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On interfacial tension calculation from the test-area methodology in the grand canonical ensemble

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We propose the extension of the test-area methodology, originally proposed to evaluate the surface tension of planar fluid-fluid interfaces along a computer simulation in the canonical ensemble, to deal with the solid-fluid interfacial tension of systems adsorbed on slitlike pores using the grand canonical ensemble. In order to check the adequacy of the proposed extension, we apply the method for determining the density profiles and interfacial tension of spherical molecules adsorbed in slitlike pore with different pore sizes and solid-fluid dispersive energy parameters along the same simulation. We also calculate the solid-fluid interfacial tension using the original test-area method in the canonical ensemble. Agreement between the results obtained from both methods indicate that both methods are fully equivalent. The advantage of the new methodology is that allows to calculate simultaneously the density profiles and the amount of molecules adsorbed onto a slitlike pore, as well as the solid-fluid interfacial tension. This ensures that the chemical potential at which all properties are evaluated during the simulation is exactly the same since simulations can be performed in the grand canonical ensemble, mimicking the conditions at which the adsorption experiments are most usually carried out in the laboratory. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3694533]

I. INTRODUCTION

During the last two decades there has been an enormous advance in the fundamental knowledge of interfacial properties of inhomogeneous complex fluids, not only in the cases of vapour-liquid and liquid-liquid free interfaces, but also in other inhomogeneous situations, such as molecules near planar walls, inside slitlike pores, and in general, in all situations concerning fluids adsorbed on structured materials as zeolites, nanotubes, and amorphous adsorbents. Molecular chains, substances with specific interactions as hydrogen bonding, and systems interacting through long-range intermolecular forces including Coulombic-type interactions are only a few examples of systems for which new methods of statistical mechanics and computer simulation techniques are now available to describe their thermodynamic and structural behaviour.

One of the main reasons of this advance is undeniably the constant development of molecular-based theories of statistical mechanics. Density gradient theory,[1–7] and more significantly, density functional theory (DFT),[8,9] have allowed to determine thermodynamic and structural properties of spherical and molecular inhomogeneous systems. Particularly relevant to this discussion are the great amount of works published for predicting and understanding the behaviour of fluids at free interfaces and adsorbed on different materials. The new generation of functional theories, such as those based on fundamental measure theory[10–12] and their different versions, have provided an important insight into the field. We recommend the work of Llovell *et al.*[13] for a recent review of the literature.

As in the case of molecular-based theories, computer simulation methods have also experienced a great development in the field of interfacial properties, particularly in new techniques for the calculation of fluid-fluid interfacial tension. The traditional method used for determining this key property has been (and still is) the mechanical route, through the evaluation of the microscopic components of the pressure tensor from the virial. However, during the last decade there has been an intense and fruitful development of new methodologies based on the thermodynamic definition of surface tension. The use of new theoretical approaches, such as the expanded ensemble,[14] wandering interface method,[15] or perturbative methods as the test-area (TA)[16] technique, or the determination of the macroscopic components of the pressure tensor (using for instance virtual volume changes, as proposed by de Miguel and Jackson[17] or Brumby *et al.*[18]) are only a few examples of the new methods available in the literature from a computer simulation perspective. These methods are becoming very popular, and as an example the TA method has been so far used by several authors to determine vapour-liquid interfacial properties of Lennard-Jones (LJ) chains,[19] several water models,[20,21] the Mie potential,[5,22] or binary fluid mixtures.[7,23]

The traditional method, and also most of the recent ones, has been applied for determining the fluid-fluid (mainly vapour-liquid) surface tension of simple and complex systems using molecular simulations carried out in the canonical ensemble, i.e., simulations in which the number of particles, volume, and temperature are kept constant. Obviously, this is the "natural" ensemble for calculating the fluid-fluid interfacial properties at direct coexistence using computer simu-

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lation. However, this is not the case if we are dealing with confined inhomogenous systems. There are only a few studies in which the solid-fluid interfacial tension of a confined fluid is calculated from computer simulation (see for instance Hamada *et al.*,[24] Singh and Kwak,[25] Das and Binder[26]), while most authors concentrate on phase behaviour (Gelb *et al.*[27]), adsorption (del Pino *et al.*[28]), or fluid structure (Evans[29]). The reason for this is that confined fluid interfacial tension is not experimentally accessible. However, its determination is important from a formal point of view because this quantity is easily calculated theoretically from DFT. A comparison between theoretical and molecular simulation predictions constitutes a strong test to check the ability of a theory in predicting the behaviour of adsorbed molecules in a pore.

