A potential distribution induced mapping of free energies for simple fluids

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\section*{Abstract}
The potential distribution theorem (PDT) is utilized to construct an effective density, the pseudo-density $\rho_\text{pseudo}(z)$, that enables mapping of the free energies of the uniform fluid exactly onto the nonuniform system values. In addition, a similar quantity, the pseudo-chemical potential $\mu_\text{pseudo}(z)$, is given as the chemical potential produced by the uniform equation of state upon using the nonuniform density $\rho_\text{w}(z)$ as input. The PDT connects three quantities: the work $W_\text{ins}$(z) for inserting a test particle into the fluid, the chemical potential $\mu_0$ of the bulk fluid, and the nonuniform singlet density $\rho_\text{w}(z)$. We perform Metropolis NVT ensemble Monte Carlo (MC) simulations to obtain the insertion work $W_\text{ins}(z)$ (via Widom’s particle insertion) and the densities $\rho_\text{w}(z)$. We illustrate the mapping on two simple fluids adsorbed on a hard wall: the Lennard-Jones and the attractive Yukawa fluids. The pseudo-density is determined via an accurate uniform-fluid equation of state for the Lennard-Jones system, and for the Yukawa fluid via direct MC simulations. We characterize the behavior of the effective density and the pseudo-chemical potential vis-à-vis the cases of enhancement and depletion of the fluid density near the wall. These quantities ($\rho_\text{pseudo}$ and $\mu_\text{pseudo}$) are found to exhibit for enhanced adsorption out-of-phase oscillations compared to $\rho_\text{w}(z)$ and $\beta W_\text{ins}(z)$. For depleted adsorption, we do not observe oscillations and the trends of $\rho_\text{pseudo}$ and $\mu_\text{pseudo}$ are in good agreement with those of $\rho_\text{w}(z)$ and $\beta W_\text{ins}$. We analyze the differences in behavior in terms of the concavity of the chemical-potential function. We also show the equivalence of the potential distribution theorem to the Euler–Lagrange equation of the density functional theory.

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1. Introduction

One of the major undertakings in the study of nonuniform fluids is to find the free energy of inhomogeneous fluid based on that of the homogeneous fluid. In this work, we formulate this mapping in terms of the well-known potential distribution theorems (PDT) \cite{1,2} of the classical theory of liquids. The gist of the approach can be simply stated. The potential distribution theorem yields the insertion works $W_\text{ins}$ of a test particle in the bulk fluid as well as in the nonuniform fluid. The two insertion works (in uniform as well as in nonuniform fluids) are, in general, different due to the presence of density gradients in the system. In addition to the nonuniform singlet density profile (which is denoted by $\rho_\text{w}(z)$, i.e. nonuniform in the z-direction perpendicular to the wall), we shall define an effective density (which is called the pseudo-density $\rho_\text{pseudo}(z)$) that, when substituted into the equations for a uniform fluid, will yield information on the nonuniform insertion work. This pseudo-density is constructed in the following way: we first calculate the work of insertion $W_\text{ins}(z)$ locally (at a certain distance $z$...
from the wall) in the nonuniform case. Then, we set \( \mu_{\text{ex}} = W_{\text{int}}(z) \) and we invert a bulk equation of state to obtain \( \rho_{\text{pseudo}}(z) \). If we knew \( \rho_{\text{pseudo}} \) beforehand, we could obtain the free energy of the nonuniform fluid from the uniform equation of state (i.e., via the very construction of \( \rho_{\text{pseudo}} \)). In general, \( \rho_{\text{pseudo}}(z) \neq \rho_{\text{pseudo}}^{(1)}(z) \). The questions we shall examine, and also the behavior we shall characterize, are how this effective density behaves for different fluid systems and for different conditions of adsorption. Historically, the effective densities were obtained via various means: e.g. the use of the weighting functions \([3, 4]\) and other coarse graining procedures \([5]\). Here, we are interested in understanding the behavior of the effective densities, which are naturally defined in terms of the PDT. The PDT had a long and indeed veritable history, and due to its basis in first principles the PDT can be applied to uniform as well as nonuniform fluids belonging to general classes of interaction potentials. The insight from PDT may lead to new theoretical frameworks for inhomogeneous fluids. In this work, instead of using theoretical methods, we shall employ Monte Carlo (MC) simulations to obtain the pseudo-densities, as the insertion work can be obtained from Widom’s particle insertion technique \([1]\).

In a parallel development, we shall also define a \textit{pseudo-chemical} potential \( \mu_{\text{pseudo}} \). It is the chemical potential produced by the uniform equation of state when we input the nonuniform density \( \rho_{\text{pseudo}}^{(1)}(z) \), thus \( \mu_{\text{pseudo}}(z) = \mu(\rho_{\text{pseudo}}^{(1)}(z)) \). Its values are not equal to the nonuniform free energy \( \mu_{\text{pseudo}}(z) \neq W_{\text{int}}(z) \), since the governing equations for nonuniform fluids are not the same as for the uniform fluids. The amount of difference between these two energies is an indication of the severity or “disturbances” of the nonuniformity on fluid properties. Obviously, in the limit of vanishing external forces, the fluid becomes uniform and the two energies become the same.

