Non-analytic curvature contributions to solvation free energies: influence of drying

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We investigate the solvation of a hard spherical cap of radius $R$, immersed in a fluid for which the interparticle forces are short ranged. For thermodynamic states lying close to the liquid binodal, where the chemical potential deviation $\delta \mu \equiv \mu - \mu_{co}(T)$ is very small and positive, complete wetting by gas (drying) occurs and two regimes of interfacial behavior can be identified. These are characterized by the length scale $R_c = 2\gamma_{gl}^\infty/(\Delta \rho \delta \mu)$, where $\gamma_{gl}^\infty$ is the planar gas-liquid surface tension and $\Delta \rho$ is the difference in coexisting densities at temperature $T$. For $R > R_c$, the interfacial free energy and the density profile of the fluid near the hard wall can be expanded in powers of the curvature $R^{-1}$, in keeping with the analysis of Stillinger and Cotter, J. Chem. Phys. 55, 3449 (1971). In the other regime, $R < R_c$, the interfacial free energy and its derivatives acquire terms depending on $\ln R$. Since $R_c^{-1}$ can be made arbitrarily small this implies non-analytic behavior, as $R^{-1} \to 0$, of the work of formation of a hard spherical cavity and of the Gibbs adsorption and the fluid density at contact with the wall. Our analysis, which is based on an effective interfacial Hamiltonian combined with exact statistical mechanical sum rules, is confirmed fully by the results of microscopic density functional calculations for a square-well fluid. We discuss the repercussions of our results for solvation phenomena, emphasizing that non-analytic behavior equivalent to that we find for complete drying in solvophobic systems will also arise in the case of complete wetting, i.e. when liquid films are adsorbed on the surface of large (colloidal) particles or at curved substrates. We re-assess various results in the important but neglected Stillinger-Cotter paper, where drying was not considered explicitly, in the light of our present analysis.

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I. INTRODUCTION

If a solute is to dissolve in a solvent the latter must pay the price of forming cavities capable of accommodating the solute molecules. This process can usefully be imagined as being carried out in two steps, with the first step involving the insertion of a hard cavity in which all attractive solute-solvent interactions are turned off. Treating the basic model of hard cavity solvation is the aim of scaled particle theory (SPT). One of the key issues in the chemistry and physics of solvation is understanding the significance of solute geometry and, in particular, the size-dependence of the free-energy of cavity insertion. If one naively equates cavity formation with bubble formation, then this issue reduces to understanding the curvature dependence of the surface tension of a bubble. Gibbs and later Tolman proposed analytic expansions of the interfacial free-energy in powers of the interfacial curvatures. This approach was adopted by the founders of SPT and remains today a commonly-used ansatz for treating inhomogeneous fluid phenomena.

There is, however, one aspect of hard cavity-solvation that SPT is unable to describe even qualitatively. Namely, when the radius of curvature is large and the liquid solvent approaches liquid-gas coexistence, i.e. the chemical potential $\mu \to \mu_{co}^\infty(T)$. In this special case, it is known from the theory of wetting/drying transitions that a thick film of gas must appear at the surface of the hard cavity. More specifically, the planar hard wall-liquid interface is dry (completely wet by gas) in the limit $\mu \to \mu_{co}^\infty(T)$ at all temperatures $T$ where liquid-gas coexistence occurs. It is straightforward to show that standard SPT is unable to accommodate the drying of a hard cavity in the large radius limit. Recently, Chandler and co-workers have proposed that a full understanding of the hydrophobic effect (of much importance in biology as well as chemistry) requires the incorporation of drying phenomena as the size of hydrophobic solutes increases. One of the key aspects of their interpretation is the realization that at standard temperature and pressure water is very close to saturation (bubble formation), i.e. the relevant thermodynamic field (chemical potential or bulk pressure) is very close to its value at bulk coexistence. Because of the ubiquitous presence of attractive power-law (dispersion) interactions between solute and solvent true drying films are not easy to create in the physical world. Even weakly attractive solute-solvent interactions will lead to partial rather than complete drying so that the thickness of the region of depleted density is greatly reduced. Nevertheless, it is argued that the incipient presence of drying should play an important role in hydrophobic phenomena at large length scales.
We focus, in the main, on model solvents where the interparticle potential is finite-ranged, say a square-well or a truncated Lennard-Jones fluid. The presence of dispersion interactions leads to different non-analyticities which will be discussed elsewhere. Our starting point will be the phenomenological interface Hamiltonian appropriate to the wetting/drying of curved substrates, assuming finite-range interactions in which the binding potential is expressed as the excess Grand potential of fluid surrounding a hard spherical cavity of radius $R$. We consider a reservoir of liquid at chemical potential $\mu > \mu_{co}(T)$ whose pressure is denoted by $p$. If $V_{tot}$ is the total system volume including the cavity then the volume accessible to the fluid is $V_{acc} = V_{tot} - 4\pi R^3/3$. The wall-fluid boundary of infinite repulsion is located at $r = R$ and this induces a film of gas to grow out to a radius $R + \ell$ where a fluctuating gas-liquid interface forms with surface tension $\gamma_{gl}$. The gas film is considered to have a pressure $p_g$, the pressure of the metastable bulk gas at the same chemical potential $\mu$, so that its grand potential is $-p_g V_g$, where $V_g = 4\pi [(R + \ell)^3 - R^3]/3$ is the volume of the film. It follows that the excess grand potential can be expressed as

$$\Omega^{ex}(\ell; T, \mu, R) \equiv \Omega + pV_{acc} = (p - p_g)V_g + 4\pi \left[ R^2 \gamma_{wg} + (R + \ell)^2 \gamma_{gl} + R^2 a(T) \xi \exp\{-\ell/\xi\} \right],$$

where $\gamma_{wg}$ is the surface tension of the wall-gas interface. The final term in Eq. (1), involving the gas-phase bulk correlation length $\xi$ (the decay length of the gas tail of the planar gas-liquid interface), is the leading-order mean-field interaction between the gas-liquid interface and the wall-gas interface. For a hard wall $a(T) > 0$ for all temperatures $T$ at which gas-liquid coexistence occurs. From the Gibbs-Duhem equation at fixed temperature $T$ we can write (defining $\Delta \rho \equiv \rho_l - \rho_g$, the difference of the coexisting densities)