How is it possible to determine the interfacial tension of a fluid confined into a pore from computer simulation? There are different possibilities for calculating the interfacial tension of a confined system using methodologies based on its thermodynamic definition, and particularly, using the TA[16] technique. However, if we are interested in determining all the involved interfacial properties, including the interfacial tension, at the same thermodynamic conditions at which the fluid adsorbed inside a pore is in equilibrium with its reservoir, the practical possibilities are limited. This situation depicted is the one occurring in most laboratory adsorption experiments, so the possibility to reproduce the same conditions determines the potential quantitative evaluation of the molecular simulation estimations. The goal in adsorption experiments is to determine the amount of molecules adsorbed as a function of the temperature and pressure of the reservoir with which the system is in contact. Since in the experimental setup the adsorbed gas is in equilibrium with the gas in the reservoir, the equilibrium conditions are that the temperature and chemical potential of the gas inside and outside the adsorbent must be identical. These conditions are exactly mimicked in the grand canonical ensemble, and hence, in a grand canonical Monte Carlo (GCMC) computer simulation.

From a computer simulation perspective, the calculation of the amount of molecules adsorbed in a pore, at a given pressure and temperature, involves a two-step procedure. In the first step, a bulk simulation is performed in the isothermal-isobaric or *NPT* ensemble at a given P and T. In order to evaluate the chemical potential of the system at the thermodynamic conditions, the particle insertion method proposed by Widom[30] is used during the production stage of the simulation. Since the density of the reservoir is usually low since the bulk phase is a gas, the Widom methodology is usually appropriate. It is important to recall here that this chemical potential μ is the corresponding value for the reservoir at the selected pressure and temperature. The second step involves a grand canonical ensemble simulation, at the same temperature and chemical potential, that allows to determine all the thermodynamic and structural properties of the adsorbed gas, including the average amount adsorbed, the density profiles, or even the isostheric heat of adsorption. However, since the TA methodology is only applicable for simulations carried out in the canonical or *NVT* ensemble, there is no possibility of determining the interfacial tension during the same simulation run. The standard procedure involves a third independent simulation, in the *NVT* ensemble, of the confined fluid at a density equal to the average amount of adsorbed molecules obtained in the GCMC simulation. During the production stage it is then possible to calculate the solid-fluid interfacial tension of the adsorbed system in the pore by performing virtual displacements in the interfacial areas, as proposed by Gloor *et al.*[16] in the TA procedure. Note that it is also possible to calculate the interfacial tension from the thermodynamic route through the relationship that connects the interfacial tension and the normal and tangential components of the pressure tensor. Consider a system confined inside a pore with a well-defined geometry, such as a slitlike pore in which the system is confined between two parallel walls that interact with the fluid through a known solid-fluid intermolecular potential. The z axis is chosen perpendicular to the walls of the pore and the x and y axis are parallel to the walls. It is important to recall here that in a inhomogeneous system the pressure is not a scalar but a tensorial quantity. In the particular case of pores with planar geometry in which the inhomogeneity of the system is along the direction perpendicular to the walls, i.e., the z axis, the microscopic perpendicular or normal (along the z axis direction) component of the pressure tensor, $P_{zz} \equiv P_{\mathrm{N}}$, is constant and equal to the "true" thermodynamic pressure inside the pore. The microscopic tangential components of the pressure tensor, parallel to the walls, $P_{xx}(z) = P_{yy}(z) \equiv P_{\mathrm{T}}(z)$, are functions of the z coordinate, or distance to the walls, and it is different to P_{N}, i.e., $P_{\mathrm{T}}(z) \neq P_{\mathrm{N}}$.

An alternative, more efficient, and faster procedure, without the need of performing the third computer simulation (the *NVT* run) would be feasible if the solid-fluid interfacial tension were calculated at the same time than the rest of thermodynamic and structural properties during the GCMC simulation. This would be possible by extending the TA methodology to be applicable in the grand canonical ensemble. The goal of this work is to extend the method proposed by Gloor *et al.*[16] to the grand canonical ensemble. We have then performed some Monte Carlo simulations in both ensembles to check the equivalence of the predictions obtained using the two methodologies. We have also determined interfacial tension using Monte Carlo simulations in the μVT ensemble by the more traditional method of Irving and Kirkwood[31] that entails the calculation of the components of the pressure tensor using the virial route.

The rest of the paper is structured as follows. In Sec. II, we derivate the extension of the formalism in the grand canonical ensemble. Molecular simulation details are provided in Sec. III. Section IV presents the comparison between the interfacial tension calculations using μVT and *NVT* ensembles for a benchmark system. Finally, we present the main conclusions of this work.

II. TEST-AREA METHODOLOGY IN THE GCMC ENSEMBLE

Consider an open system of particles at a given temperature T, occupying a volume V, and at chemical potential μ. In the grand canonical or μVT ensemble, the key free energy is the grand canonical potential energy $\Omega = \Omega(\mu, V, T) \equiv \Omega_{\mu VT}$.

