Congruent Chemical Potentials and Insertion Works in Establishing Nonuniform-Fluid Structures via Uniform-Fluid Properties

Lloyd L. Lee

Department of Chemical & Materials Engineering, California State Polytechnic University, Pomona, California, United States

Supporting Information

ABSTRACT: We propose an effective density \( \rho_{\text{pseudo}} \) that engenders direct mapping of the free energy \( F_U \) of uniform fluids to the free energy \( F_N \) of nonuniform fluids by requiring \( F_N = F_U \) (at \( \rho_{\text{pseudo}} \)). The equality is called the congruence condition. It is made possible by considering the statistical mechanical theory: the potential distribution theorem (PDT). The PDT connects three quantities: the work \( W_{\text{ins}}(z) \) needed for inserting a test particle into the fluid, the chemical potential \( \mu_0 \) of the bulk fluid, and the nonuniform singlet density \( \rho_w^{(1)}(z) \). We use Monte Carlo (MC) data to obtain the insertion work \( W_{\text{ins}}(z) \) (via the Euler–Lagrange equation) from the probability densities \( \rho_w^{(1)}(z) \). The concept of the congruent effective density \( \rho_{\text{pseudo}} \) is applicable to general interaction potentials, not restricted to the hard sphere type. We examine thus two simple fluids adsorbed on a hard wall: (i) the hard spheres and (ii) the Lennard-Jones fluid. We discern the differences in behavior of the effective density vis-à-vis whether there is enhancement or depletion of the fluid density near the wall (namely, if there is accumulation of molecules at the wall, or if there is deficit of molecules at the wall). \( \rho_{\text{pseudo}}(z) \) is found to exhibit for enhanced adsorption out-of-phase oscillations compared to \( \rho_w^{(1)}(z) \). For depleted adsorption, we do not observe oscillations, and the trends of \( \rho_{\text{pseudo}}(z) \) are in line with those of \( \rho_w^{(1)}(z) \). Explanation is sought in terms of the concavity of the chemical-potential function.

1. INTRODUCTION

Nonuniform fluids are encountered in many engineering processes:1–4 adsorption of gas/liquid at a solid substrate (desiccation, molecular sieves), solid–fluid phase contact operations, sedimentation, crystallization, colloid stabilization, membrane separation, and many other chemical and biological processes. The situations of fluids subjected to a density gradient or pressure/temperature gradients involve a myriad phenomena and a variety of structures. It is a challenging problem to handle effectively. In engineering design and calculations, it is desirable to find a way of employing the simpler uniform fluids to mirror the properties of the nonuniform fluids. This gives a convenient pathway, if it is at all possible.

This thread of thoughts has not been lost and has been pursued in the past 30 years or so in the density functional theories5–9 (DFT) for nonuniform fluids. They are called the weighted density approach. It culminated in 1989 in the fundamental measure theory (FMT) of Rosenfeld.10 For the hard sphere fluid, Rosenfeld constructed a set of weighting functions \( \omega \) that produced the weighted densities \( n_w \) to be used in mapping effectively the free energies \( F_U \) of the uniform hard spheres to the free energies \( F_N \) of the nonuniform hard spheres that are found near a hard wall. The original theory was developed for hard sphere fluid only. It achieved high accuracy in structural properties.11 We shall have occasion to discuss the FMT later.

In this article, we shall use direct matching. We, at the outset, set \( F_N = F_U \) and ask under what conditions this equality can be fulfilled? One advantage of this picture is that this approach is not necessarily limited to the hard-sphere fluid, being applicable to other types of fluids with soft and attractive forces. Next question is: is this a possible approach? In this work, we shall examine the feasibilities for the hard spheres and the attractive Lennard-Jones fluid as well. There are at least two tasks at hand: one is to characterize the quantities involved; the other is to construct a method for obtaining these quantities. We concentrate on the first task in this article.

The singlet probability density \( \rho_w^{(1)} \) in a nonuniform fluid is a function of position \( z \) from the confining wall as given by the Euler–Lagrange equation (EL)

\[
\ln \left( \frac{\rho_w^{(1)}(z)}{\rho_0} \right) = -\beta w(z) + C_w^{(1)}(z) + \beta \mu_0
\]

(1.1)

where \( \rho_0 \) is the bulk number density, \( w(z) \) is the one-body wall potential (as a function of the vertical distance \( z \)), \( \mu_0 \) is the bulk fluid chemical potential. \( C_w^{(1)}(z) \) is the singlet direct correlation function which can be shown (see the Supporting Information).

