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Comparison of mesoscopic solvation pressure at constant density and at constant chemical potential

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ABSTRACT

The solvation pressures arising from the confinement of a fluid by surfaces are calculated under two different thermodynamic conditions, namely at constant density and at constant chemical potential, through mesoscopic scale simulations. We consider two types of fluids, a model monomeric solvent on the one hand, and a fluid composed of linear polymers dissolved in a monomeric solvent, on the other. For these systems our simulations show that the prediction of the solvation (or disjoining) pressure when the chemical potential is kept fixed is different from that obtained when the total density is fixed. We find however, that the same trend between both types of simulations can be obtained when the value of the fixed density is chosen as the average value of the density obtained at constant chemical potential.

1. Introduction

Ensemble equivalence is one of the most cherished tenets of statistical mechanics [1]. It is advantageous though to keep in mind that it occurs only when certain conditions are met. Generally speaking, for short range interacting potentials ensemble equivalence is guaranteed in the thermodynamic limit [2]; however, for long range interactions, such as the electrostatic one, ensemble equivalence does not hold [3]. The choice of statistical ensemble is typically given by the conditions of the physical situation at hand, and for finite systems different values of measureable quantities might be obtained for different ensembles. The question then arises as to how is one to choose the most adequate ensemble when dealing with systems that are not in the thermodynamic limit. The purpose of this paper is to address this point through computer simulations of fluids confined by effective surfaces, where a solvation (or disjoining) pressure arises precisely because of the confinement. We shall show that for finite systems the solvation pressure computed in the canonical ensemble (constant particle number, *N*, volume, *V*, and temperature, *T*), is generally different from that calculated in the grand canonical ensemble (constant chemical potential, μ, *V*, and *T*), although the discrepancy disappears as the thermodynamic limit is approached.

When fluids are confined by surfaces the pressure experienced by the fluid particles is in general different from the pressure of the (unconfined) bulk fluid; such pressure is defined as the solvation pressure [4]. It is an important property to know when studying colloidal dispersions, where the disparity of sizes between the fluid's molecules and the colloidal particles allows one to model the colloids as planar walls, because it yields information about the stability of the dispersion. It can be measured through atomic force microscopy (AFM), or with the surface force apparatus (SFA). In those experimental arrangements the fluid is confined in only in one direction, and remains free to exchange particles with the rest of the fluid. Hence, the μVT ensemble is the natural choice of ensemble for this physical situation, but since simulations in the NVT ensemble are usually faster to perform and they can provide information about transport properties, one might want to know how different can the averages of the solvation pressure be between these ensembles.

With this aim in mind we have chosen a mesoscopic short range interaction model for the fluid's molecules, known as the dissipative particle dynamics (DPD) model [5], which has proved to be successful when modeling complex polymeric systems, among others. In addition to the short range nature of the interparticle interactions, it has the advantage of being faster than atomistically

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detailed molecular dynamics [6] and by construction it has a built-in thermostat. In the next section we present briefly the DPD model, the effective surface interaction, and the characteristics of the fluid. In Section 3, complete details of our simulations are found, while our results and their discussion are shown in Section 4. Finally, our conclusions are drawn in Section 5.

2. Methods

In the DPD model, the total force between any two given particles *i* and *j* is given by $\mathbf{F}_{ij} = \mathbf{F}^{\mathrm{C}}{}_{ij} + \mathbf{F}^{\mathrm{D}}\mathrm{ij} + \mathbf{F}^{\mathrm{R}}{}_{ij}$, where $\mathbf{F}^{\mathrm{C}}{}_{ij}$, $\mathbf{F}^{\mathrm{D}}{}_{ij}$, and $\mathbf{F}^{\mathrm{R}}{}_{ij}$ are the conservative, dissipative and random forces respectively, and have the functional forms shown below:

$$\mathbf{F}_{ij}^{\mathrm{C}} = a_{ij}\omega(r_{ij})\hat{\mathbf{e}}_{ij}\mathbf{F}_{ij}^{\mathrm{D}} = -\gamma\omega^2(r_{ij})\left[\hat{\mathbf{e}}_{ij}\cdot\vec{\mathbf{v}}_{ij}\right]\hat{\mathbf{e}}_{ij}\mathbf{F}_{ij}^{\mathrm{R}} = \sigma\omega(r_{ij})\hat{\mathbf{e}}_{ij}\xi_{ij} \quad (1)$$

where $\hat{\mathbf{e}}_{ij} = \mathbf{r}_{ij}/r_{ij}$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, $\mathbf{r}_i$ being the position and $\mathbf{v}_i$ the velocity of particle *i*, respectively. The variable ξ_{ij} is a random number uniformly distributed between 0 and 1 with Gaussian distribution and unit variance; a_{ij}, γ and σ are the strength of the conservative, dissipative and random forces, respectively. The $\omega(r_{ij})$ factor is a spatial weight function which can be simply chosen as:

$$\omega(r_{ij}) = \begin{cases} 1 - r_{ij}/R_c, & r_{ij} \le R_c \\ 0, & r_{ij} \ge R_c \end{cases} \quad (2)$$

where R_c is a cut off distance, which is taken equal to 1. At inter-particle distances larger than R_c all forces are equal to zero. This simple distance dependence of the forces allows one to use relatively large integration time steps in the dynamics. The relation between the strengths of the dissipative and random forces defines the built-in thermostat [7],$k_BT = \sigma^2/2\gamma$; k_B is Boltzmann's constant. The natural probability distribution function of the DPD model is that of the *NVT* ensemble. For more details and applications of the DPD technique, see for example [8],