The change in grand canonical free energy when the temperature, volume, and chemical potential are changed with their corresponding infinitesimal amounts is given by the well-known change of free energy in the grand canonical ensemble. However, density variations produce an extra contribution to the thermodynamic state functions, in general, and to the grand canonical free energy in particular. In the presence of an interface the free energies and particularly Ω need to be modified to include the work that has to be imposed by external forces in order to change the interfacial area $\mathcal{A}$ by $d\mathcal{A}$,

$$d\Omega(\mathcal{A}) = -SdT - PdV - Nd\mu + \gamma d\mathcal{A}. \qquad (1)$$

The contribution $\gamma d\mathcal{A}$ is the work needed and the coefficient γ is the interfacial tension of the system. Note that $\Omega = \Omega(\mu, V, T, \mathcal{A}) \equiv \Omega_{\mu VT}(\mathcal{A})$ is also a function of the interfacial area $\mathcal{A}$. Its thermodynamic definition follows from the expression:

$$\gamma = \left(\frac{\partial \Omega}{\partial \mathcal{A}}\right)_{\mu VT}, \qquad (2)$$

where the partial derivative must be evaluated at constant chemical potential μ, volume V, and temperature T. Note that in the case of a two-phase vapour-liquid or liquid-liquid interface, the usual definition of the surface tension invokes a similar derivative but in the the canonical or *NVT* ensemble. This is the "natural" ensemble for studying a two-phase fluid-fluid interface since the number of particles N, volume V, and temperature T are constant.

Similarly the case of the canonical ensemble, the interfacial tension can be computed efficiently from the previous expression by using fictitious increasing and decreasing surface area. The grand canonical free energy is related with the grand canonical partition function $\Xi_{\mu VT}$ through the well-known statistical mechanics relationship

$$\Omega \equiv \Omega_{\mu VT}(\mathcal{A}) = -k_B T \ln \Xi_{\mu VT}, \qquad (3)$$

where k_B is Boltzmann's constant, and the grand canonical partition function $\Xi_{\mu VT}$ is expressed as

$$\Xi_{\mu VT} \equiv \Xi_{\mu,V,T}(\mathcal{A}) = \sum_{N=0}^{+\infty} \exp[\beta\mu N]\, Q_{NVT}, \qquad (4)$$

where Q_{NVT} is the canonical partition function of a system formed by N particles (at temperature T and volume V) and $\beta = (k_B T)^{-1}$. The partition function of a system of spherical molecules without internal degrees of freedom can be written as

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!}\int d\mathbf{r}^N \exp[-\beta U_N(\mathbf{r}^N)] = \frac{1}{\Lambda^{3N} N!} Z_{NVT}, \qquad (5)$$

where Λ is the de Broglie wavelength associated with the translational degrees of freedom of the system, $U_N \equiv U_N(\mathbf{r}^N)$, the intermolecular potential energy of a system formed by N particles that depends on all the positions $\mathbf{r}^N \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$, and Z_{NVT} is the configurational partition function of the system

$$Z_{NVT} = \int d\mathbf{r}^N \exp[-\beta U_N(\mathbf{r}^N)]. \qquad (6)$$

Although we have used explicitly the relationship given by Eq. (5) valid for systems that interact through spherical intermolecular potentials, with no internal degrees of freedom, the methodology is equally applicable to molecular systems, as it will be explained.

Perturbative methods in computer simulation allow to calculate a number of thermodynamic properties from estimation of the change in the appropriate free energy under fictitious perturbation. The works of Eppenga and Frenkel,[32] Harismiadis *et al.*,[33] and de Miguel and Jackson,[17] in the case of pressure or components of the pressure tensor, and that of Gloor *et al.* in the case of surface tension are clear examples of this methodology. Following the work of Gloor *et al.*, the interfacial tension can be easily evaluated in the grand canonical ensemble using the appropriate thermodynamics definition. Using Eq. (2), the interfacial tension can be expressed as the difference in grand potential free energy between two states with different surface areas

$$\gamma = \left(\frac{\partial \Omega}{\partial \mathcal{A}}\right)_{\mu VT} = \lim_{\Delta\mathcal{A}\to 0} \frac{\Omega_{\mu VT}(\mathcal{A}+\Delta\mathcal{A}) - \Omega_{\mu VT}(\mathcal{A})}{\Delta\mathcal{A}} \approx \frac{\Delta\Omega_{\mu VT}}{\Delta\mathcal{A}}. \qquad (7)$$

The difference in free energy can be written in terms of the grand canonical partition functions of the system having surface areas $\mathcal{A}' = \mathcal{A} + \Delta\mathcal{A}$ and $\mathcal{A}$, with $\Delta\mathcal{A} > 0$,

$$\Delta\Omega_{\mu VT} = \Omega_{\mu VT}(\mathcal{A}') - \Omega_{\mu VT}(\mathcal{A}) = -k_B T \ln\left[\frac{\displaystyle\sum_{N=0}^{+\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!}\int d\mathbf{r}^N \exp[-\beta U(\mathcal{A}')]}{\displaystyle\sum_{N=0}^{+\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!}\int d\mathbf{r}^N \exp[-\beta U(\mathcal{A})]}\right], \qquad (8)$$

where $U(\mathcal{A}) \equiv U_N(\mathbf{r}^N;\mathcal{A})$ and $U(\mathcal{A}') \equiv U_N(\mathbf{r}^N;\mathcal{A}')$ denote the intermolecular potential energy of the system with surface area $\mathcal{A}$ and $\mathcal{A}'$, respectively. It is straightforward to write the previous equation in a more convenient way as