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to be equal to the (negative) work of insertion: \(C_1^0(z) = -\beta W_{\text{ins}}(z) (t = 1/(kT), k = \text{Boltzmann constant}, T = \text{absolute temperature}).\) Thus the insertion work \(W_{\text{ins}}(z)\) (work required to introduce a test particle at a position \(z\) in the nonuniform fluid) is also a function of \(z\). If \(W_N = W_z\), then, according to the potential distribution theorem,\(^{12}\) the chemical potential \(\mu_0\) of the uniform fluid should be equal to this insertion work: \(\mu_0 = W_{\text{ins}}(z)\). To make this possible, we shall find an effective density \(\rho_{\text{pseudo}}(z)\) for use with the uniform fluid that also changes with position \(z\) such that \(\rho_{\text{pseudo}}(z) = W_{\text{ins}}(z)\) (see Table 1).

This equality is called the congruence condition between the uniform and nonuniform systems. The effective density \(\rho_{\text{pseudo}}\) is purely hypothetical, and the uniform fluid it supports is also hypothetical, meaning that the pair \((\rho_{\text{pseudo}}\) and \(\mu_0\)) is not physically present to the experiment. But they are useful in transferring the properties of the uniform fluid to those of the nonuniform system. If we have means of determining these \(\rho_{\text{pseudo}}\) we can, through the Euler—Lagrange equation,\(^3\) obtain all properties of the nonuniform system.

First we set out to characterize this pseudodensity. We can use the simulation data (e.g., Monte Carlo simulations, MC) on hard spheres\(^{14}\) or on Lennard-Jones fluid to evaluate the pseudodensity \(\rho_{\text{pseudo}}\). The MD data give the singlet density \(\rho_{\text{singlet}}\). From the Euler—Lagrange eq 1.1, we can solve for the singlet density \(\rho_{\text{pseudo}}(z)\) that will give a \(\beta \mu_0\) so that \(\beta \mu_0(\rho_{\text{pseudo}}(z)) = W_{\text{ins}}(z)\). (This has to be done for each position \(z\)). In general, \(\rho_{\text{pseudo}}(z) \neq \rho_{\text{singlet}}(z)\). The behavior we shall examine is how this effective density behaves for different fluid systems and at different conditions of adsorption. We shall focus our attention first on simple fluid adsorption: such as hard spheres adsorbed at a structure-less planar hard wall (HS/HW). Then we shall look at the fluid with attractive forces, the Lennard-Jones fluid at a hard wall (LJ/HW). A note on notation: \(\mu_0\) refers to the configurational chemical potential, that is, the excess chemical potential \(\mu_{\text{ex}}\) beyond the ideal gas contribution. For simplicity, we also shall write \(\mu_0 = \mu_{\text{ex}}\).

By varying the temperature or the bulk density, adsorption of the fluid on a planar wall can change from wall-enhanced density profile (contact density on the wall being higher than the bulk density, \(\rho_{\text{wall}}^1(z = \text{contact}) > \rho_0\)) to wall-depleted density profile (contact density on the wall being lower than the bulk density, \(\rho_{\text{wall}}^0(z = \text{contact}) < \rho_0\)). We call the former the adhesive adsorption, and the latter is the depletive adsorption. The depletion occurs on weak or repulsive walls especially when the bulk phases are near the vapor—liquid coexistence or the critical point. We shall show from the MC data that for the cases of depletion at the wall, the pseudquantities exhibit distinct features that differentiate them from those cases of adsorptive adsorption at the wall. The origin of this behavior is to be sought in the “concavity” of the chemical potential curves. All quantities we need shall be obtained from Monte Carlo (MC) simulation, in order to avoid introduction of uncertainties from theoretical approximations. For example, the insertion work \(W_{\text{ins}}\) can be obtained from Widom’s particle-insertion\(^{15}\) technique and the singlet density \(\rho_{\text{singlet}}^1\) can be obtained from the Metropolis Monte Carlo methods.\(^{16}\)

In a parallel development, we shall also define a pseudochemical potential \(\mu_{\text{pseudo}}\). It is the bulk-fluid chemical potential value \(\mu_0\) produced by the equation of state when we substitute the nonuniform density \(\rho_{\text{pseudo}}^0(z)\) as its argument, thus \(\mu_{\text{pseudo}}(z) = \mu_0(\rho_{\text{pseudo}}^0(z))\). Its values are not equal to the nonuniform free energy \(\mu_{\text{pseudo}}(z) \neq W_{\text{ins}}(z)\), since the governing equations for nonuniform fluids are not the same as those for the uniform fluids. The degree of difference between these two energies is an indication of the deviation of nonuniformity from uniform behavior. (In the limit of vanishing external forces, the fluid becomes uniform and the two energies will become the same.) Details will be given in section 3.