To demonstrate the pseudo quantities, we examine simple fluids such as molecules interacting with Lennard-Jones (LJ) potential or with Yukawa (Yu) potential. By varying the temperature or the bulk density, adsorption of the fluid on a planar wall can change from wall-enhanced density profiles (densities near the wall being higher than the bulk density) to wall-depleted density profiles (densities near the wall being lower than the bulk density). The depletion occurs on weak or repulsive walls especially at bulk phases near the vapor–liquid coexistence or the critical point \([6]\). We shall show from the MC data that for the cases of depletion at the wall, the pseudo quantities exhibit distinct features in contrast to the cases of enhanced adsorption at the wall. The cause of this behavior is to be sought in the “concavity” of the chemical potential curves.

The article is organized as follows. In Section 2 we trace the derivations of the potential distribution theories for an inhomogeneous \( N \)-body system. In Section 3, we describe the methods and numerical details of our Monte Carlo simulations. We study two adsorptive systems: all simple enough for a clear elucidation of the PDT based quantities: the pseudo-densities and pseudo-chemical potentials. Section 4 is for Lennard-Jones (LJ) molecules adsorbed on a hard wall (LJ/HW), and Section 5 is for hard-core attractive Yukawa fluid adsorbed on a hard wall (Yu/HW). Section 6 offers a further examination of the potential distribution theory and its connection to the Euler–Lagrange equation arising in the Density Functional Theory (DFT). We draw conclusions in Section 7.

### 2. The potential distribution theories for nonuniform systems

In this Section, we shall show the derivations of the potential distribution theories for nonuniform fluids in the canonical ensemble. (This can also be done in the grand canonical ensemble \([2]\). We distinguish two types of test particles: one that is under the influence of the external one-body potential \( w \), and the other, free from it, i.e. at \( w = 0 \). Our emphasis is on the second type: wall-free test particles. The \( N \)-body system consists of \( N \) fluid molecules and they border on a planar solid surface. The Hamiltonian \( H_N \) is written as \( H_N(p^N, r^N) = \mathcal{K}_N(p^N) + \mathcal{U}_N(r^N) + W_N(r^N) \), where \( r^N = (r_1, r_2, \ldots, r_N) \) is a shorthand for the \( N \)-vector of the positions of \( N \) particles, \( p^N \) is the \( N \)-momenta vector, \( \mathcal{K}_N \) is the kinetic energy, while \( \mathcal{U}_N(r^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u^{(2)}(r_{ij}) \) is the potential energy between fluid particles (assumed to be pairwise additive), and \( W_N(r^N) = \sum_{i=1}^{N} w(r_i) \) is the sum of one-body energies arising from the external one-body potential \( w \). It is the last energy term that drives the inhomogeneities in the system. Now we consider an \((N-1)\)-body system: the sum of pair energies becomes \( \mathcal{U}_{N-1}(r^{N-1}) = \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} u^{(2)}(r_{ij}) \), and the sum of one-body energies \( W_{N-1}(r^{N-1}) = \sum_{k=1}^{N-1} w(r_k) \). The test particle is introduced in the \((N-1)\)-body system as a particle with label “\( N \)” located at the vector position \( r_N \). This test particle can interact with the other \( N-1 \) molecules through the pair potential \( u^{(2)}(r_{i,N}) \), \( i < N \), as well as with the wall through the one-body potential \( w(r_N) \). This particle is designated the type-1 test particle. The excess potential energy \( \Psi_w(r_N) \) due to the presence of the type-1 test particle is

\[
\Psi_w(r_N) \equiv \mathcal{U}_{N-1}(r^{N-1}) + \mathcal{W}_N(r^N) - \mathcal{W}_{N-1}(r^{N-1}) = \sum_{i=1}^{N-1} u^{(2)}(r_{iN}) + w(r_N).
\]

On the other hand, the type-2 test particle, by choice, does not interact with the wall \( w(r_N) = 0 \). The excess potential energy \( \Psi_{-w}(r_N) \) is (subscript “\(-w\)” stands for “without wall interaction”) \[
\Psi_{-w}(r_N) \equiv \sum_{i=1}^{N-1} u^{(2)}(r_{iN}).
\]

Then the potential distribution theory for the type-1 test particles (interacting with \( w \)) is obtained from the \((N-1)\)-body canonical ensemble average of \( \Psi_w(r_N) \)

\[
\ln \left( \exp \left( -\beta \Psi_w \right) \right)_{N-1:w} = -\beta \mu_w + \ln \left[ \rho^{(1)}_w(r_N) \right] + 3
\]
since
\[
\langle \exp[-\beta \Psi_w] \rangle_{N-1:w} = \frac{1}{Q_{N-1}} \int \mathcal{D}r^{N-1} \exp[-\beta U_{N-1} - \beta W_{N-1}] \cdot \exp \left\{ -\beta \left[ \sum_{i=1}^{N-1} u^{(2)}(r_{iN}) + w(r_N) \right] \right\}.
\] (2.4)

The singlet density \( \rho^{(1)}_w(r_N) \) is defined as
\[
\rho^{(1)}_w(r_N) = \frac{N}{Q_N} \int \mathcal{D}r^{N-1} \exp[-\beta U_N - \beta W_N].
\] (2.5)

Eq. (2.3) has been obtained earlier [1,2]. Note that \( Q_N \) is the \( N \)-body configurational integral, \( \Lambda \) is the de Broglie wavelength, and
\[
\beta \mu_w = \ln(Q_{N-1}/Q_N) + \ln(\rho_0 \Lambda^3),
\] (2.6)

where \( \rho_0 \) is the bulk density.