$$p - p_g = \Delta \rho \delta \mu,$$

where $\delta \mu \equiv \mu - \mu_{co}(T)$ denotes the difference between the chemical potential and its value at bulk saturation. The equilibrium thickness of the gas film $\ell_{eq}(T, \mu, R)$ follows by minimizing the Grand potential as a function of $\ell$ at fixed $T, \mu, R$ (and hence at fixed pressures and surface tensions). To leading-order in $\ell_{eq}/R$ this yields

$$\frac{\ell_{eq}}{\xi} = \ln \left\{ \frac{aR}{\Delta \rho \delta \mu R + 2\gamma_{gl}^{\infty}} \right\},$$

where superscript $\infty$ denotes the planar limit at saturation. Noting that at worst $\ell_{eq}$ is no bigger than order $\ln R$, we can substitute (4) back into Eq. (1) to identify the first two terms in a curvature expansion of the equilibrium interfacial free-energy:

$$\Omega_{eq}^{\infty}(R, \mu) = 4\pi R^2 \left\{ \gamma_{wg}(R, \mu) + \gamma_{gl}(R) + (\xi + \ell_{eq}(R, \mu)) \left[ \Delta \rho \delta \mu + \frac{2\gamma_{gl}^{\infty}}{R} \right] \right\}.$$
one to reassess the possible need to include additional terms and/or thermodynamic field variations of the quantities appearing in the interface binding potential Eq. 11. For example, for our purposes we do not need to distinguish between $\gamma_{gl}(R + \ell_{eq}, \mu)$ and $\gamma_{gl}(R)$.

The key conclusion of our work is already apparent from the introductory analysis above. Namely, the presence or absence of non-analytic $\ln R$ contributions is controlled by a length scale

$$R_c \equiv \frac{2\gamma_{gl}}{\Delta \rho \mu},$$

through the asymptotic approach to the planar limit at gas-liquid coexistence (where both $R$ and $R_c$ are infinite).

$$\ell_{eq} \rightarrow \begin{cases} \ln \left\{ \frac{a R}{2 \gamma_{gl}} \right\}, & R \ll R_c \\ \ln \left\{ \frac{1}{2 \Delta \rho \mu} \right\}, & R \gg R_c. \end{cases}$$

The length scale $\ell_{eq}$ is identical to the length that controls capillary evaporation between planar hard walls, or, indeed, capillary condensation between planar walls that are completely wet. Chandler and co-workers have linked this length scale to the hydrophobic attraction between large solutes in water; for water at room temperature and pressure $R_c \approx 1.4 \mu$m, a surprisingly large length scale.

In the following section we re-analyze the arguments of Stillinger and Cotter, that might otherwise lead the reader into rejecting outright the presence of non-analyticity (terms involving $\ln R$) in the curvature expansion of interfacial free energies and order parameters. In Secs. III-V we detail the cross-over between a non-analytic and an analytic approach to the planar limit, both for the interfacial free energy and for interfacial order parameters. Sec. VI presents Density Functional Theory (DFT) results for a square-well fluid, that illustrate the existence of this cross-over. We conclude in Sec. VII with a discussion of the physical significance of our analysis and comments on some of the additional interesting material to be found in the paper by Stillinger and Cotter.

II. STILLINGER AND COTTER SUM RULE ANALYSIS

There are three exact results that can be applied to a spherical hard cavity immersed in an arbitrary solvent:

$$\frac{\partial \Omega_{eqz}^z(R, \mu)}{\partial R} = 4\pi R^2 k_B T [\rho_w(R, \mu) - \rho_w(\infty, \mu)] \quad \text{Eq. (7)}$$

$$\frac{\partial \Omega_{eq}^z(R, \mu)}{\partial \mu} = \Gamma(R, \mu) \equiv 4\pi \int_{R}^{\infty} dr r^2 [\rho(r) - \rho_b(\mu)] \quad \text{Eq. (8)}$$

$$\frac{\partial \Gamma(R, \mu)}{\partial R} = -4\pi R^2 k_B T \frac{\partial}{\partial \mu} [\rho_w(R, \mu) - \rho_w(\infty, \mu)] \quad \text{Eq. (9)}$$

The first two of these results are virial route and compressibility route sum rules, respectively. A brief review of their derivation and physical content is given in the appendices to Ref. 10. The quantity $\rho_w(R, \mu)$ denotes the limiting value of the density profile $\rho(r)$ at the surface of the cavity ($r = R$) and $\rho_w(\infty, \mu) = p/k_B T$, where $p$ is the pressure of the reservoir, is its zero curvature (planar) limit. Eq. 8 is the Gibbs adsorption equation for this problem; $\rho_b(\mu)$ is the reservoir density. The third equation 9 is the Maxwell relation that follows directly from the previous two sum rules. It is equivalent to the derivative w.r.t. $R$ of Eq. (4.13) of Stillinger and Cotter although the latter was derived by a much less direct route. Note that Eq. 9 is interesting in that it relates the derivative w.r.t. the field $\mu$ of a local quantity $\rho_w$ to the derivative w.r.t. $R$ of an integrated quantity, the Gibbs adsorption $\Gamma$. Stillinger and Cotter consider the consequences of the assumption of an analytic curvature expansion of the adsorption $\Gamma$ and the contact density $\rho_w$, in the context of the Maxwell relation 9. We re-visit their argument. Let us introduce the variable $z \equiv r - R$ and assume following Ref. 10 an analytic expansion of the density profile, thus

$$\rho(z; R) = \rho(z; \infty) + \frac{\rho'(z)}{R} + \frac{1}{2!} \frac{\rho''(z)}{R^2} + \frac{1}{3!} \frac{\rho'''(z)}{R^3}, \quad \text{Eq. (10)}$$