The present work is organized as follows. We formulate two potential distribution theorems: one for the Type 1 test particle and the other for the Type 2 test particle. The Type 1 test particle is the usual kind in literature that interacts with the wall potential, while the Type 2 test particle does not interact with the wall. The Type 2 test particle is in fact the object of study in this paper. Owing to their lengths, the derivations of the potential distribution theorems are given in the Supporting Information. The reader may want to glance through the Supporting Information to get familiarized with the notation. The second PDT is the focus of the present work. In section 2, we examine the pseudodensities in the hard-sphere/hard wall system at moderate to high bulk fluid densities. We also compare the pseudodensities with the weighted densities derived from the FMT theory. Section 3 is devoted to the study of a soft repulsion + attraction potential: the Lennard-Jones (LJ) molecules adsorbed on a hard wall. We formally introduce the pseudochemical potential \(\mu_{\text{pseudo}}\) there. In addition, we design a \(W - \mu - \rho\) plot for further characterization of the free energies from the uniform and from the nonuniform fluid. Section 4 draws the conclusions.

2. HARD SPHERE FLUID ADSORBED ON A HARD WALL (HS/HW)

We first examine the simple case of hard spheres adsorbed on a structureless planar hard wall (HS/HW). The hard wall interaction potential is given by (the molecular centers can approach the hard wall at the closest \(z = \frac{d}{2}\), half diameter):

\[
\phi(z) = \infty, \quad z < \frac{d}{2}
\]

\[
= 0, \quad z \geq \frac{d}{2}
\]

(2.1)

For this case, there are Monte Carlo data on the density profiles as given by Groot, Faber, and Eerden.\(^{14}\) In one study, they have simulated five cases with densities ranging from \(\rho d^3 = 0.5745, 0.715, 0.758, 0.813,\) to 0.9135. We shall adopt their Monte Carlo data as inputs. First we shall obtain the work of insertion from the PDT-2 (see eq A.10 in the Supporting Information).

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Table 1. Construction of the Pseudodensity, \(\rho_{\text{pseudo}}\) to Achieve the Congruence Condition

<table>
<thead>
<tr>
<th>(\rho_{\text{pseudo}})</th>
<th>(\rho_{\text{singlet}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_{\text{ins}}) (the free energy as insertion work, (W_{\text{ins}}))</td>
<td>(F_{\text{ch}}) (the free energy as chemical potential, (\mu_0))</td>
</tr>
<tr>
<td>(\rho_{\text{pseudo}}(z) = \rho_{\text{singlet}}(z))</td>
<td>(\rho_{\text{singlet}}(z))</td>
</tr>
<tr>
<td>(W_{\text{ins}}(z)) obtained from PDT/ Widom’s Test Particle Insertion</td>
<td>(\rho_{\text{singlet}}(z))</td>
</tr>
<tr>
<td>(\mu_0) obtained from equation of state, e.g., the Carnahan-Starling Equation</td>
<td>(\rho_{\text{singlet}}(z))</td>
</tr>
</tbody>
</table>

\(\rho_{\text{pseudo}}(z)\) is the configurations part, i.e., \(\rho_{\text{total}} = \rho_{\text{ideal gas}} + \rho_{\text{pseudo}}\).
We can calculate $W_{\text{ins}}$ from the MC data on the singlet density $\rho^{(1)}_{\text{MC}}$ that is,
\[
\beta W_{\text{ins}}(z) = \beta \mu_0^\text{ex} - \beta w(z) - \ln[\rho^{(1)}_{\text{MC}}(z)/\rho_0]
\]  
We consider the $W_{\text{ins}}$ calculated this way as MC-based data. For the bulk fluid, we have the accurate Carnahan–Starling (CS) equation
\[
\frac{P_{\text{CS}}}{\rho_0 kT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} = Z_{\text{CS}}
\]
The chemical potential of hard spheres is then given by
\[
\beta \mu_0^{\text{HS}} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + (Z_{\text{CS}} - 1)
\]  
where $\eta = (\pi/6)\rho_0^3$ is the packing fraction. The pseudodensity $\rho_{\text{pseudo}}$ is obtained by setting $\beta \mu_0^{\text{HS}} = \beta W_{\text{ins}}$ (forcing the free energies of the uniform and of the nonuniform fluid to be equal), and solve for the density (i.e., $\rho_{\text{pseudo}}$) of a hypothetical homogeneous hard sphere fluid that gives rise to this equality: $\beta W_{\text{ins}}(z) = \beta \mu_0^{\text{HS}}(\rho_{\text{pseudo}}(z))$. This is done for each $z$-position in the nonuniform fluid. Thus $\rho_{\text{pseudo}}$ is also a function of $z$: $\rho_{\text{pseudo}}(z)$. We note, while the nonuniform system is presently at hand (a given physical system), the uniform counterpart is purely hypothetical. A fictitious uniform hard-sphere fluid is made up so as to give the equal free energy. In the unlikely situation that the pseudodensity $\rho_{\text{pseudo}}(z)$ is the same as the nonuniform singlet density $\rho^{(1)}_{\text{ff}}(z)$ (these hypothetical uniform fluids have identical density values as the $\rho^{(1)}_{\text{ff}}$ of the nonuniform fluid), then we would have an extremely simple mapping of the free energies of the uniform/nonuniform pair. This cannot be the case, because various density gradients in the nonuniform fluid will give different insertion works while the uniform systems have no density gradients.