The potential distribution theorem for the type-2 test particles (without \( w \)) is obtained instead from the \( (N-1) \)-body ensemble average of the wall-less excess potential \( \Psi_{-w}(r_N) \) Eq. (2.2), i.e.
\[
\ln \langle \exp[-\beta \Psi_{-w}] \rangle_{N-1:w} = -\beta \mu_w + \beta w(r_N) + \ln[\rho^{(1)}_w(r_N) \Lambda^3]
\] (2.7)

since
\[
\langle \exp[-\beta \Psi_{-w}] \rangle_{N-1:w} = \frac{\exp[\beta w(r_N)]}{Q_{N-1}} \int \mathcal{D}r^{N-1} \exp[-\beta U_{N-1} - \beta W_{N-1}] \cdot \exp \left\{ -\beta \left[ \sum_{i=1}^{N-1} u^{(2)}(r_{iN}) + w(r_N) \right] \right\}.
\] (2.8)

The insertion work \( W_{\text{ins}} \) required to insert a type-2 test particle with the excess potential \( \Psi_{-w}(r_N) \) is thus (noting that \( \beta \mu_w = \beta \mu_0^w + (\ln(\rho_0 \Lambda^3)) \))
\[
\beta W_{\text{ins}}(r_N) \equiv -\ln \langle \exp[-\beta \Psi_{-w}] \rangle_{N-1:w} = \beta \mu_w - \beta w(r_N) - \ln \left[ \rho^{(1)}_w(r_N) \Lambda^3 \right]
\] (2.9)

where \( \mu_0^w \) is the bulk excess chemical potential.

This quantity \( \beta W_{\text{ins}} \) can be simulated directly via the Monte Carlo method using the Widom particle-insertion technique (see Section below). \( W_{\text{ins}} \) can also be considered as the intrinsic work of insertion. Eqs. (2.8) and (2.9) will be related to the Euler–Lagrange equation of the DFT (see Section 6).

3. Monte Carlo simulations

We shall examine two adsorptive systems: (i) Lennard–Jones spheres over a hard wall (LJ/HW); and (ii) Attractive Yukawa spheres over a hard wall (Yu/HW). For the first system (LJ/HW), we have performed independently new MC simulations [7] at the states of \( T^* = kT/\epsilon = 1.35 \) and densities \( \rho^* = \rho \Lambda^3 = 0.50, 0.65, \) and 0.82. For the system Yu/HW, we perform new simulations here at an isotherm \( T^* = 0.76 \), and densities \( \rho^* = 0.215, 0.368, 0.473, \) and 0.557.

NVT Monte Carlo simulations [8] were carried out for two parallel planar (structureless) walls separated in the \( z \)-direction by \( z_{\text{max}} = 24 \sigma \), and boxed in at dimensions of \( 12 \sigma \) in the \( x \)-and \( y \)-directions. Periodic boundary conditions were applied in the \( x \)-and \( y \)-directions only. For this volume to give the desired reduced densities, one would require \( N = 1728, 2246, \) and 2834 particles for the Lennard–Jones system and \( N = 743, 1271, 1635, \) and 1994 particles for the Yukawa system. However, due to the oscillations of the density profiles near the wall (thus causing drying/depletion at the wall), the actual numbers of particles used were adjusted so that the correct bulk densities (in the middle of the simulation box) were attained. For each state we made simulations consisting of 10 independent runs with \( 1 \times 10^6 \) cycles in each run, following an equilibration with \( 1 \times 10^5 \) MC cycles. A single MC cycle is defined as carrying out of \( N_{\text{att}} \) attempted moves of particles equal to the number of particles in the system \( (N_{\text{att}} = N) \). The acceptance ratio was adjusted between 35% and 45%. The density distributions \( \rho^{(1)}_w(z) \) were obtained with a bin size of 0.05\( \sigma \). These singlet density profiles were obtained by taking averages for every 10 cycles in the 10 runs. Much longer simulation runs were made for the LJ systems, i.e. from 2 to \( 3 \times 10^6 \) cycles. In addition, in order to provide data for the insertion probabilities, we used the Widom fictitious particle-injection method [9], injecting \( N \) “ghost” (test) particles \( (N = \text{size of the system in question, e.g. } N = 1728, 2246, \text{etc.}) \) at every 10 cycles into the same bins as used for accumulation of the \( \rho^{(1)}_w(z) \) statistics. We then collected statistics for the ensemble averages \( \langle \exp[-\beta \Psi_{-w}] \rangle_{N-1:w} \) i.e. the potential distributions in each bin.