$$\rho_w(R, \mu) \equiv \rho_w(R) = \rho_w(\infty) + \frac{\rho'(0)}{R} + \frac{1}{2!} \frac{\rho''(0)}{R^2} + \frac{1}{3!} \frac{\rho'''(0)}{R^3}, \quad \text{Eq. (11)}$$

where a prime denotes a partial derivative with respect to curvature ($R^{-1}$) and all the coefficients belong to the planar limit (at a given chemical potential). When 10 is substituted into the definition of the adsorption $\Gamma$, in Eq. 8,
we see that $\Gamma(R)$ will then also possess an analytic curvature expansion provided the integrals over the expansion coefficients exist (are non-divergent). In particular, the only obvious requirement is for the existence of the planar limit integral

$$\int_0^\infty dz z^2 [\rho(z; \infty) - \rho(b)] .$$

Interestingly, in the presence of an $r^{-6}$, but not $r^{-7}$, dispersion contribution to the intermolecular potential of the solvent, this integral is ill-defined because when an $r^{-6}$ energy is integrated over the semi-infinite volume occupied by solvent it generates a $z^{-3}$ asymptotic decay in the planar density profile $\rho(z; \infty)$ away from the wall. Thus, one does in fact anticipate the presence of a term or terms involving ln $R$ in the adsorption when $r^{-6}$ dispersion interactions are included. Indeed it has been shown explicitly that the free-energy $\Omega_{eq}^{ex}$ then has a $\ln R$ contribution. However, this non-analyticity is of higher-order than the corresponding result for the wetting/drying case with finite ranged potentials detailed below.

For a strictly finite ranged model potential one might expect the integrals over the expansion coefficients to exist and therefore the adsorption to possess an analytic expansion in powers of the curvature. From the compressibility sum rule (5), this property is also transferred to the interfacial free energy (apart from unlikely terms independent of the chemical potential). Assuming $\Gamma(R)$ is analytic in $R^{-1}$ the right-side of the Maxwell relation (9) cannot contain a term of order $R^{-1}$, so that $\partial \phi^{0′}(0)/\partial \mu$ in expansion (11) must be zero for arbitrary values of the chemical potential $\mu$. Stillinger and Cotter then argue that for the case of vanishing bulk density, $\rho_b(\mu) \to 0$, $\rho''(0)$ is zero and therefore $\rho''(0) = 0$ for all $\mu$. If this condition is not met then one has a clear inconsistency with (9). Note that since there is no reason to expect $\rho''(z)$ to be zero away from the wall, a failure to appreciate the special significance of the Maxwell relation (9) would lead one to expect a $\ln R$ term in the interfacial free energy. In fact, the enforcement of this unexpected condition on the limiting value of the density profile at a hard wall cavity has recently been demonstrated numerically within density functional theory for a hard sphere solvent. The corollary to the argument of Stillinger and Cotter is that non-analytic terms in the curvature expansion of the interfacial free energy demand analogous non-analytic terms to be present in the interfacial order parameters $\rho_w$ and $\Gamma$. Although Stillinger and Cotter did not contemplate drying at a hard cavity it is clear that wetting/drying non-analyticity must behave consistently with their sum rule arguments. In the following sections we provide an explicit analysis, based on Eq. (11) and the sum rules listed above, which ascertain leads order non-analytic behavior.

### III. SURFACE TENSION ROUTE

Substituting Eq. (11) into Eq. (12) we can write the interfacial free energy as

$$\Omega_{eq}^{ex}(R, \mu) = 4\pi R^2 \left\{ \frac{\gamma_{wg}(R, \mu)}{R} + \frac{2\xi}{\gamma_{gl}} \right\} + \xi \Delta \rho \delta \mu + \xi \left[ \Delta \rho \delta \mu + \frac{2\gamma_{gl} \gamma_{gl} \delta \mu}{\Delta \rho \delta \mu R + 2\gamma_{gl}^\infty} \right] .$$

The behavior of this quantity depends on whether $R > R_c$ or $R < R_c$, where $R_c$ is defined by Eq. (5). There are two qualitatively different regimes. Let us consider these two regimes separately, in each case discarding terms beyond the leading-order curvature dependence.

For $R \ll R_c$, for which $\delta \mu$ must be kept sufficiently small, we have to our desired order in the curvature expansion

$$\Omega_{eq}^{ex}(R, \mu) = 4\pi R^2 \left\{ \gamma_{wg}(R, \mu) + \gamma_{gl}^\infty + \frac{2\xi \gamma_{gl} \gamma_{gl}^\infty}{R} \ln \left\{ \frac{aR}{2\gamma_{gl}^\infty} \right\} \right\} .$$

If we now invoke sum rule (7) it follows that in this regime

$$k_B T [\rho_w(R, \mu) - \rho_w(\infty, \mu)] = \frac{2}{R} \left\{ \gamma_{wg}(R, \mu) + \gamma_{gl}^\infty \right\} + \frac{2\xi \gamma_{gl} \gamma_{gl}^\infty}{R^2} \ln \left\{ \frac{aR}{2\gamma_{gl}^\infty} \right\} ,$$

where we remind the reader that terms of higher-order than those specified are omitted. This is the result obtained by Evans et al. in Ref. 12, based on setting $\delta \mu = 0$ at the outset. Here, we note that for any non-zero $\delta \mu$ the planar
limit must lie outside this regime; i.e. at \( R = R_c \) there must be a cross-over to analytic behavior.

