Eq. (6), good accuracy was obtained for decreasing steps, but the returning curve showed a small drift. This behaviour reflects the fact that, for potentials with repulsive cores, the perturbation method works best when the system is compressed. As described above, in the perturbation method, configurations at separation h_0, are used to generate configurations at h_1 by scaling of z-coordinates with the factor h_1/h_0. If the system is being expanded, i.e., $h_1 > h_0$, the average distance of closest approach (obtained by scaling) at the larger separation will be greater than at the smaller separation. Thus, finite length simulations at h_0, will not sample certain configurations which make a significant contribution to the function $e(S, h_0, h_1)$, defined by

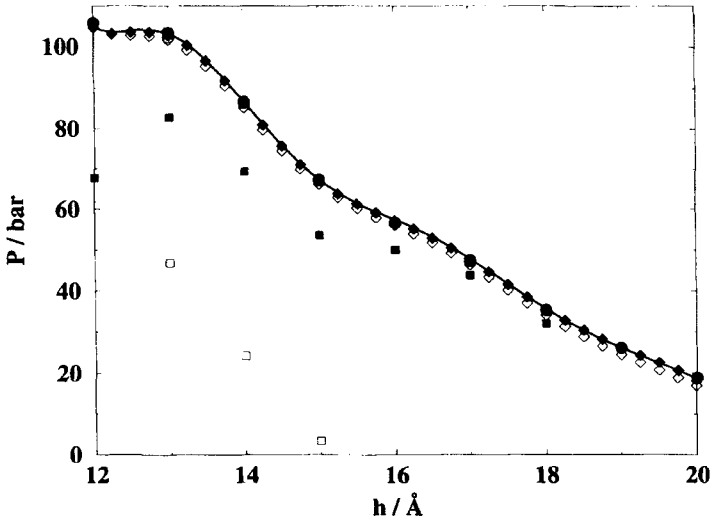

FIGURE 1 Mean parallel pressure as a function of separation. The solid line provides a reference, in which a small step, $\delta h = -0.1$ Å, was chosen to solve Eq. (6). In the other curves, $|\delta h|$ was larger and the simulations were performed going first from $h = 20$ Å to 12 Å (filled symbols) and then back to 20 Å (empty symbols). Diamonds and the solid squares denote simple perturbation results with $|\delta h| = 0.25$ and 1.0 Å, respectively. Circles denote $|\delta h| = 1.0$ Å results, using Bennet's method, Eq. (12).

Eq. (7). This problem becomes more serious the larger is δh. This failure of the perturbation method is not shared by Bennet's method as the Fermi function is bounded above and below by 1 and 0 respectively. A step length of 1 Å gave rise to a complete failure with the simple perturbation method. On the other hand, using Bennet's method with a step length of1 Å no hysteresis was found and the data was about as accurate as those from the perturbation method with the smallest step (0.1 Å). Considering these results, it appears that Bennet's method can decrease the CPU effort in these types of calculations by at least a factor four. A similar CPU reduction has been found in simulations of confined water models [10].

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