At the densities studied, the statistics of successes in bins is between 3% and 85%, depending on the \( z \)-locations of the bins. In the run for Yu/HW at \( \rho^* = 0.577 \) for example, about \( 3.4 \times 10^5 \) attempted insertions were made. The successes of insertion ranged from about \( 1 \times 10^7 \) times to \( 2.9 \times 10^8 \) times at different \( z \) locations.
Fig. 1. Substantiation of the potential distribution theorem (2.9) via Monte Carlo simulation. System: Yukawa fluid on Hard wall (Yu/HW). Temperature \( T^* = 0.76 \), bulk density \( \rho^* = 0.215 \). Red squares: the insertion work term \( -\beta W_{\text{ins}} - \beta \mu_0^* \); blue dots: the structural term as expressed by the singlet cavity distribution function \( -\ln[\rho_0^{(1)} \exp(\beta w)/\rho] \). We use the hard core diameter \( \sigma \) as unit length; thus the \( z \)-axis is in \( z/\sigma \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The MC simulations provide direct means of obtaining the singlet density \( \rho_0^{(1)}(z) \) as well as the potential distribution \( \langle -\beta \Psi_w \rangle_{N-1,w} \) (or equivalently the insertion work \( \beta W_{\text{ins}} \)). These quantities are to be used in the analyses below. Since these quantities were obtained from the MC simulations, they are considered as "exact" data (to within the statistical errors of MC). We thus avoid the potential errors associated with any analytical theory (e.g. from the mean-spherical approximation).

For the Yu/HW system, we present below some examples on the insertion work. First, we evaluate the singlet density profile \( \rho_0^{(1)}(z) \) close to the wall (from \( z \sim 0.5\sigma \) to \( 12\sigma \)); then we use Widom's insertion method [1,9] for estimation at different \( z \) values of (i) the bulk chemical potential \( \beta \mu_0^* \), and (ii) the insertion probability \( \langle -\beta \Psi_w \rangle_{N-1,w} \). Finally, we calculate the two independently obtained PDT quantities:

\[
\begin{align*}
Q_1 &= -\ln[\rho_0^{(1)}(r_N)/\rho_0] - \beta W(r_N), \quad (a) \\
Q_2 &= -\beta \mu_0^* - \langle -\beta \Psi_w \rangle_{N-1,w}. \quad (b)
\end{align*}
\]

(3.1)

Quantity \( Q_1 \) is a "structural" quantity: namely it is essentially the density distribution \( \langle -\ln[\rho_0^{(1)}(z)/\rho_0] \rangle \); while quantity \( Q_2 \) is a "work" quantity \( (W_{\text{ins}} = -kT \ln \langle -\beta \Psi_w \rangle_{N-1,w}) \). According to Eq. (2.9), the two should be equal, i.e. \( Q_1 = Q_2 \).

Fig. 1 compares \( Q_1 \) vs. \( Q_2 \) obtained from the MC data at \( \rho_0^* = 0.215 \); and Fig. 2 shows the comparison at \( \rho_0^* = 0.577 \). We observe that quantity \( Q_1 \) (blue circles) is closely matched by the insertion work \( Q_2 \) (red squares) in both cases. A similar accord is also in evidence for the other systems studied but not shown here. We note furthermore that the red squares "invade" the region \( 0 < z < 0.5 \), which is inside the wall. This shows that \( \beta W_{\text{ins}} \) being the intrinsic insertion work (with the wall force turned off) can assume (similar to the cavity function \( y(r) \) in uniform fluids) finite non-zero values in the overlap region. Note that all data points were obtained directly from MC calculations. Since the PDT is an exact relation in statistical mechanics, the degree of agreement between \( Q_1 \) and \( Q_2 \) indicates the correctness of the numerical procedures employed in the present MC simulation. Throughout the paper, the unit length is the Lennard-Jones size parameter \( \sigma \).

4. Lennard-Jones fluid on a hard wall

We shall examine the adsorption of Lennard-Jones molecules on a hard wall. The LJ pair potential is given by

\[
u^{(2)}(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}
\]

(4.1)

where \( \sigma \) is the size parameter, and \( \varepsilon \) is the energy parameter. The temperature is \( T^* = kT/\varepsilon = 1.35 \) and the densities are \( \rho_0^* = 0.50, 0.65, \) and \( 0.82 \). (as noted, \( \sigma \) will be taken as the unit length.)

The wall potential \( w(z) \) (in the \( z \)-direction) is

\[
\begin{align*}
w(z) &= \infty \quad z \leq \sigma/2 \\
w(z) &= 0 \quad z > \sigma/2.
\end{align*}
\]

(4.2)