For \( R \gg R_c \), an approach to the planar limit at non-zero \( \delta \mu \), the free-energy curvature expansion \([12]\) changes character to yield an analytic form whose leading term is

\[
\Omega_{eq}^{\|}(R, \mu) = 4\pi R^2 \left\{ \gamma_{wg}(\infty, \mu) + \gamma_\infty + \xi \Delta \rho \delta \mu \left\{ \ln \left( \frac{a}{\Delta \rho \delta \mu} \right) \right\} + 1 \right\}.
\]  (15)

When this result is inserted into sum rule \([14]\) one obtains

\[
k_B T [\rho_w(R, \mu) - \rho_w(\infty, \mu)] = \frac{2}{R} \left[ \gamma_{wg}(\infty, \mu) + \gamma_\infty + \xi \Delta \rho \delta \mu \left\{ \ln \left( \frac{a}{\Delta \rho \delta \mu} \right) \right\} + 1 \right].
\]  (16)

The next term is \( O(R^{-2}) \); one has an expansion analytic in \( R^{-1} \). Eq. (16) can be re-expressed as

\[
k_B T [\rho_w(R, \mu) - \rho_w(\infty, \mu)] = \frac{2}{R} \gamma_wl(\infty, \mu) + O(R^{-2}) ,
\]  (17)

where \( \gamma_wl(\infty, \mu) \) is the surface tension of the planar wall-liquid interface at chemical potential \( \mu \); this quantity contains the \( \delta \mu \ln \delta \mu \) term associated with complete wetting/drying for short-ranged forces. Thus, provided \( R \gg R_c \), one can read off the planar surface tension from the leading term in the curvature expansion of the contact density (which is Stillinger and Cotter’s route to their exact formula for the planar surface tension discussed in Sec. VII below) even when drying is present.

IV. SURFACE ADSORPTION ROUTE

When Eq. (12) is inserted into the compressibility sum rule \([8]\) we obtain

\[
\Gamma(R, \mu) - \Gamma_{wg}(R, \mu) = -4\pi R^2 \xi \Delta \rho \ln \left\{ \frac{a R}{\Delta \rho \delta \mu R + 2 \gamma_\infty} \right\} ,
\]  (18)

which can be re-written as

\[
\frac{\Gamma(R, \mu) - \Gamma_{wg}(R, \mu)}{4\pi R^2} = -\xi \Delta \rho \left\{ \ln \left( \frac{1}{R} + \frac{1}{R_c} \right)^{-1} \right\} + b(T) ,
\]  (19)

where \( b(T) = \ln(a/2 \gamma_\infty) \). One can expand the logarithmic term in Eq. (19) about \( \ln R_c \) and note that the radius of convergence (and hence the extent of the analytic regime) is \( R_c/R < 1 \). One can also read off the limiting forms of the two regimes. For the non-analytic case at \( R \ll R_c \), examined by Evans et al. in Ref. \([12]\)

\[
\Gamma(R, \mu) - \Gamma_{wg}(R, \mu) \rightarrow -4\pi R^2 \xi \Delta \rho \ln \left\{ \frac{a R}{2 \gamma_\infty} \right\} ,
\]  (20)

and for the non-zero \( \delta \mu \) analytic case at \( R \gg R_c \)

\[
\Gamma(R, \mu) - \Gamma_{wg}(R, \mu) \rightarrow -4\pi R^2 \xi \Delta \rho \ln \left\{ \frac{a}{\Delta \rho \delta \mu} \right\} .
\]  (21)

V. SURFACE MAXWELL RELATION ROUTE

In this section we will check directly the consistency of our curvature expansions for the case of drying with the surface Maxwell relation \([9]\). For the analytic regime \( R \gg R_c \) one can demonstrate consistency by simply inserting \([16]\) into the right side of \([9]\) and comparing with the derivative of Eq. (21). From both routes one obtains

\[
\frac{\partial (\Gamma - \Gamma_{wg})}{\partial R} \rightarrow -8\pi R \xi \Delta \rho \ln \left\{ \frac{a}{\Delta \rho \delta \mu} \right\} .
\]  (22)
The non-analytic regime $R \ll R_c$ is not so straightforward because one must first retain the leading order term varying with chemical potential (missing from the right-side of Eq. (14)). This requires us to keep the non-dominant term in the prefactor of the logarithmic contribution to the interfacial free-energy (12); it is also helpful to expand the logarithm and note that at next to leading-order it cancels the sub-dominant $\xi \Delta \rho \delta \mu$ term:

$$
\Omega_{ex}^x(R, \mu) \to 4\pi R^2 \left\{ \gamma_{wg}(R, \mu) + \gamma_{gl}^\infty + \xi \left[ \Delta \rho \delta \mu + \frac{2\gamma_{gl}^\infty}{R} \right] \ln \left\{ \frac{aR}{2\gamma_{gl}^\infty} \right\} \right\} .
$$

Thus, keeping appropriate terms, at non-zero $\delta \mu$ we have

$$
k_B T \left[ \rho_w(R, \mu) - \rho_w(\infty, \mu) \right] = \frac{2}{R} \left[ \gamma_{wg}(R, \mu) + \gamma_{gl}^\infty + \xi \left[ \Delta \rho \delta \mu + \frac{2\gamma_{gl}^\infty}{R} \right] \ln \left\{ \frac{aR}{2\gamma_{gl}^\infty} \right\} \right]
$$

where despite appearances the prefactor of the logarithmic term is not missing a factor of two in front of $\gamma_{gl}^\infty$. When Eq. (24) is inserted into the surface Maxwell equation (9) one immediately rederives the result for $\partial T / \partial R$ obtained from (20), to leading order as required.

VI. RESULTS FROM DENSITY FUNCTIONAL THEORY FOR A SQUARE-WELL FLUID

The explicit results for surface thermodynamic functions that we have presented in earlier sections are based upon the ansatz (1) for the excess grand potential of a fluid adsorbed on a hard spherical cavity. This ansatz, as in all interface Hamiltonian approaches to wetting/drying, relies upon the introduction of the length $\ell$, the thickness of the drying layer around the sphere. In a fully microscopic approach only the fluid-fluid pair potential should appear, once the wall-fluid (external) potential has been specified. The properties of the fluid are determined by the behavior of the average one-body density $\rho(r)$, which depends, in turn, on the nature of the wall-fluid and fluid-fluid potentials, as well as on the thermodynamic state point $(T, \mu)$ of the fluid reservoir. In order to test the predictions of the (coarse-grained) interface Hamiltonian approach we employ the same microscopic density functional theory (DFT) used in Ref. 12. Specifically we consider an attractive square-well fluid adsorbed at the hard spherical cavity of radius $R$.