$$\Delta\Omega_{\mu VT} = -k_B T \ln\left[\frac{\displaystyle\sum_{N=0}^{+\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!}\int d\mathbf{r}^N \exp(-\beta\Delta U^{+}) \exp[-\beta U(\mathcal{A})]}{\displaystyle\sum_{N=0}^{+\infty} \frac{e^{\beta\mu N}}{\Lambda^{3N} N!}\int d\mathbf{r}^N \exp[-\beta U(\mathcal{A})]}\right], \qquad (9)$$

where $\Delta U^{+} = U(\mathcal{A}+\Delta\mathcal{A}) - U(\mathcal{A})$ is the change in potential energy when the interfacial area changes from $\mathcal{A}$ to $\mathcal{A}+\Delta\mathcal{A}$. According to Eq. (9), the difference in grand potential free energy is proportional to the logarithm of the average of the Boltzmann factor associated with the surface area perturbation over the unperturbed system of surface area $\mathcal{A}$. This configurational average can be written as

$$\Delta\Omega_{\mu VT} = -k_B T \ln \langle \exp[-\beta\Delta U^{+}]\rangle_{\mu VT}. \tag{10}$$

The interfacial tension can be then calculated in the grand canonical ensemble through the following expression:

$$\gamma^{+} = -\frac{k_B T}{\Delta\mathcal{A}} \ln \langle \exp[-\beta\Delta U^{+}]\rangle_{\mu VT}. \tag{11}$$

In principle, one could also have selected a backward, finite difference scheme to approximate the first derivative of the free energy. In this case, one can write

$$\gamma = \left(\frac{\partial\Omega}{\partial\mathcal{A}}\right)_{\mu VT} = \lim_{\Delta\mathcal{A}\to 0} \frac{\Omega_{\mu VT}(\mathcal{A}) - \Omega_{\mu VT}(\mathcal{A}-|\Delta\mathcal{A}|)}{|\Delta\mathcal{A}|}, \tag{12}$$

which results in an expression for the interfacial tension of the form

$$\gamma^{-} = -\frac{k_B T}{|\Delta\mathcal{A}|} \ln \langle \exp[-\beta\Delta U^{-}]\rangle_{\mu VT}, \tag{13}$$

where $\Delta U^{-} = U(\mathcal{A}) - U(\mathcal{A}-|\Delta\mathcal{A}|)$ is the change in potential energy when the interfacial area changes from $\mathcal{A}$ to $\mathcal{A}-|\Delta\mathcal{A}|$.

For systems of particles interacting through continuous potentials, γ^{+} and γ^{-} are expected to be equal to the value of the interfacial tension as long as $\Delta\mathcal{A}\to 0$. In practical implementations, small but finite values of $\Delta\mathcal{A}$ must be used, and the forward and backward approaches will not yield exactly the same value. As in previous works,[14,16,17,19–21,34–36] the central finite-difference approximation should provide a more reliable estimate of the derivative given by Eqs. (7) and (12). In this case, the interfacial tension can be expressed as

$$\gamma = \frac{\gamma^{+}+\gamma^{-}}{2}, \tag{14}$$

where γ^{+} and γ^{-} are given by Eqs. (11) and (13), respectively. Special care must be taken when using Eq. (14) for determining the interfacial tension of systems that interact through non-continuous intermolecular interactions. The use of Eq. (14) assumes implicitly that both expansion and compression perturbations are appropriate to gauge the value of interfacial tension. This is not expected for systems with discontinuous intermolecular potentials, as was first noted by Eppenga and Frenkel[32] some years ago, and more recently by de Miguel and co-workers.[17,18] However, as we deal with continuous intermolecular potentials, the use of Eqs. (11), (13), and (14) is fully justified from a theoretical point of view.

III. SIMULATION DETAILS

We have applied the methodology proposed in the previous section to study the interfacial properties of a simple fluid confined inside a pore. In particular, the geometry selected for this evaluation is a planar slit pore, composed by two nonstructured flat parallel walls separated by a fixed distance, the pore width H. The molecules confined inside this pore will be described using a simplified albeit widely used molecular model, consisting of symmetrically spherical molecules whose intermolecular interaction energy is described through the classical LJ potential

$$u_{ff}(r_{ij}) = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ff}}{r_{ij}}\right)^{6}\right], \tag{15}$$

where $u_{ff}(r_{ij})$ is the intermolecular potential energy between particles i and j that depends only on the distance between the centres of molecules $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$. The interactions are spherically truncated but not shifted at a given distance r_c. No long-range corrections are applied and all the calculations are carried out considering a cutoff distance of $r_c = 4\sigma_{ff}$. As it is well known, σ_{ff} stands for the diameter of the molecular spherical core, and ε_{ff} is the depth of the pairwise interaction potential. The subscript *ff* stands for fluid-fluid molecular interactions. The confinement of LJ spheres inside a planar pore has been studied using Monte Carlo molecular simulations by several authors.[24,37,38]