For the modeling a confined fluid in contact with a reservoir bulk we use a hybrid Monte Carlo algorithm in the μVT ensemble (GCMC) where the DPD particles are evolved in space and time through integration of Newton's second law with the forces given by equation (1) for 10 time steps, then the total energy of the tenth configuration is compared with the total energy of the first one, and applying the standard Metropolis algorithm [9], only one of those configurations is kept. One then proceeds to attempt solvent particle insertions and deletions with equal probability to keep μ (of the solvent) fixed, using only the DPD configurational energy in the Metropolis algorithm, since particles do not move in this part of the computer code. Full details of the hybrid GCMC − DPD algorithm have been given elsewhere [10]. To model the colloidal particles dispersed in the fluid we have chosen for simplicity an effective, linearly decaying force. More accurate, self − consistent models for DPD surfaces are available [11] but they are beyond the scope of the present work. The so-called wall force is given by equation (3), below, for distances $z \le R_c$, and it is zero otherwise.

$$F_w(z) = a_w\left[1 - \frac{z}{R_c}\right]. \quad (3)$$

In the equation above, a_w is the intensity of the particle–wall interaction, and *z* is the distance between a fluid particle and the position of the surface. The wall force in equation (3) is clearly short ranged also, as are those among the DPD fluid particles. Two types of fluid shall be considered here. The first one is a simple monomeric solvent; in the second we introduce linear polymers in addition to the solvent monomers. Polymers are modeled as monomers joined with freely rotating harmonic springs. The property we are interested in studying, i. e., the solvation pressure (Π), is calculated as the difference between the component of the pressure tensor which is perpendicular to the planar walls, P_{zz}, and the bulk pressure, P_B. The latter is obtained from simulations of the same fluid but without confining walls, namely,

$$\Pi(z) = [P_{zz}(z) - P_B], \quad (4)$$

where the components of the pressure tensor are obtained in our simulations from the virial theorem [6]. The solvation pressure is also calculated using the standard DPD algorithm in the *NVT* ensemble; details of such algorithm have been published elsewhere [12] and need not be repeated here.

3. Simulation details

We use dimensionless units throughout this work. The constants in the dissipative and random forces in equation (1) were set to 4.5 and 3, respectively, to keep the temperature fixed at $k_BT = 1$.We carried out simulations for two types of systems: the first one is a monomeric solvent confined by two walls along the *z*-axis. The second is a mixture of 20 linear polymer molecules dissolved in the fluid. Periodic boundary conditions were used for the *x*- and *y*- axes, but not for the *z*-axis where the walls were placed at the ends of the simulation box. The chemical potential was fixed at $\mu = 37.7$ units for all cases, except where indicated otherwise; this value yields an average total density close to 3 units. We carried out simulations with at least 200 blocks, with each block comprising 10^4 MC configurations; the first 50 blocks were used to equilibrate the system and the rest were used for the production phase, to get good statistical averages of the physical properties. For the DPD simulations we carried out calculations of at least 200 blocks, with each block composed of 10^4 time steps, and again discarded the first 50 blocks. A time step of $\delta t = 0.03$ was used for the dynamics part of the GCMC, and for the standard DPD simulations (not MC). Each polymer molecule is composed of 7 identical DPD beads freely joined by springs. For the harmonic springs used to represent bonds between beads in a polymer, a spring constant *K* equal to 100.0, and equilibrium distance $r_{eq} = 0.7$ were chosen. The dimensions of the simulation box were $7 \times 7 \times L_z^*$, with L_z^* varying from 1 up to 14 units. We chose a conservative force intensity (see equation (1)), $a_{ij} = 78.3$, when $i = j$, while $a_{ij} = 79.3$ for $i \ne j$. For the interaction between a solvent monomer and the wall (see equation (3)), a constant $a_w = 120.0$ was chosen, and to promote polymer adsorption on the walls, $a_w = 60.0$ for each polymer bead. The acceptance rate for the GCMC-DPD was in the range from about 15% up to 30%, depending on the compression exerted by the walls on the fluid.

4. Results and discussion

Let us start by examining the density profiles along the direction perpendicular to the walls, to see how the confined fluid acquires a structure imparted on it by the walls, breaking the three-dimensional symmetry of bulk fluid. In Fig. 1(a) we find the density profile of the pure monomeric solvent, showing symmetric density oscillations close to each wall, as is expected to occur due to the ordering of the molecules into layers [13]. This structuring disappears as the distance from the surfaces increases, until the fluid behaves as if it was not perturbed at all (see data in the center of the box in the *z*-direction), with an average density equal to its bulk density. Fig. 1(b) displays the density profiles of the solvent and of the 20 polymer molecules, where it is clear that the polymer is completely (and symmetrically) adsorbed on the walls. Since the entire surface of each wall gets covered by the polymers, we call them "surface modifying" polymers.