The fluid-fluid potential is given by

$$
\rho(r) = \begin{cases} 
\infty, & r < \sigma \\
-\varepsilon, & \sigma < r < 3\sigma/2 
\end{cases}
$$

with $\varepsilon > 0$ and the wall-fluid potential is

$$
V(r) = \begin{cases} 
\infty, & r < R \\
0, & r > R 
\end{cases}
$$

The grand potential functional is taken to be

$$
\Omega_V[\rho] = F_{id}[\rho] + F_{ex}[\rho] + \int d\rho(r)(V(r) - \mu) ,
$$

where $F_{id}[\rho]$ is the Helmholtz free energy functional of the ideal gas and the excess (over ideal) part of the free energy functional is approximated by

$$
F_{ex}[\rho] = F_{hs}[\rho] + \frac{1}{2} \int d\rho(r) \int d\rho'(r') \phi_{att}(|r - r'|) ,
$$

with $\rho(r) \equiv \rho(r)$. Here $F_{hs}[\rho]$ is the excess Helmholtz free energy functional of a hard-sphere fluid which we treat by means of Rosenfeld’s24 successful fundamental measures theory. Attractive interactions are treated by means of a simple mean-field approximation24 we take the attractive part of the potential to be $\phi_{att}(r) = -\varepsilon$ for $r < 3\sigma/2$ and zero otherwise. The equilibrium density profile $\rho_{eq}(r)$ is obtained by solving numerically the Euler-Lagrange equation resulting from minimizing the functional (27) at fixed $\mu$, $R$, and $T$. As usual, $\Omega_V[\rho_{eq}]$ yields the estimate of the grand potential $\Omega$ and, hence, of the surface excess quantity $\Omega_{ex}^x$ defined in Eq. (1) from which other surface thermodynamic quantities follow. As emphasized in Ref. 12 this particular DFT approach has the advantages that
i) the coexisting densities \( \rho_t \) and \( \rho_g \) can be calculated precisely from the bulk free energy density arising from (28), ii) the results from the DFT defined by (27) and (28) satisfy the Gibbs adsorption theorem (8) and the sum rule (7) for the contact density \( \rho_w(R, \mu) \), (this was confirmed earlier in extensive numerical calculations for hard-spheres adsorbed at hard curved cavities (22)), and iii) the planar surface tension \( \gamma_{gl}^\infty \) and the bulk correlation length \( \xi \) of the wetting phase (in this case gas) can be obtained from independent calculations. Specifically, we compute \( \gamma_{gl}^\infty \) from a separate DFT calculation for a planar free interface and we calculate \( \xi \) by evaluating the leading-order pole of the fluid structure factor obtained by taking two functional derivatives of Eq. (28). Note that the quantity \( \xi \) entering Eq. (11) is also the true correlation length which determines the exponential decay of the bulk pair correlation function \( g(r) \) for \( r \to \infty \). The functional (28) is, of course, mean-field in character in that it omits some of the effects of capillary wave fluctuations that occur in a wetting/drying film. We shall return to this issue later.

In our numerical work we chose to focus on the surface adsorption route to surface thermodynamic functions, i.e. we chose to test the validity of Eq. (19) within the context of the microscopic DFT approach. It should be clear from the previous discussion that if the form of (19) is verified then all the relevant predictions from the coarse-grained approach must also hold within the microscopic treatment. Note that in Ref. 12 we had already confirmed, via DFT, the validity of the predictions of the coarse-grained theory for \( \delta \mu = 0 \), i.e. for \( R_c = \infty \). Here we are considering finite but large \( R_c/\sigma \). We must also focus on the situation where \( R/\sigma \gg 1 \) since the mesoscopic arguments based on (1) are reliable only when the equilibrium layer thickness \( \ell_{eq}/\sigma \) is large, i.e. when \( \delta \mu \) is small and the cavity radius \( R \) is large.

In Fig. 11 we plot the difference in adsorption \( \Gamma(R, \mu) - \Gamma_w(R, \mu) \), divided by the surface area \( 4\pi R^2 \), obtained from the DFT calculations, with \( \Gamma \) defined by the integral in Eq. (8), versus the dimensionless quantity \( x \) where

\[
\frac{x}{\xi^2} = -\xi^2 \Delta \rho \ln \left( \frac{k_B T \sigma^{-3}}{2\gamma_{gl}^\infty (R^{-1} + R_c)} \right)
\]

for fixed \( R_c = 5000\sigma \) and \( k_B T/\epsilon = 1 \). The predictions of Eq. (19), namely that this plot should be a straight line with positive gradient unity, are satisfied accurately both for \( R \ll R_c \) and \( R \gg R_c \). We have confirmed that for \( R/\sigma \geq 250 \) Eq. (19) remains valid for a wide selection of values of \( R_c/\sigma \). At smaller values of \( R \) deviations of order \( \sigma/\sigma \) become apparent to the eye. We conclude from the DFT results that provided \( R/\sigma \) is sufficiently large (and \( \delta \mu \) is sufficiently small) the adsorption is given accurately by Eq. (19) and thus the excess grand potential is well-accounted for by the starting equation (4).

The results in Fig. 11 are appropriate to a typical colloidal particle in ‘water’ at 1 atmosphere. As mentioned in the Introduction, we take \( R_c = 1.4\mu m \) for water at room temperature and pressure. In Fig. 2 we chose to fix \( R_c \) to be 250\( \sigma \), corresponding to a thermodynamic state much further from bulk coexistence, and varied the colloid radius \( R \). The difference in adsorption varies linearly with \( x \) for large radii \( R \) but deviations from a straight line of slope unity can be discerned for smaller values of \( R \).

In Fig. 3 we plot the difference between the contact density at the spherical cavity and that a planar wall, i.e. \( [\rho_w(R, \mu) - \rho_w(\infty, \mu)] \), versus \( 1/R \) for a fixed value of \( \delta \mu \) corresponding to \( R_c = 250\sigma \). For \( R > R_c \) the data lie on a straight line whose slope is given by \( 2\gamma_{wl}(\infty, \mu) \sigma^2/k_B T \). Thus, the DFT results also confirm the validity of Eq. (17): the planar wall-liquid surface tension \( \gamma_{wl}(\infty, \mu) \) at a non-zero value of \( \delta \mu \) can be obtained from plots of the contact density versus \( 1/R \) provided one has sufficient data in the range \( R > R_c \).