We first apply this construction to the HS/HW system at $\rho^{*} = 0.5745$. The pseudodensity thus obtained is given in Figure 1a. We observe that the pseudodensity curve $\rho_{\text{pseudo}}(z)$ is much subdued in magnitude as compared to the singlet density $\rho^{(1)}_{\text{ff}}$. While $\rho^{(1)}_{\text{ff}}(z)$ shows vigorous oscillations, the $\rho_{\text{pseudo}}(z)$ is only slightly oscillatory. In addition, the oscillations of the latter are out-of-phase with respect to the former. In Figure 1b, we plot the MC-based insertion work $\beta W_{\text{ins}}$ as a function of $z$. The $\beta W_{\text{ins}}(z)$ also has oscillations, damping down eventually to the bulk chemical potential value at large $z$. The periods of $\beta W_{\text{ins}}(z)$ are in sync with the pseudodensity $\rho_{\text{pseudo}}(z)$ as shown in Figure 1a, while out-of-phase with the singlet density $\rho^{(1)}_{\text{ff}}(z)$. This phase shift behavior is general for the hard sphere systems. As will be shown later for soft spheres, there is in-phase as well as out-of-phase behavior.

As anticipated, we next compare the pseudodensities with the weighted densities $n_{\alpha}$ of the FMT. According to FMT, there are six weighted densities $n_{\alpha}$ (with index $\alpha = 0,1,2,3,V1$, and $V2$) arising from the six geometric weighting functions, $\omega_{\alpha}$.

The weighting functions $\omega_{\alpha}$ are generated from a basis set consisting of only three functions: (i) the Dirac delta function $\delta$, (ii) the Heaviside function $\Theta$, and (iii) the vector weight $\omega_{\alpha}V$. We choose two weighted densities (a) $n_0$ (obtained from Dirac delta), and (b) $n_1/V$ (obtained from the Heaviside function, and normalized by the spherical volume $V$). In Figure 2, these $n_{\alpha}$ are compared with the pseudodensity (for the case of $\rho^{*} = 0.5175$). We observe that (i) the values of $n_0$ and $n_1/V$ are commensurate with the pseudodensity, as they are of similar magnitude and all show smaller amplitudes than the singlet density; (ii) there are noticeable differences between the weighted densities and the pseudodensity. This is not surprising, since they are obtained from different principles: the former from the geometric measures, and the latter from the congruence condition.

At a higher density, $\rho^{*} = 0.715$, the pseudodensities were obtained in a similar manner and shown in Figure 3a. The
MC simulations are available from Balabanic et al.\textsuperscript{17} for adsorption of Lennard-Jones molecules bordering on a planar hard wall. The temperature $T^* = kT/\varepsilon = 1.35$ (note that the critical temperature $T^*_c$ of pure LJ fluid is 1.312), and densities are at $\rho_0^* = \rho_0^S = 0.5$, 0.65, and 0.82 (the critical density $\rho^*_c$ is 0.316); $\varepsilon$ and $\sigma$ are energy and size parameters, respectively, of the Lennard-Jones potential:

$$u_{\text{LJ}}(r) = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6$$

where $r$ is the intermolecular distance. Adsorption can be broadly classified into two types (see Introduction): (i) adhesive adsorption and (ii) depletive adsorption. In the adhesion type, the singlet density $\rho_w^{(1)}(z)$ near the wall ($z = 0$) is higher than the bulk density $\rho_0^*$ meaning that there is accumulation of molecules near the wall; while in the depletion type, the singlet density $\rho_w^{(1)}(z)$ at the wall is lower than the bulk value $\rho_0^*$ meaning that the molecules “shy away” from the wall and prefer to remain in the bulk. By these criteria, the LJ/HW cases with bulk densities at 0.50 and 0.65 are of the depletion type (i.e., there is deficit of molecules at the wall as compared to the bulk fluid), and the case of 0.82 is of the adhesion type (i.e., there is an excess of molecules at the wall as compared to the bulk). For the temperature $T^* = 1.35$, the pseudodensity obtained is shown together with the singlet density $\rho_w^{(1)}$ in Figure 5. First we notice that the singlet density $\rho_w^{(1)}(z)$ oscillates with large amplitudes. Its contact value is $\rho_w^{(1)}(z = \sigma/2\sigma) = 0.82$.

![Figure 3](image)

**Figure 3.** Hard spheres on the hard wall HS/HW at $\rho^* = 0.715$. (a) The singlet density $\rho_w^{(1)}$ (from MC\textsuperscript{9}, solid line) and the effective (pseudo) density $\rho_{\text{pseudo}}(z)$ (green circles). The values of the pseudodensity are smaller than $\rho_w^{(1)}$ and show much subdued oscillations. (b) The insertion work $\beta W_{\text{ins}}(z) = -C_w^{(1)}(z)$ (orange triangles) obtained from the Euler–Lagrange eq 1.1 based on MC data (Groot et al.\textsuperscript{8}).

Figure 4. Hard spheres on the hard wall HS/HW at $\rho^* = 0.715$. Comparison of the effective (pseudo) density $\rho_{\text{pseudo}}$ (green circles) with the weighted densities $n_0$ (red line) and $n_{1/2}/V$ (purple line) from the FMT theory of Rosenfeld.\textsuperscript{8}

![Figure 4](image)

![Figure 5](image)

**Figure 5.** Lennard-Jones fluid on the hard wall (LJ/HW) at $\rho_0^* = 0.82$ ($T^* = 1.35$). The effective (pseudo) density $\rho_{\text{pseudo}}$ (green circles, obtained according to the congruence condition shown in Table 1) and the insertion work $\beta W_{\text{ins}}$ (red dashes, from Euler–Lagrange eq 1.1 based on the MC data). The singlet density profile $\rho_w^{(1)}(z)$ (black full line) is the Monte Carlo data of Groot et al.\textsuperscript{9} The pseudodensity $\rho_{\text{pseudo}}(z)$ oscillates weakly around the bulk value $\rho_0^* = 0.82$, but out-of-phase (+180°) as compared to $\rho_w^{(1)}(z)$. The insertion work $\beta W_{\text{ins}}$ also oscillates and is in phase with $\rho_{\text{pseudo}}(z)$, while out-of-phase with $\rho_w^{(1)}(z)$. Insertion work is shown in Figure 3b. The pseudodensity as before has smaller amplitudes. The singlet density $\rho_w^{(1)}$ and pseudodensity $\rho_{\text{pseudo}}$ have opposite periods of oscillations. The weighted densities $n_0$ and $n_{1/2}/V$ from FMT are compared in Figure 4. Again we see differences between $n_0$ and $n_{1/2}/V$ and $\rho_{\text{pseudo}}$. We have also examined cases at higher densities (e.g., at $\rho_0^* = 0.813$). The same behavior is in evidence. Next we examine the cases of adsorption of the soft spheres.

3. LENNARD-JONES FLUID ADSORBED ON A HARD WALL (LJ/HW)

The singlet density $\rho_w^{(1)}$ obtained from the Euler

$$\partial_n (\rho^* - \rho_w^{(1)}) = 0$$

and the insertion work is shown in Figure 3b. The pseudodensity as before has smaller amplitudes. The singlet density $\rho_w^{(1)}$ and pseudodensity $\rho_{\text{pseudo}}$ have opposite periods of oscillations. The weighted densities $n_0$ and $n_{1/2}/V$ from FMT are compared in Figure 4. Again we see differences between $n_0$ and $n_{1/2}/V$ and $\rho_{\text{pseudo}}$. We have also examined cases at higher densities (e.g., at $\rho_0^* = 0.813$). The same behavior is in evidence. Next we examine the cases of adsorption of the soft spheres.