The molecules are supposed to interact with both confining walls. Among the extensive collection of models proposed in the literature to account for solid-fluid molecular interactions, the so-called Steele[39] 10–4–3 potential is very popular as it has been used to reproduce the interaction with realistic planar solid substrates as for instance graphite. This model considers that the atoms constituting the solid substrate are placed in layers equispaced by a distance Δ and placed in parallel to the solid-fluid dividing surface. Each of the solid substrate atoms is supposed to interact with every individual fluid molecule through a LJ potential. With this setting, and considering that the atom density in each solid substrate layer is constant, the total interacting energy between a given molecule and one confining wall may be integrated, yielding the following expression:

$$u_{sf}(r) = 2\pi\varepsilon_{sf}\sigma_{sf}^{2}\rho_S\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{r}\right)^{10} - \left(\frac{\sigma_{sf}}{r}\right)^{4} - \left(\frac{\sigma_{sf}^{4}}{3(r+0.61\Delta)^{3}}\right)\right], \tag{16}$$

where r is the distance from the centre of the molecule to one of the walls. The subscript *sf* denotes in this case wall-fluid interactions. These characteristic interacting parameters are defined using the usual Lorentz-Berthelot rules, i.e., $\sigma_{sf} = \frac{1}{2}(\sigma_{ss}+\sigma_{ff})$, and $\varepsilon_{sf} = (\varepsilon_{ss}\,\varepsilon_{ff})^{1/2}$, where σ_{ss} and ε_{ss} are the diameter and dispersive energy parameters corresponding to the LJ wall atoms, respectively. Typical graphite values of $\rho_S = 0.114$ and $\Delta = 3.35$ were selected, representing the solid substrate atom density within each layer, and interlayer spacing, respectively. Since the walls are oriented perpendicular to the z axis and each molecule interacts with two walls, one located at $z = 0$ and the other one at $z = H$, the total solid-fluid interaction energy felt by a molecule placed at a distance z

from one of the walls is given by

$$U_{sf}^{\mathrm{TOT}}(z) = u_{sf}(z) + u_{sf}(H - z). \tag{17}$$

In the calculations presented here, the range of both attractions has been considered to be the same, hence $\sigma_{ss} = \sigma_{ff}$, and the ratio $\varepsilon_{sf}/\varepsilon_{ff}$ has been tuned considering different values in order to explore the effect of the relative strength of both interactions on the confined fluid interfacial properties.

We have performed computer simulations in the grand canonical or μVT ensemble, as well as in the canonical or *NVT* ensemble, in order to check the methodology proposed in Sec. II. The simulation box selected was a parallelepipedic box of dimensions L_x, L_y, and L_z. The flat parallel walls were placed at $z = 0$ and $z = L_z = H$, which means that periodic boundary conditions no longer apply along the z axis. The pore width, which plays an important role in any study concerning slab geometries as it determines the capillarity effects induced by the confinement, remained constant in every case, i.e., $L_z \equiv H$ is fixed during Monte Carlo simulations, whatever the thermodynamic ensemble is used.

All simulation runs were organized in cycles. For GCMC simulations, each cycle consisted in N displacement movements and a molecule deletion or insertion trial. The type of movement was in every case selected at random according to their fixed probabilities, and the maximum displacements were tuned along the simulation to approach a 30% acceptance ratio. Initially, $N = 512$ Lennard-Jones molecules were placed inside the simulation box using a fcc grid. A typical run consisted of 5×10^5 equilibration cycles followed by a production stage of at least 2×10^6 cycles. During this last stage averages of the desired interfacial properties were computed (density profiles, interfacial tension, normal and tangential components of the pressure tensor). Simulation box profiles along the z axis were determined by dividing the box in 100 equal width slabs parallel to the confining surfaces. The uncertainties for the calculated interfacial tension values presented were in all case determined using the block averaging technique, described in Ref. 40. The *NVT* runs were identical, except of course for the fact that only translation moves were considered.

Interfacial tension of the system was calculated using the TA methodology explained in Sec. II in the *NVT* and μVT ensemble. In addition, the Irving and Kirkwood[31] method was independently applied to determine interfacial tension during GCMC simulations. This last method allows to determine the normal and tangential components of the pressure tensor for the case of planar confinement studied. The pressure is obtained in this case as the contributions from the fluid intermolecular interactions to the normal and tangential components, as follows:

$$P_N^{IK}(z) = \rho(z)k_BT - \frac{1}{2\mathcal{A}}\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \frac{|z_{ij}|}{r_{ij}}\frac{du(r_{ij})}{dr}\Theta\left(\frac{z-z_i}{z_{ij}}\right)\Theta\left(\frac{z_j-z}{z_{ij}}\right)\right\rangle, \tag{18}$$

$$P_T^{IK}(z) = \rho(z)k_BT - \frac{1}{4\mathcal{A}}\left\langle \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \frac{\left(x_{ij}^2 + y_{ij}^2\right)}{r_{ij}\cdot|z_{ij}|}\frac{du(r_{ij})}{dr}\Theta\left(\frac{z-z_i}{z_{ij}}\right)\Theta\left(\frac{z_j-z}{z_{ij}}\right)\right\rangle, \tag{19}$$