VII. DISCUSSION

In this paper we have used an interface Hamiltonian appropriate to (mean-field) wetting/drying to explore the curvature dependence of the interfacial free energy \( \Omega_{\square}^{\square}(R, \mu) \). We have concentrated on the solvation of a hard spherical cavity of radius \( R \), a problem tackled originally by scaled particle theory, since for this system the exact sum rules (7) (8) (9) provide direct insight. In particular, the surface Maxwell relation (9) implies that terms non-analytic in \( 1/R \) cannot be present in the curvature expansion of the interfacial free energy unless there exist corresponding non-analytic terms in the Gibbs adsorption \( \Gamma(R, \mu) \) and in the contact density \( \rho_w(R, \mu) \). Our main conclusion is that in the neighborhood of complete drying one must distinguish two regimes of behavior: i) \( R \ll R_c \), where non-analytic terms involving \( \ln R \) (see Eqs. (19) (13) (20)) are present and ii) \( R \gg R_c \), where the curvature expansions involve only powers of \( 1/R \). The length scale \( R_c \) is given by Eq. (6); the closer the bulk liquid is to coexistence, the smaller is the chemical potential deviation \( \delta \mu \) and the larger is \( R_c \). In Ref. 12 we considered only the case \( R_c = \infty \).
\((\delta \mu = 0)\), identifying the leading-order, non-analytic contributions and confirming their existence by means of DFT calculations. Here we elucidate the crossover between the two regimes and verify the predictions from the interface Hamiltonian by performing DFT calculations of the Gibbs adsorption for a wide range of \(R\) and \(R_c\) - see Sec. VI. As the DFT yields density profiles and surface thermodynamic functions consistent with the sum rules (7), it follows that the leading-order curvature predictions contributed by the interface Hamiltonian analysis are all consistent with our DFT results.

Of course, both theoretical approaches omit effects of capillary-wave fluctuations. In three-dimensional systems with short-ranged wall-fluid and fluid-fluid forces the mean-field theory of complete wetting/drying is expected to be affected marginally by fluctuations; the upper critical dimension is \(d_c = 3\). The linear renormalization group is sufficient to handle these effects and amounts to a Gaussian smearing of the interfacial binding potential\(^{28}\). Since, to leading-order in \(1/R\), incorporation of curvature merely replaces \(\Delta \rho \delta \mu\) for a planar wall by \(\left(\Delta \rho \delta \mu + 2\gamma gl/\omega R\right)\) we conjecture\(^{22}\) by analogy with results for the planar problem, that our present mean-field results for the leading non-analytic contribution to \(\Omega_{eq}(R, \mu)\), the third term on the right of Eq. (13), should be unaltered when fluctuations are included, apart from replacing the bulk correlation length \(\xi\) by \((1 + \omega/2)\xi\), for \(\omega < 2\)\(^{28}\). Here \(\omega = k_B T/(4\pi \gamma gl/\xi^2)\) is the usual parameter measuring the strength of capillary-wave fluctuations in \(d = 3\). Note that in the case of power-law potentials, arising from dispersion forces, the upper critical dimension \(d_c < 3\) and fluctuation effects are not expected to alter the results of the corresponding mean-field treatment.

We turn now to the physical relevance of our results. As mentioned in the Introduction, there are potential implications for understanding aspects of hydrophobicity at large length scales, specifically for big solvophobic solute particles and for planar substrates\(^{6}\). In order to appreciate some of these we recall from the definition in Eq. (11) that the excess chemical potential for inserting a single hard cavity into the solvent at fixed \((\mu, T)\), equivalent to the work required to create an empty cavity of radius \(R\), is given by

\[
\mu_{hs}(R, \mu) = p_4 \pi R^3 + \Omega_{eq}(R, \mu),
\]

where \(p\) is the pressure of the reservoir. Thus, a theory for the interfacial free energy constitutes a theory for the excess chemical potential associated with the insertion of a hard-sphere into the solvent, precisely the quantity that SPT attempts to calculate. The present analysis shows that striking logarithmic contributions can occur in \(\mu_{hs}\) for large \(R\) and sufficiently small \(\delta \mu\). It is clear that no simple extension of SPT can hope to accommodate such subtle contributions. Indeed drying per se is not incorporated into standard SPT treatments.\(^{28}\) Moreover, it is evident that theoretical approaches to solution which start from an approximate description of the Helmholtz free energy of the homogeneous mixture and obtain \(\mu_{hs}\) by taking the derivative with respect to the solute density in the limit of vanishing solute will not normally be able to capture the subtle physics associated with drying films.

It is likely that the physical situation for which our theory is most directly relevant is not drying but one in which a big colloidal particle is wet by a liquid film in the approach to liquid-gas \((\mu \rightarrow \mu_r(T))\) or liquid-liquid coexistence\(^{14}\). The arguments that lead to Eq. (11) are valid for complete wetting by either fluid phase, provided the wall-fluid potential has finite range or decays on a length scale shorter than the bulk correlation length of the wetting phase. In these circumstances the interfacial free energy per unit area will acquire a non-analytic \(R^{-1}\) in \(R\) contribution provided \(R < R_c \equiv 2\gamma gl/(\Delta \rho \delta \mu)\). Of course the sum rule (7) is modified when the wall-fluid potential \(V_{wf}(r)\) is not purely hard\(^{28,29,30}\).

\[
\frac{\partial \Omega_{eq}(R, \mu)}{\partial R} = -4\pi \int_0^\infty dr r^2 \rho(r) \frac{dV_{wf}(r)}{dr} - 4\pi R^2 p
\]

(31)