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2) \approx 2.06, much higher than the bulk value of 0.82. By our classification, this adsorption belongs to the adhesion type \((\rho_w^{(1)}(z = \sigma/2) = 2.06 > \rho_0 = 0.82)\). On the other hand, the pseudodensity \(\rho_{\text{pseudo}}(z)\) has much smaller variations. The periods of the latter are about 180° out-of-phase from those of \(\rho_w^{(1)}(z)\). The reason of such a décalage can be explained thusly: smaller values in \(\rho_w^{(1)}(z)\) mean higher values in the insertion work \(W_{\text{ex}}\) (examine the Euler—Lagrange eq 1.1); and larger values of \(W_{\text{ex}}\) mean larger values of the pseudodensities, provided that \(\rho_{\text{pseudo}}\) increases with \(\beta \mu_0\). This trend, that increasing density causes increased excess chemical potential, will be called the prevailing curve. The opposite trend, that increasing density entails “decreased” excess chemical potential, will be called the countervailing curve. We have more to comment on this matter later.

The next density we examine is \(\rho_0^* = 0.65 (T^* = 1.35)\). The contact value \(\rho_w^{(1)}(z = \sigma/2) \approx 0.60\) (from MC). Thus there is slight depletion of molecules in the interfacial region (since \(0.60 < 0.65\)). The pseudodensities are shown in Figure 6a. The insertion work is shown in Figure 6b (together with a quantity \(\mu_{\text{pseudo}}\) to be explained below). The pseudodensity \(\rho_{\text{pseudo}}(z)\) shows opposite period with respect to the singlet density \(\rho_w^{(1)}(z)\) once again. At this juncture, we shall introduce a new pseudoquantity, the pseudochemical potential \(\beta \mu_{\text{pseudo}}\). It is the (excess) chemical potential of a hypothetical homogeneous fluid evaluated at the experimental singlet density, that is, \(\beta \mu_{\text{pseudo}}(z) = \beta \mu_0(\rho_w^{(1)}(z))\). Table 2 shows this particular construction. For Lennard-Jones fluids, the uniform \(\beta \mu_0\) can be obtained from the Nicolas equation of state\(^\text{12} \) which was based on the simulation data on pure Lennard-Jones fluids. Figure 7 gives the chemical potentials of the uniform LJ fluid as a function of density \(\rho_0^*\) (at \(T^* = 1.35\)). Two chemical potentials are given: (i) the total chemical potential \(\beta \mu_{\text{total}}\) and (ii) the excess chemical potential \(\beta \mu_{\text{ex}}\) (the total chemical potential \(\beta \mu_{\text{total}}\) = ideal gas part + excess part = \(\beta \mu_{\text{id}} + \beta \mu_{\text{ex}}\)). Note that the total chemical potential \(\beta \mu_{\text{total}}\) is an increasing function of the density \(\rho_0\) (always prevailing), while the excess chemical potential \(\beta \mu_{\text{ex}}\) has a minimum at \(\rho_0^*\approx 0.52\) (i.e., it is countervailing from \(\rho_0^*\approx 0\) to 0.52; and then prevailing from 0.52 upward, being a concave function of \(\rho_0^*\)).

\[
\beta \mu_{\text{total}} = \beta \mu_{\text{id}} + \beta \mu_{\text{ex}} = \text{(ideal gas part)} + \text{(excess part)}
\]

This pseudochemical potential has been evaluated for LJ/HW at \(\rho_0^* = 0.65\) and is shown in Figure 6b. Also shown is the insertion work \(\beta W_{\text{ex}}\). These two quantities (\(\beta W_{\text{ex}}\) and \(\beta \mu_{\text{pseudo}}\)) are different, with opposite periods (one curve is almost the mirror image of the other). Thus there is no possibility of “mapping” free energies from uniform to nonuniform fluid this way. This opposite periodicity is symptomatic, in terms of the curve of the bulk chemical potential \(\beta \mu_0\) vs bulk density \(\rho_0^*\), (i.e., witnessing the \(\beta \mu_0^*\) vs \(\rho_0^*\) trends), when the relative position of the adsorbed density \(\rho_0^* = 0.65\) is greater than the minimum 0.52 in the \(\beta \mu_0^*\) vs \(\rho_0^*\) curve (\(\rho_0^* = 0.65 > \rho_0^*\approx 0.52\)).
shall have out-of-phase oscillations (prevailing). If the adsorbed density were less than 0.52, to the left of $\rho_{0,\text{min}}^s < \rho_{0,\text{min}}^s$, as shall be seen, we would have synchronous oscillations (countervailing).