We first examine a high density case, \( \rho_0^* = 0.82 \). The insertion work \( \beta W_{\text{ins}}(z) \) is evaluated from the newly generated MC data according to Widom's insertion. This is plotted (as a dashed line) in Fig. 3. The bulk chemical potentials for the Lennard-Jones fluid are calculated from the Nicolas equation of state [10] (which gives an accurate representation of the simulated
Lennard-Jones properties). We can thus evaluate the pseudo-density $\rho_{\text{pseudo}}(z)$ via the Nicolas equation given the insertion work $\beta W_{\text{ins}}(z)$. The mapping is schematically depicted in Table 1. The values are displayed in Fig. 3 (circles) together with the MC singlet density $\rho_w^{(1)}(z)$ (black line). We observe that the LJ fluid “wets” the surface at this high density $\rho_b^* = 0.82$ with a contact value $\rho_w^{(1)}(\sigma) = 2.06$ well above the bulk $\rho_0 = 0.82$. The $\rho_w^{(1)}(z)$ shows rapid oscillations along the $z$-axis with large amplitudes, while the pseudo-density $\rho_{\text{pseudo}}(z)$ “hugs” the bulk value $\rho_b^* = 0.82$, undulating only slightly above and below 0.82. It oscillates in phase with the $\beta W_{\text{ins}}(z)$ but out of phase with respect to $\rho_w^{(1)}(z)$.

For the density $\rho_0 = 0.65$, we experience a similar behavior: namely opposite oscillations between $\rho_w^{(1)}(z)$ and $\rho_{\text{pseudo}}(z)$, although much subdued in this case (See Fig. 4). This state condition ($T^* = 1.35$, and $\rho_0 = 0.65$) is closer to the phase boundaries between liquid and vapor. The density profile becomes relatively flat, and the strong oscillations (at $\rho_0 = 0.82$) disappear. We have also calculated the pseudo-chemical potential $\beta \mu_{\text{pseudo}}$. It is the hypothetical chemical potential calculated (via a uniform fluid equation) with input density values $\rho_w^{(1)}(z)$ of the nonuniform fluid (see diagram in Table 1). Namely, if we imagine a fictitious uniform fluid associated with the density value $\rho_b = \rho_w^{(1)}(z)$ at given $z$, the Nicolas equation will yield a bulk chemical potential value at this density $\rho_b$. This hypothetical chemical potential will be, by analogy with the pseudo-density, called the pseudo-chemical potential $\beta \mu_{\text{pseudo}}(z)$. It is a fictitious quantity because no uniform fluid exists at such a density $\rho_b$ in the LJ/HW system. The pseudo-chemical potential $\beta \mu_{\text{pseudo}}(z)$ thus obtained is shown (as a blue line) in Fig. 5 and compared with the MC insertion work $\beta W_{\text{ins}}(z)$ (the red line). It is seen that the amplitudes of oscillations in $\beta \mu_{\text{pseudo}}$ are opposite to those of $\beta W_{\text{ins}}(z)$. These two energies are almost mirror images of each other; except that there is in $\beta \mu_{\text{pseudo}}$ a curious “bump” (a) local maximum, marked by an arrow in Fig. 5. To explain this peak, we need to consider the insertion of an LJ molecule near the location $z \sim 1.1$ (see Fig. 4, where a representative circle
Fig. 4. Lennard-Jones fluid/hard wall (LJ/HW) system at bulk density $\rho_0^* = 0.65$ and temperature $T^* = 1.35$. Case of “drying”. (MC simulation from Lee et al. [7]). Black line = singlet density $\rho^0_1(z)$; green circles = pseudo-density $\rho_{\text{pseudo}}(z)$. The pseudo-density is obtained via the method of Table 1 by using the Nicolas equation for Lennard-Jones fluid. The dotted circle is to show the insertion of an LJ sphere centered at $z \sim 1.1$. This picture is used to explain the “local maximum” in the $\beta \mu_{\text{pseudo}}(z)$ curve of Fig. 5. See explanations in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Lennard-Jones fluid/hard wall (LJ/HW) system at bulk density $\rho_0^* = 0.65$ and temperature $T^* = 1.35$. Comparison of the pseudo-chemical potential $\beta \mu_{\text{pseudo}}(z)$ (lower blue line) with the PDT-derived insertion work $\beta W_{\text{ins}}$ (upper red line). We mark by an arrow the “local maximum” in the pseudo-chemical potential $\beta \mu_{\text{pseudo}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Inserting a sphere of diameter $\sigma$