However, we expect the density profile in the neighborhood of the wall to acquire contributions equivalent to those appearing on the r.h.s. of Eq. (11). More specifically, for a complete wetting situation, with \(R < R_c\), the first term on the right in Eq. (31) should acquire both a contribution \(8\pi R \gamma gl\) and a non-analytic \(8\pi \gamma gl \ln R\) contribution from the fluid-fluid interface located near \(R + \ell_{eq}\). In real fluids dispersion forces are ubiquitous and these give rise to power-law divergences of the wetting film thickness at a planar wall. Analysis of the appropriate interface Hamiltonians and extensive DFT calculations for a Lennard-Jones liquid adsorbed at a hard spherical cavity show that wetting/drying lead to non-analytic terms in the curvature expansion of the interfacial free energy and of the surface order parameters that are power laws in \(R^{-1}\) (not logarithms), provided \(R < R_c\). For example, for \(R_c = \infty\), the \(r^{-6}\) decay of the fluid-fluid pair potential gives rise to the adsorption increasing as \(R^{2/3}\), a term proportional to \(R^{-2/3}\) in the interfacial free energy per unit area, and a term \(R^{-5/3}\) in the contact density\(^{15}\).
Throughout our discussion we have referred, somewhat loosely, to the presence of non-analytic contributions to surface thermodynamic functions. It is important to understand precisely what physical repercussions such contributions, which involve ln $R$, might have. We choose to fix $\delta \mu$ to be small, so that drying films develop, but non-zero so that $R_c$ is very large but finite, and vary the curvature $R^{-1}$. For large curvature, $R < R_c$, the interfacial free energy per unit area has a term in $R^{-1} \ln R$ (see Eq. 31). On reducing the curvature a crossover occurs and for $R > R_c$ the same quantity has an expansion in powers of $R^{-1}$, i.e.

$$\frac{\Omega_{eq}(R, \mu)}{4\pi R^2} = \gamma_{wl}(\infty, \mu) + O(R^{-1}) \ .$$

(32)

It follows that the adsorption and the contact density differ from their planar limiting values by terms $O(R^{-1})$ and higher powers of the curvature; no singularity develops in derivatives as $R^{-1} \to 0^+$. This means that one can also consider the situation of negative curvature, $R^{-1} < 0$, corresponding to adsorption from the liquid confined inside the hard cavity. (One can imagine solvent particles `ghosted' into the cavity from a reservoir at the same fixed $(\mu, T)$ - a situation also considered in Sec. VI of Ref. 10.) By continuity one expects thick films of gas to develop on the hard wall. Their equilibrium thickness is still given by Eq. 3, and for the same $\delta \mu$, films are thicker than at the planar wall since $R^{-1} < 0$. Thus one expects a continuous (analytic) dependence of surface thermodynamic functions on curvature in the neighborhood of $R^{-1} = 0$. As the curvature becomes more negative (the radius of the spherical cavity becomes smaller), the film thickens further and eventually the denominator of the logarithm in Eq. 3 vanishes when the curvature approaches $-R_c^{-1}$, signaling the breakdown of the theory. However, in reality this scenario will be prevented by the prior occurrence, at some larger radius, of capillary evaporation, i.e. the cavity will empty leaving only the `gas phase'.

If we make $\delta \mu$ smaller the regime $R \gg R_c$, where the surface thermodynamic functions exhibit power-law dependence on the curvature, shrinks. Nevertheless, provided $R_c$ remains finite there should be a (narrow) regime where Eq. 32 and the corresponding result 17 for the contact density remain valid. (The latter is especially important as it forms the starting point for deriving the planar wall-liquid tension in the analysis of Stillinger and Cotter, see Eq. 11.) Of course, one is free to work at bulk coexistence, $R_c = \infty$, and then the regime where a power series expansion in the curvature exists is of vanishing extent and $\Gamma \sim -R^2 \ln R$; this is the situation considered earlier in Ref. 12.

In this case capillary evaporation occurs for an infinitesimal negative curvature; the phase transition intervenes immediately to prevent our taking the logarithm of a negative number! Another situation one might contemplate is that in which the radius $R$ of the hard cavity is fixed at some (large) value and the chemical potential $\mu$ is varied. For sufficiently large $\delta \mu$, $R \gg R_c$ and one expects power-law curvature contributions, whereas on approaching coexistence $\delta \mu \to 0$ and there will necessarily be crossover to the regime $R \ll R_c$ where logarithmic contributions will arise.

There are practical reasons for investigating the realm of validity of power-series expansions in the curvature. Helfrich’s seminal analysis of fluctuating membranes is based on the assumption that the free energy can be written as such an expansion which includes three terms in addition to the bulk contribution. Very recently König et al. have argued that the interfacial free energy per unit area, $\Omega_{eq}(R, \mu)/(4\pi R^2)$, and other surface thermodynamic quantities can be written as a constant plus only two contributions, one linear in the mean curvature and the other linear in the Gaussian curvature of the convex surface bounding the fluid. They support their conjecture with numerical DFT results for a hard-sphere fluid bounded by a curved wall. It is clear from our analysis that the occurrence of wetting/drying negates the possibility that power-series expansions, with a finite or an infinite number of terms, could provide a valid description of the interfacial free energy for every state point of the fluid. For fluids with short-ranged wall-fluid and fluid-fluid forces, exhibiting gas-liquid coexistence, the existence of a large interfacial length scale $\ell_{eq} \gg \xi$ precludes such a simple description. In the case of power-law (dispersion) forces the situation is worse. As mentioned in Sec. II, for $r^{-6}$ interactions $\Omega_{eq}^{\text{ex}}$ has a ln $R$ contribution for a non-wet spherical cavity.

We return now to discussion of the Stillinger-Cotter paper and enquire whether their conclusions require revision in the light of our present analysis. Recall that these authors postulate the existence of a power-series expansion (11) for the density profile and on this basis they conclude that the work of cavity formation, and therefore the interfacial free-energy, is “free of contributions varying logarithmically with the radius, in the large size limit.” As we argued in Sec. II, their argument cannot be valid for power-law forces. In the case of short-ranged forces there were sound reasons for accepting initially the validity of expansions (11) and (13) but we have ascertained that the occurrence of drying may lead to logarithmic contributions to the contact density: compare Eqs. (11) and (12). Consistency with the sum rules then requires the presence of logarithmic contributions in the interfacial free energy, in contradiction to Stillinger and Cotter’s conclusion. However, if we restrict consideration to thermodynamic states and radii for which $R \gg R_c$ then the power-series expansions are appropriate and Stillinger and Cotter’s conclusion could be deemed valid. We re-iterate that these authors did not contemplate drying so the length scale $R_c$ does not enter
their analysis; effectively they set $R_c = \sigma$ or $\xi$.