To further compare the uniform free energies with the nonuniform free energies, we construct a so-called $W-\mu-\rho$ plot. We plot two separate curves on the same graph (Figure 8): (i) the first curve is the uniform fluid $\mu_0-\rho_0$ and (ii) the second curve is the nonuniform $W_{\text{ins}}-\rho_0^{(1)}$ (to do this, we plot the quantity $W_{\text{ins}}(z)$ vs $\rho_0^{(1)}(z)$ by picking the same $z$). For the cases at $\rho_0^s = 0.82$ and 0.65, the slopes of the nonuniform fluid $W_{\text{ins}}-\rho_0^{(1)}$ curves are at an angle with respect to the slope of the uniform $\mu_0-\rho_0$ curve (slopes of the $W_{\text{ins}}-\rho_0^{(1)}$ in adsorption are “negative”, countervailing, while slope of $\mu_0-\rho_0$ in the bulk is “positive”, prevailing.), whereas, as shall be seen below, at a lower density, for example, $\rho_0^s = 0.50$ ($<\rho_{0,\text{min}}^s = 0.52$), the slope of the $\mu_0-\rho_0$ curve also becomes negative (countervailing) and is similar in sign to the slope of the $W_{\text{ins}}-\rho_0^{(1)}$ curve (countervailing). At $\rho_0^s = 0.50$, there is more “congruence” between the two curves $W_{\text{ins}}-\rho_0^{(1)}$ and $\mu_0-\rho_0$ partly because they are both countervailing.

For the highest density (0.82) the $\rho_0^{(1)}(z)$ values (the abscissa) span $\rho_0^{(1)} \approx 0.25$ to 2.06, while $W_{\text{ins}}$ (the ordinate) covers ca. 1.2 to -0.3. This results from tracing the oscillations in $\rho_0^{(1)}$ (see Figure S) at temperature $T^* = 1.35$ and bulk density $\rho_0^s = 0.82$. It is of interest to see that the tracing of oscillation $W_{\text{ins}}-\rho_0^{(1)}$ from Figure S gives a single curve on the $W-\mu-\rho$ plot, instead of multivalued. We rearrange the Euler–Lagrange eq 1.1 to read:

$$
\ln[\rho_0^{(1)}(z)] - C_w^{(1)}(z) = \ln[\rho_0^{(1)}(z)] + \beta W_{\text{ins}}(z)
$$

$$
= -\beta w(z) + \beta \mu_0^s + \ln \rho_0
$$

(3.2)

Since the wall interaction is of the hard-wall kind, $w(z) = 0$ for all $z > 0$, that is, a constant, the relation between $W_{\text{ins}}$ and $\rho_0^{(1)}$ is thus a constant. We have a single curve for $W_{\text{ins}}-\rho_0^{(1)}$ (independent of the $z$-coordinate!).

To understand the trends (countervailing or prevailing), the PDT says that at lower $\rho_0^s$, the insertion work required is higher (see Supporting Information, eq A.10). In other words increasing $\rho_0^s$ means decreasing $\beta W_{\text{ins}}$ countervailing; whereas the pure fluid $\mu_0^s-\rho_0$ curve has a positive slope here, prevailing. These slopes of opposite signs give the observed “orthogonal” crossings as shown. At $\rho_0^s = 0.65$, we are still in the prevailing branch of $\mu_0^s-\rho_0$ (since $0.65 > \rho_{0,\text{min}}^s = 0.52$, the minimum in $\mu_0^s$). Thus we have again the crossing of the $W_{\text{ins}}-\rho_0^{(1)}$ curve with the $\mu_0^s-\rho_0$ curve.

At density $\rho_0^s = 0.50$ ($T^* = 1.35$), the pseudodensity is shown in Figure 9a. Interestingly, at this lower density, the singlet density $\rho_0^{(1)}$ and the pseudodensity $\rho_{\text{pseudo}}$ are quite close in magnitude. There are no opposite oscillations. This adsorption shows significant depletion of molecules at the wall (contact value of $\rho_0^{(1)}(z = \sigma/2) = 0.2$ as opposed to its density in the bulk $\rho_0^s = 0.50$). The pseudodensity $\rho_{\text{pseudo}}$ also shows this depletion. Its values $\rho_{\text{pseudo}}(z)$ lie even lower than the $\rho_0^{(1)}(z)$. The differences between $\rho_{\text{pseudo}}(z)$ and $\rho_0^{(1)}(z)$ are within 5% of each other for most of the points examined. The pseudochemical potential $\beta \mu_{\text{pseudo}}$ is plotted in Figure 9b. It is also close to the insertion work $\beta W_{\text{ins}}$. We show the $W-\mu-\rho$ plot for this density in Figure 8 as the red line. The nonuniform $W_{\text{ins}}-\rho_0^{(1)}$ curve now closely hugs along the uniform $\mu_0^s-\rho_0$ curve.
curve (black line) with similar slopes. We note that the section of the $\mu_p - \rho_0$ curve being compared is at the countervailing branch, negative slopes ($\rho_0^* = 0.5 < \rho_0^{\text{ins}} \approx 0.52$): on this branch higher density means lower excess chemical potential. This trend conforms to the PDT requirement on the $W_{\text{ins}} - \rho_w$ relation (lower probability density implies that the work of insertion is higher) (see Supporting Information, eq A.10), meaning countervailing. Thus we have the observed parallelism between the $W_{\text{ins}} - \rho_w$ curve and the $\mu_p - \rho_0$ curve (both are countervailing).