is drawn roughly at this location). The range of densities covered by the diameter of the circle is around 0.45–0.54. Namely, we are inserting a sphere at a density value centered around $\rho_0 = 0.5$ but spread over to 0.45–0.54 (see Fig. 6: the chemical potential of pure LJ fluid as a function of the bulk density $\rho_0$). We inquire what is the “work” required for this insertion. While in the nonuniform fluid the correct answer is given by the potential distribution value $\beta W_{\text{ins}}$ at $z \sim 1.1$, the interpretation in terms of the pseudo-chemical potential comes from the bulk fluid. We need to calculate the “bulk” chemical potentials $\beta \mu_0^\alpha$ in the range of $\rho_0 = 0.45–0.54$. Fig. 6 shows the pure LJ fluid excess chemical potentials $\beta \mu_0^\alpha$, which are obtained from the Nicolas equation, as a function of the bulk density $\rho_0$ at the isotherm $T^* = 1.35$. This “excess” chemical potential for the pure LJ fluid is a concave function of $\rho_0$, possessing two branches: a falling branch for $0 < \rho_0 < 0.50$, and a rising branch for $0.50 < \rho_0 < 0.9$. (Fig. 6); namely $\beta \mu_0^\alpha$ first decreases with increasing density until it reaches the minimum (at a value $\beta \mu_0^\alpha_{\text{min}} \sim -1.9$). In the density window (shown as a rectangle in Fig. 6) we see that the surrounding excess chemical potentials are for the most part higher than the minimum value at $\rho_0 \sim 0.5$. This observation suggests that if one inserts an LJ sphere at, say, $\rho_0 \sim 0.3$ (where $\beta \mu_0^\alpha \sim -1.44$) on the left side of $\rho_0 = 0.5$, it requires more work than inserting at $\rho_0 \sim 0.5$ (where $\beta \mu_0^\alpha \sim -1.9$); whereas insertion at higher densities, say, at $\rho_0 \sim 0.65$ (where $\beta \mu_0^\alpha \sim -1.53$) again requires more work than at $\rho_0 \sim 0.5$. This behavior is counter-intuitive at first, since one would expect that at lower densities, it is “easier” (less work is needed) to insert a particle. The fact is that we are dealing with the “excess” chemical potentials (values in excess of the ideal-gas value of the chemical potential). If we add back the ideal gas value ($\ln(\rho_0 A^3)$) to restore to the “total” chemical potential ($\mu_0^\text{TOTAL} = kT \ln(\rho_0 A^3) + \mu_0^\alpha$), we would not have a minimum at $\rho_0 \sim 0.5$ but a monotonously increasing function, i.e. the total chemical potential always increases with the density $\rho_0$.

In this insertion window, the excess chemical potential is higher at surrounding distances, thus we have a local maximum in the $\beta \mu_{\text{pseudo}}$ curve (Fig. 5). The above observations are applicable to the pseudo-chemical potentials, but not to the $\beta W_{\text{ins}}$. 
Fig. 6. Pure Lennard-Jones fluid at $T^* = 1.35$. The bulk excess chemical potential $\beta \mu _{\text{ex}}^0$ is plotted as a function of the bulk density $\rho_0$ (based on the Nicolas equation). The square marks the “insertion window” covering the density range corresponding to the “insertion” of an LJ sphere. See the text for explanations.

Fig. 7. Lennard-Jones fluid/hard wall (LJ/HW) system at bulk density $\rho_0^* = 0.50$ and temperature $T^* = 1.35$. Case of “drying”. Black line: singlet density $\rho_{w}^{(1)}(z)$; green circles: pseudo-density $\rho_{\text{pseudo}}(z)$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The next state considered is at $\rho_0 = 0.50$. At this condition the LJ density profile becomes depleted near the wall. The $\rho_{\text{pseudo}}$ (green circles) are plotted in Fig. 7. Compared to the nonuniform density $\rho_{w}^{(1)}(z)$ (black line), $\rho_{\text{pseudo}}(z)$ runs slightly lower but exhibits the same trend (no indication of opposite oscillations). This is in marked contrast to the earlier cases at $\rho_0^* = 0.82$ and $0.65$. The pseudo-chemical potential (lower blue line) is given in Fig. 8 along with the MC insertion work $\beta W_{\text{ins}}$ (upper red line). These two quantities closely follow each other, and we have reasonably good agreement of the pseudo quantities with the nonuniform quantities. Note that the state point ($\rho_0^* = 0.50$ and $T^* = 1.35$) is very close to the bulk bubble point line. There is a severe depletion of the liquid at the wall—the contact value is $\rho_{w}^{(1)}(\sigma/2) = 0.2$ as compared to the bulk value of 0.5. The surface layers are vapor-like in their depressed density values, even though there is no thermodynamically stable vapor phase. The depleted region extends to distances over approximately 5 molecular diameters (from $z = 0.5$ to $z \approx 5$), before the profile reaches back to the bulk value 0.5.

5. Attractive hard-core Yukawa fluid on a hard wall

In this Section, we study the adsorption of the attractive Yukawa fluid (with a hard spherical core) on a hard wall. The pair potential $u^{(2)}(r)$ for this fluid is

$$
\begin{cases}
  u^{(2)}(r^*) = \infty & r^* \leq 1 \\
  u^{(2)}(r^*) = -\varepsilon \exp[-\lambda(r^*-1)] & r^* > 1,
\end{cases}
$$

where $r^* = r/\sigma$, $r$ is the intermolecular distance, $\sigma$ is now the hard sphere diameter, $\varepsilon$ is the energy parameter, and $\lambda$ is the range parameter. The wall potential is for a smooth hard planar surface as given by Eq. (4.2). We study the isotherm: $kT/\varepsilon = T^* = 0.76$ with four bulk density values $\rho_0 = \rho_0\sigma^3 = 0.215, 0.358, 0.473$, and 0.557 (all with range parameter $\lambda = 3$). We carried out new Monte Carlo simulations for these densities. The singlet densities $\rho_{w}^{(1)}(z)$ (lines) are presented in Fig. 9 for the four cases. We observe that near the wall ($z \sim 0.5$), depletion occurs again: the density profiles are depressed below the corresponding bulk values.
Fig. 8. Lennard-Jones fluid/Hard wall (LJ/HW) system at bulk density \( \rho_0^* = 0.50 \) and temperature \( T^* = 1.35 \). Comparison of the pseudo-chemical potential \( \beta \mu_{\text{pseudo}}(z) \) (lower blue line) with the PDT-derived insertion work \( \beta W_{\text{ins}} \) (upper black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**

“Mapping” of properties between the non-uniform system and uniform systems.