where Θ is the Heaviside function and the subscript r_{ij} refers to the distance between molecules i and j. The contribution of the interacting walls produces an additional term to the normal pressure component, which may be described, taking into account that the walls are placed in the geometry selected at $z = 0$ and $z = L_z$, according to

$$P_N^{walls,IK}(z) = \frac{1}{\mathcal{A}}\left[\left\langle\sum_{i=1}^{N} F_w(z_i)\Theta(z_i - z)\cdot\Theta(z)\right\rangle - \left\langle\sum_{i=1}^{N} F_w(L_z - z_i)\Theta(L_z - z)\cdot\Theta(z - z_i)\right\rangle\right], \tag{20}$$

where N is the number of confined fluid molecules, and $F_w(z)$ is given by

$$F_w(z) = \frac{du_w(z)}{dz}. \tag{21}$$

The calculation of the interfacial tension from the computed normal and tangential components of pressure tensor is then straightforward, using the classical mechanical route definition

$$\gamma_{IK} = \int_0^{L_z}\left(P_N^{IK}(z) + P_N^{walls,IK}(z) - P_T^{IK}(z)\right)dz. \tag{22}$$

IV. RESULTS

Once the technical and theoretical justification for the application of the TA method in the grand canonical ensemble has been established, a test will be performed on a benchmark system, with the aim to provide a first insight into the quantitative equivalence of the application of TA method in the canonical and grand canonical ensembles. In particular, we compare the quantitative performance of the TA approach in the calculation of interfacial tension for a slab confined fluid in the *NVT* and μVT ensembles. Keeping this in mind, it is very important to set the thermodynamic conditions for both runs to be as equivalent as possible, and with this aim the calculation routes exposed in Sec. II, comprising, respectively, two or three simulation runs were followed.

In the following discussion, the fluid-fluid dispersive energy parameter ε_{ff} and the diameter σ_{ff} are chosen as the units of energy and length, respectively. According to this, we define the following reduced quantities: temperature, $T^* = k_B T/\varepsilon_{ff}$; pressure, $P^* = P\sigma_{ff}^3/\varepsilon_{ff}$; density profile, $\rho^* = \rho\sigma_{ff}^3$; chemical potential, $\mu^* = \mu/\varepsilon_{ff}$; surface tension, $\gamma^* = \gamma\sigma_{ff}^2/\varepsilon_{ff}$; pore size, $H^* = H/\sigma_{ff}$; and distance from one of the walls, $z^* = z/\sigma_{ff}$.

The procedure has been then the following. Initial values of $T^* = 2.001$ and $P^* = 0.136$ have been selected as reference working conditions. The reason for this choice is that, if the molecule of methane is modeled as a single LJ sphere, these reduced coordinates correspond to the usual conditions found in real tight gas reservoirs,[41] a case study that is very relevant from a practical perspective, and where the fluid interfacial properties play a crucial role. As mentioned in Sec. II, the calculation of the solid-fluid interfacial tension of a confined system involves, if the TA methodology could be applied during a GCMC simulation, a two-step procedure. In the first step, a simulation of the described bulk LJ fluid was performed in the isothermal-isobaric or *NPT* ensemble at the selected P^* and T^* conditions, in order to determine the chemical potential value. The chemical potential was determined using the classical Widom particle insertion method.[30] This preliminar simulation yielded a value of $\mu^* = -10.86\,(3)$.

In a second step, the information obtained in the preliminar simulation is then used to perform a simulation of the confined fluid in the grand canonical ensemble at the chemical potential obtained during the (bulk) *NPT* simulation. It is important to recall here that this is the standard procedure if one intends to mimick the setup used in experimental adsorption studies, i.e., a gas reservoir in equilibrium with the confined system at the same temperature and chemical potential. During this second simulation, the average density of molecules inside the pore (adsorbed molecules) is calculated. In particular, the average density value inside the pore, in equilibrium with the bulk phase at $T^* = 2.001$ and $P^* = 0.136$, was $\rho^* = 0.0739(6)$. In addition to that, we apply the extension of the TA procedure proposed in Sec. II and calculate the solid-fluid interfacial tension of LJ molecules confined in the pore. We also apply the Irving-Kirkwood method for determining independently along the grand canonical simulation the normal and tangential components of the pressure tensor, and hence, the interfacial tension.

Although this procedure is enough to have reliable values of the solid-fluid interfacial tension, we have performed an additional and independent simulation of the confined system in the canonical ensemble at the same (constant) density as that obtained in the second simulation previously mentioned ($\rho^* = 0.0739$) and calculate the solid-fuid interfacial tension of the confined system using the TA method in the canonical or *NVT* ensemble as originally described by Gloor *et al.*[16]