4. CONCLUSIONS

We present the link, the pseudodensity $\rho_{\text{pseudo}}$ that enables direct mapping of the free energy of a uniform fluid to the free energy of a nonuniform fluid, $F_{\text{ins}} = F_{\text{fl}}$. We equate the uniform chemical potential to the nonuniform work of insertion, $\mu = W_{\text{ins}}$ then solve for the $\rho_{\text{pseudo}}$ that enforces this equality. To do this, we need to derive the potential distribution theorem in a nonuniform system, especially for the so-called type-2 test particles (see the Supporting Information). We distinguish two types of test particles: (i) those under the influence of the wall potential $w(z)$, that is, the type 1 test particles; and (ii) those free from the wall influence, that is, the type 2 test particles. Monte Carlo simulation\(^{19}\) is used to obtain the $W_{\text{ins}}$ of the type-2 test particle and the singlet density $\rho_0^W$. These quantities are connected by the PDT\(^{20}\) (Supporting Information, eq A.10). To implement this concept, we examine two adsorptive systems: the repulsion-only hard spheres, and the attractive Lennard-Jones fluid, both adsorbed on a hard wall.

We are able to characterize the pseudodensity $\rho_{\text{pseudo}}$ plus a complementary quantity, the pseudochemical potential $\mu_{\text{pseudo}}$ in these systems. We show that due to the “concavity” of the chemical potential-density curve (with both the countervailing (falling) branch and the prevailing (rising) branch), the pseudodensity (or the pseudochemical potential) shows either parallelism behavior, namely, with similar slopes to the singlet density $\rho_0^W$, or orthogonal behavior, with slopes opposite to the singlet density $\rho_0^W$. For state conditions of the countervailing trend, the pseudodensities $\rho_{\text{pseudo}}$ and pseudochemical potentials $\mu_{\text{pseudo}}$ are commensurate (with similar magnitudes and slopes) with the singlet density $\rho_0^W$, and the nonuniform insertion work $W_{\text{ins}}$ respectively. On the other hand, for state conditions in the prevailing region, it is shown that $\rho_{\text{pseudo}}$ and $\mu_{\text{pseudo}}$ are poor estimates of the nonuniform density $\rho_0^W$, and of the insertion work $W_{\text{ins}}$ respectively. The exact position or this threshold is demarked by the minimum value $\rho_{\text{amin}}^{\text{ins}}$ of the $\mu_p - \rho_0$ curve in the $W - \mu - \rho_0$ plots. The present results were entirely based on Monte Carlo simulations, thus absent inaccuracies introduced from any approximate theories. The only theoretical formulas used were the Carnahan--Starling equation for hard spheres and the Nicolas equation of state for Lennard-Jones fluid.

For hard sphere fluid, we compare the pseudodensities with the weighted densities $n_a$ derived from the fundamental measure theory of Rosenfeld. We determine that the pseudodensities $\rho_{\text{pseudo}}$ are not equivalent to $n_a$ given that they arise from different theoretical principles: the potential distribution theorem versus the geometrical measures based on the Mayer clusters.

At present the quantity $\rho_{\text{pseudo}}$ is a “descriptive” one, in that it does not “construct” the actual density distributions for a given adsorptive system. To make property calculations, a separate theory needs to be established to yield either $\rho_{\text{pseudo}}$ as a function of position $z$, or $W_{\text{ins}}$ as a function of $z$. Here lies the advantage of the FMT, since it is constructive: for hard spheres on a wall, we have $n_a$ as a function of $z$, $n_a(z)$, that can be used as inputs to the free energy $F_{\text{ins}}$ expression. It is hoped that with the analyses provided above, a constructive DFT theory based on the congruence idea can be developed in the future for general interaction potentials (not limited to hard spheres). Preliminary work has been done, and work in this direction is in progress.

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