<table>
<thead>
<tr>
<th>Nonuniform Systems:</th>
<th>Singlet Densities: ( \rho^{(1)}_{\text{ex}}(z) )</th>
<th>PDT-Insertion Work: ( \beta W_{\text{ins}} = -C_w^{(1)}(z) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through Nicolas Equations*</td>
<td>( \rho_{\text{pseudo}}(z) )</td>
<td>( \rho_{\text{pseudo}}(z) )</td>
</tr>
<tr>
<td>Uniform Systems:</td>
<td>Pseudo-Densities: ( \rho_{\text{pseudo}}(z) )</td>
<td>Pseudo-Chemical Potentials: ( \beta \mu_{\text{pseudo}}(z) )</td>
</tr>
</tbody>
</table>

We calculate the pseudo-densities (as symbols in Fig. 9) based on the MC values of \( \beta W_{\text{ins}}(z) \) at each density. The uniform-fluid chemical potentials have been obtained from MC simulation. For \( \rho_0 = 0.215 \), \( \rho_{\text{pseudo}}(z) \) (pluses) is shown in Fig. 9. Near the wall, the values of \( \rho_{\text{pseudo}}(z) \) are lower than the singlet density \( \rho^{(1)}_{\text{ex}}(z) \). This implies that if we base our free energy calculations on an equation of state (EOS) of the uniform fluid, the input densities to the EOS should be \( \rho_{\text{pseudo}}(z) \) and are smaller than the nonuniform \( \rho^{(1)}_{\text{ex}}(z) \). Fig. 10 shows the actual insertion work \( \beta W_{\text{ins}}(z) \) (lines). When the “real” density \( \rho^{(1)}_{\text{ex}}(z) \) was used in the EOS, it would give work values being overly negative (see green pluses of Fig. 10). To understand this, we need to make comments based on Fig. 11, which depicts the bulk excess chemical potential \( \beta \mu^{(0)}_{\text{ex}}(\rho_0) \) of pure Yukawa fluid as a function of the bulk density \( \rho_0 \). \( \beta \mu^{(0)}_{\text{ex}}(\rho_0) \) is a decreasing function of \( \rho_0 \) within the range of densities (0.215–0.557) studied. The higher the density \( \rho_0 \) the lower (more negative) the chemical potential \( \beta \mu^{(0)}_{\text{ex}}(\rho_0) \). Thus, to achieve an insertion work \( \beta W_{\text{ins}}(z) \) that is higher, the effective density must be lower.

The higher densities \( \rho^*_0 = 0.358, 0.473, \) and 0.557 can be similarly analyzed (Figs. 9 and 10). The insertion work \( \beta W_{\text{ins}}(z) \) is higher than the pseudo chemical potential \( \beta \mu_{\text{pseudo}}(z) \), and the pseudo density \( \rho_{\text{pseudo}}(z) \) is lower than the singlet density \( \rho^{(1)}_{\text{ex}}(z) \). At large \( z \) all quantities approach the uniform fluid values, since \( \lim_{z \to \infty} \rho_{\text{pseudo}}(z) = \rho^{(1)}_{\text{ex}}(z) = \rho_0 \), and \( \lim_{z \to \infty} \beta \mu_{\text{pseudo}}(z) = \beta W_{\text{ins}}(z) = \beta \mu^{(0)}_{\text{ex}}(\rho_0) \) because the distribution of molecules is no longer influenced by the presence of the wall.

Fig. 11 summarizes the insertion works from (i) the bulk fluid (where \( w(z) \approx 0 \)) and (ii) the wall region (with inhomogeneous density gradients). The solid black line indicates the bulk excess chemical potential \( \beta \mu^{(0)}_{\text{ex}}(\rho_0) \) as a (falling) function of bulk density \( \rho_0 \). Four branches in the graph (green, purple, blue, and red in color) indicate the nonuniform insertion works \( \beta W_{\text{ins}}(z) \) at four different bulk densities \( (\rho^*_0 = 0.215, 0.368, 0.473, \) and 0.577, respectively). They go from the near-wall to the bulk fluid region (from the left to the right in Fig. 11) and terminate at the bulk \( \beta \mu^{(0)}_{\text{ex}}(\rho_0) \) values (shown as four big red dots on the black line). We observe that the highest density branch \( (\rho_0 = 0.577, \) red line) shows the largest deviations from the bulk chemical potential (black line). The discrepancies tend to fade out successively from higher densities \( (\rho^*_0 = 0.473) \) to lower densities \( (\rho^*_0 = 0.215) \).