We have applied the procedure explained in the previous paragraphs to calculate the solid-fluid interfacial tension of spherical molecules inside a slitlike pore for different confining conditions of pore widths H and solid-fluid relative strength $\varepsilon_{sf}/\varepsilon_{ff}$. We first consider the influence of the pore width for a fixed ratio $\varepsilon_{sf}/\varepsilon_{ff} = 2.0$. Figure 1 shows the density profiles inside the pore at $T^* = 2.001$ and $P^* = 0.136$ for different values of the pore width. As can be seen, simulations in the grand canonical (μVT) and canonical (*NVT*) ensembles give identical profiles, as expected since the same system is simulated using different ensembles but at equivalent thermodynamic conditions. Results indicate that the system develops the expected structure and layering effects inside the pore, and more importantly, the correct behaviour as the pore size is varied. In particular, the system exhibits three layers, two of them located at one sigma of distance from the each wall (located approximately at positions at which the solid-fluid intermolecular potential exhibits two minima), and the third located in the centre of the pore. As the pore size is increased, the confined system exhibits four ($H^* = 5$), and six layers ($H^* = 8$ and 10) located symmetrically inside the pore. Note that for the larger pores ($H^* = 8$ and 10), the system develops a nearly homogenenous adsorption or bulklike behaviour in the centre of the pore, an expected behaviour since interactions between the walls and molecules located in this region become smaller in comparison with fluid-fluid interactions as H^* increases.

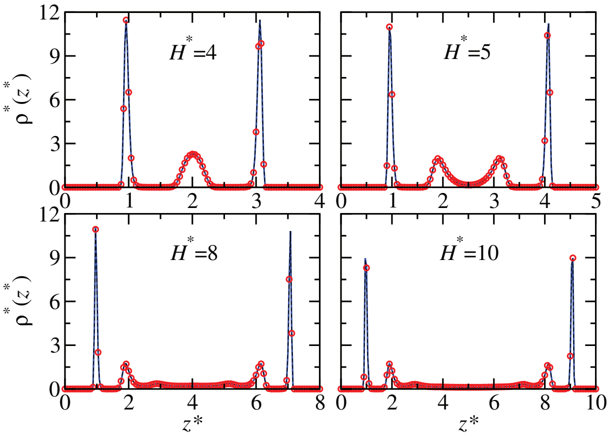

FIG. 1. Density profiles of LJ molecules adsorbed on slitlike pores with different pore widths H^*. Blue solid lines represent GCMC results at $\mu^* = -10.86$ and $T^* = 2.001$, and red circles represent *NVT* results at the same temperature and $\rho^* = 0.0739$.

Results corresponding to the solid-fluid interfacial tension for the fixed ratio $\varepsilon_{sf}/\varepsilon_{ff} = 2.0$ and different pore widths calculated using three independent methods are presented in Table I. As it can be seen, the interfacial tension values are nearly identical in all cases using three alternative methods, demonstrating the complete equivalence between the use of the TA methodology in the canonical and grand canonical ensembles when using similar thermodynamic conditions. It is important to recall here that the use of the TA method in the grand canonical ensemble allows to evaluate the interfacial tension and all the thermodynamic and structural properties of the confined system in the same simulation, without the need of any additional calculation. As can be seen in Fig. 2(a), the solid-fluid interfacial tension becomes larger (less

TABLE I. Solid-fluid interfacial tension of LJ molecules adsorbed on slitlike pores of different pore widths H^* and dispersive energy ratio $\varepsilon_{sf}/\varepsilon_{ff} = 2.0$. $\gamma^*_{TA-\mu VT}$, γ^*_{TA-NVT}, and γ^*_{IK} are the interfacial tensions obtained from the TA method in the grand canonical ensemble, from the TA in the canonical ensemble, and from the Irving-Kirkwood procedure in the grand canonical ensemble, respectively.

H^*	$\gamma^*_{TA-\mu VT}$	γ^*_{TA-NVT}	γ^*_{IK}
4	−43.67(7)	−43.64(3)	−43.70(8)
5	−33.1(5)	−33.7(5)	−33.20(6)
8	−27.2(5)	−27.7(5)	−27.27(7)
10	−28.2(5)	−28.8(5)	−28.16(6)

negative) as the pore size increases, and it seems to develop an asymptotic limiting behaviour as the pore size approaches to 8–10 (in reduced units), approximately. The structure of the adsorbed layers, at sufficiently large pores, does not change significantly as the pore size is increased, and it is expected that the solid-fluid interfacial tension does not vary too much in these cases.

A similar behaviour in the structure of the adsorbed systems is obtained when considering a fixed pore size, $H^* = 8$, and the relative strength $\varepsilon_{sf}/\varepsilon_{ff}$ is varied. Although we have not shown the results here, we have observed the expected behaviour, i.e., increase of the molecules adsorbed inside the pore and a more structured density profiles as $\varepsilon_{sf}/\varepsilon_{ff}$ increases from 0.5 up to 2.0.

The influence between the relative strength between the fluid molecules and the fluid-wall interactions was studied by setting the ratio $\varepsilon_{sf}/\varepsilon_{ff} = 0.5$, 1, 1.5, and 2.0, for a fixed pore width of $H^* = 8$. Agreement between interfacial tensions obtained with the three methods is also excellent within the statistical uncertainty of the simulations, as can be observed in Table II. Figure 2(b) shows the solid-fluid interfacial tension, as a function of $\varepsilon_{sf}/\varepsilon_{ff}$, for the pore considered. As can be seen, the interfacial tension becomes more negative as the energy ratio increases since the walls become more attractive, and hence, interact more cohesively with the fluid adsorbed. The agreement between interfacial tension values obtained from different methods to within their statistical uncertainty is remarkable, underlining the advantage of using the TA procedure along a grand canonical Monte Carlo simulation when studying adsorbed fluids on pores.