We may draw an interesting conclusion from the results obtained in the last two Sections. We notice that for the attractive pair interactions (LJ or attractive Yukawa), the uniform-fluid “excess” chemical potential \( \beta \mu^{(0)}_{\text{ex}}(\rho) \) is a concave function of the
bulk density $\rho_0$ (Figs. 6 and 11), consisting of a falling branch (at low densities), followed by a rising branch (at high densities), with a minimum occurring at $\rho_0 \sim 0.5$ (for the LJ fluid). This “concavity” can be used to explain the observed different behavior of $\rho_{\text{pseudo}}$ in the cases of enhanced and depleted fluid density near the wall. At high bulk densities (on the rising branch), normally we observe enhanced wall densities and we also see that both the insertion work $\beta W_{\text{ins}}(z)$ and the pseudo-density $\rho_{\text{pseudo}}(z)$ oscillate out of phase with respect to the singlet density $\rho^{(1)}(z)$. On the other hand, at low bulk densities (on the falling branch) where depletion of the fluid near the wall may (or not) occur, the oscillations of the pseudo-quantities are in phase with $\rho^{(1)}(z)$. Apparently, the existence of two branches of the bulk chemical potential impacts the different oscillatory behavior.

6. The singlet direct correlation and the insertion work

In this section we show the connection of the potential distribution theorem to the Euler–Lagrange equation in DFT [5]. The singlet direct correlation function (1-DCF) $C^{(1)}_{\text{w}}(r_N)$ can be identified [11] as the (negative) work required for insertion of a test particle “N” in the absence of $w(r_N)$—i.e. wall force on “N” is turned off, $w(r_N) = 0$ (i.e., for the type-2 test particle discussed earlier). Thus $C^{(1)}_{\text{w}}(r_N) = -\beta W_{\text{ins}}(r_N)$ as defined by Eq. (2.9):

$$C^{(1)}_{\text{w}}(z) = -\beta W_{\text{ins}}(z) = \ln \langle \exp(-\beta \Psi_{-w}(z)) \rangle_{N-1, w} . \tag{6.1}$$

Therefore

$$C^{(1)}_{\text{w}}(z) = -\beta \mu_{\text{w}} + \beta w(z) + \ln[\rho^{(1)}_{\text{w}}(z)A^3] = -\beta \mu_{\text{w}} + \beta w(z) + \ln[\rho^{(1)}_{\text{w}}(z)/\rho_0] \tag{6.2}$$

where $\beta \mu_{\text{w}} = \ln(\rho_0 A^3) + \beta \mu_{\text{w}}$. Comparison with the well-known Euler–Lagrange equation (6.2)

$$\rho^{(1)}_{\text{w}}(r) = \rho_0 \exp[-\beta w(r) + C^{(1)}_{\text{w}}(r) - C^{(1)}_{\text{w}}(0)] \tag{6.3}$$
or its rearrangement

\[ C_w^{(1)}(r) = C_0^{(1)}(r) + \beta w(r) + \ln[\rho^{(1)}(r)/\rho_0] \]  

(noting \( C_0^{(1)} = -\beta \mu_0^{(1)} \)) shows that these two formulas (the PDT for type-2 test particles (6.2) and the Euler–Lagrange equation (6.4)) express the same relation. Recalling that we have established that \( \beta W_{\text{ins}} \) is the work of insertion of the test particle in the PDT, we can now use Monte Carlo simulation with test particles to directly evaluate the quantity \( C_w \) for use in the Euler–Lagrange equation.

7. Conclusions

We present in this work the potential distribution theorems for two types of test particles (i) those under the influence of the wall potential \( w(z) \), and (ii) those free from the wall influence. The PDT is used in Monte Carlo simulations of simple adsorptive systems to obtain the works of insertion \( \beta W_{\text{ins}} \). These include the Lennard-Jones and attractive Yukawa fluids on a hard wall.

To enable mapping of the free energy of the uniform system to that of the nonuniform system, we construct a pseudo-density \( \rho_{\text{pseudo}} \) and a complimentary quantity, i.e. the pseudo-chemical potential \( \beta \mu_{\text{pseudo}} \). For conditions where the depletion of contact-layer liquids takes place, the pseudo-densities and pseudo-chemical potentials are found to be commensurate with the singlet density and the nonuniform insertion work, respectively. On the other hand, for conditions where the fluid density is enhanced near the wall, it is shown that \( \rho_{\text{pseudo}} \) and \( \beta \mu_{\text{pseudo}} \) are poor estimates of the nonuniform density \( \rho^{(1)}(z) \) and of the insertion work \( \beta W_{\text{ins}} \), respectively.

We show that the intrinsic insertion work \( \beta W_{\text{ins}} \) is identified with the singlet direct correlation \( -C_w^{(1)} \), and the potential distribution theorem is equivalent to the Euler–Lagrange equation of the density functional theory.

The present results were based on Monte Carlo simulations, thus avoiding inaccuracies that might have derived from approximate theories. The only theoretical formula used was the Nicolas equation of state for Lennard-Jones fluid.

The remaining task is to construct the pseudo-density \( \rho_{\text{pseudo}} \) by analytical means, instead of through MC simulations. For hard spheres, one normally employs the fundamental measure theories due to Rosenfeld [4]. For attractive interaction potentials, some initial explorations [7,12] were made and this research may help in paving the way for its eventual realization.

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References