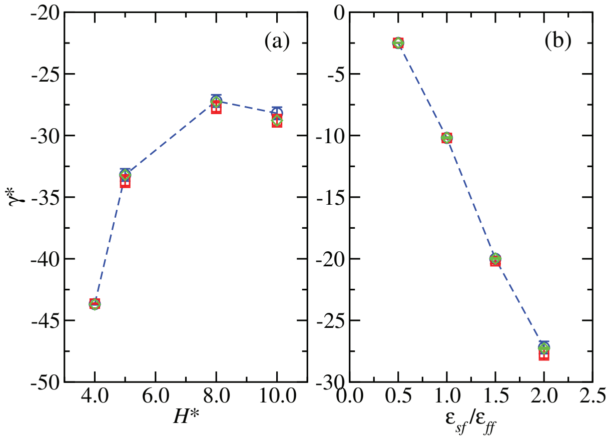

FIG. 2. Solid-fluid interfacial tension of LJ molecules adsorbed on slitlike pores of (a) different pore widths H^* and dispersive energy ratio $\varepsilon_{sf}/\varepsilon_{ff} = 2.0$ and (b) pore width $H^* = 8$ and different dispersive energy ratios $\varepsilon_{sf}/\varepsilon_{ff}$ obtained from the TA method in the grand canonical ensemble (blue circles), from the TA method in the canonical ensemble (red squares), and from the Irving-Kirkwood procedure in the grand canonical ensemble (green triangles). The blue dashed line is a guide to the eye.

TABLE II. Solid-fluid interfacial tension of LJ molecules adsorbed on slitlike pores of pore width $H^* = 8$ and different dispersive energy ratios $\varepsilon_{sf}/\varepsilon_{ff}$. $\gamma^*_{TA-\mu VT}$, γ^*_{TA-NVT}, and γ^*_{IK} represent the same as in the caption of Table I.

$\varepsilon_{sf}/\varepsilon_{ff}$	$\gamma^*_{TA-\mu VT}$	γ^*_{TA-NVT}	γ^*_{IK}
0.5	−2.49(2)	−2.49(2)	−2.49(1)
1	−10.19(6)	−10.20(6)	−10.18(5)
1.5	−20.0(2)	−20.2(3)	−19.98(5)
2	−27.2(5)	−27.8(5)	−27.27(7)

V. CONCLUSIONS

We have extended the TA methodology, originally proposed to evaluate the surface tension of vapour-liquid interfaces along a computer simulation in the canonical ensemble, i.e., at constant number of particles, volume, and temperature, to calculate solid-fluid interfacial tension of systems adsorbed on slitlike pores. This has been done by using the generalization of the grand potential free energy for systems exhibiting two-phase direct coexistence and expressing the interfacial tension as the derivative of the corresponding free energy with respect to the interfacial area. Thus, the interfacial tension can be computed along a simulation in the grand canonical ensemble, i.e., at constant chemical potential, volume, and temperature, by performing fictitious increasing and decreasing interfacial area changes and averaging the corresponding Boltzmann factor associated with the surface area perturbation over the unperturbed system.

The main advantage of this methodology is that it allows to calculate simultaneously the density profiles and the amount of molecules adsorbed onto a slitlike pore, as well as the solid-fluid interfacial tension. On the contrary, the evaluation of the solid-fluid interfacial tension using the original TA methodology requires an additional and independent simulation in the *NVT* ensemble, at the same average chemical potential and density, which makes the proposed methodology clearly more advantageous than the original one. In addition to that, the new method ensures that the chemical potential at which all properties are evaluated during the simulation is exactly the same since the simulation is performed in the grand canonical ensemble, mimicking the conditions at which the adsorption experiments are most usually carried out in the laboratory.

We have applied the new methodology performing grand canonical Monte Carlo computer simulations to calculate the density profiles and interfacial tension of spherical molecules, interacting through the Lennard-Jones intermolecular potential, adsorbed in slitlike pores with different pore sizes and solid-fluid dispersive energy parameters. In order to check that predictions obtained from the new methodology give the same results as those using the original technique, we have also performed computer simulations in the *NVT* ensemble with a number of particles equal to the average obtained at constant chemical potential. Density profiles obtained from computer simulations in the *NVT* and μVT ensembles are nearly identical for all tested pore sizes and solid-fluid dispersive energies. An excellent agreement has been also found, to within the statistical uncertainties, between solid-fluid interfacial tension obtained from simulation in both ensembles, for all the cases considered. We have also determined the interfacial tension from the mechanical expression by determining the normal and tangent components of the pressure tensor using the Irving-Kirkwood recipe, finding the same results as those obtained from the TA technique.

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