Another important result of Stillinger and Cotter is their formula for $\gamma_{wl}(\infty, \mu)$, the surface tension of the planar hard-wall liquid interface - see Eq. (3.22) of Ref. 11. The formula, which involves integrals over the pair correlation function of the inhomogeneous fluid, can with hindsight be identified with exact compressibility route expressions for the planar surface tension (discussed below). Stillinger and Cotter obtain their formula by deriving a result for the quantity $\rho'(0)$ entering Eq. (11). They then identify $\rho'(0)$, the coefficient of the $R^{-1}$ term in the curvature expansion of the contact density, with $2\gamma_{wl}(\infty, \mu)/k_B T$. This is equivalent to employing Eq. (15) or (17). The latter are valid provided $R \gg R_c$. However, this is not a handicap as one can always take the planar limit by fixing $\delta \mu$ to be small but non-zero and allow $R^{-1} \to 0$16,35. As emphasized earlier, the resultant formula for $\gamma_{wl}(\infty, \mu)$ does capture the gas-liquid tension plus the $\delta \mu \ln \delta \mu$ contribution which characterizes complete drying in systems with short-ranged forces.

As with much of their paper, Stillinger and Cotter’s derivation of the planar hard-wall-liquid surface tension was ahead of its time and appears to have been missed or ignored by later workers. The subsequent history of their result is interesting since the formula played a key role in unraveling some of the more subtle aspects of wetting/drying10,35. Usually the first published compressibility route expression for the planar surface tension is attributed to Triezenberg and Zwanzig.27 It turns out that the earlier formula of Stillinger and Cotter is equivalent to the functional inverse of the Triezenberg-Zwanzig (pair direct correlation function) formula, with the latter applied to the hard wall interface rather than the free liquid-gas interface; see for example Appendix A of Ref. 29. It was not until some years later that Schofield38 proved the equivalence of the two compressibility route expressions with the much earlier virial expression of Kirkwood and Buff. Subsequently, without being aware of the work of Stillinger and Cotter, one of us rederived their approach for the surface tension by taking curvature derivatives of the Grand potential in order to isolate surface terms in the curvature expansion29,39. A succinct general derivation, valid for arbitrary dimensionality and wall-fluid potentials, is given in Sec. IIIIC of Ref. 51. Specializing to three-dimensions and hard spherical cavities, the general formula reduces to

$$\frac{1}{R} \left( \frac{\partial}{\partial R} - \frac{R}{2} \frac{\partial^2}{\partial R^2} \right) \mu (R^2 \gamma(R, \mu)) = -\frac{1}{2} k_B T \rho_w^2 \left( \frac{\partial \rho_w}{\partial R} \right) \mu$$

$$= \frac{\pi}{2} k_B T \rho_w^2 \int_0^{2R} dr \rho_w r^3 \left[ g_w(r_{12}; R) - 1 \right], \quad (33)$$

where, as previously, $\gamma(R, \mu) \equiv \Omega_{eq}^c(R, \mu)/(4\pi R^2)$ is the surface excess grand potential per unit area and $\rho_w \equiv \rho_w(R, \mu)$ is the contact density of the fluid. $g_w(r_{12}; R)$ is the pair distribution function for pairs of particles 1 and 2 positioned at the surface of the cavity. It is clear that the exact result (33) allows one, in principle, to investigate curvature corrections to the planar tension; only the latter was extracted by Stillinger and Cotter. In earlier papers it was assumed that the leading curvature correction would correspond to a Tolman term. Now we can see that in the presence of wetting/drying in the $R \ll R_c$ regime, curvature corrections must generate the stronger $R^{-1} \ln R$ term in $\gamma(R, \mu)$ predicted by Eq. (15).

The compressibility route sum rule29,39 implies pronounced fluctuation effects in the presence of drying. These are well-documented for the case of a planar wall10,35, but have not been investigated in any detail for a curved wall. Consider Eq. (33) in the limits where $R \to \infty$ and $\delta \mu \to 0$, where the gas-liquid interface will be located far from the hard wall, near $+ \ell_{eq}$. Nevertheless, $\gamma(R, \mu)$ remains dominated by contributions from this distant interface. The inescapable conclusion is that both the one-body contact density $\rho_w(R \to \infty, \mu)$ and the pair distribution, $g_w(r_{12}; R \to \infty)$ contain much information about the distant gas-liquid interface; capillary-wave like fluctuations of the latter manifest themselves at the wall. In principle, knowledge of the capillary-wave correlation contribution to $g_w(r_{12}; R)$ would enable one to derive both the gas-liquid surface tension contribution and the leading-order, $R^{-1} \ln R$ curvature contribution to $\gamma(R, \mu)$ predicted by the interface Hamiltonian approach. This is an ambitious program, as previous work on the planar interface will confirm39.

There are other interesting topics discussed in the Stillinger-Cotter paper. These include the free energy for a droplet with a fixed number of solvent particles and some speculations on the behavior of the interfacial free energy near the bulk critical point - see Sec. VII of Ref. 10. Both topics warrant further attention; we cannot do justice to these in the present paper. In concluding, however, we do wish to return to what we believe is an important and intriguing issue in the statistical mechanics of inhomogeneous fluids. This concerns the vanishing of the coefficient $\rho''(0)$ of the $R^{-3}$ term in the expansion of the contact density $\rho_w$ - see Eq. (11). As we pointed out in Sec. II, Stillinger and Cotter argue, on the grounds of consistency with the sum rules, that $\rho''(0)$ must vanish.
at all thermodynamic state points, with the caveat (see Sec. VII of their paper) that their curvature expansions will themselves become inapplicable at or near the gas-liquid critical point where the bulk correlation length is diverging. Stillinger and Cotter do not write down an explicit expression for $\rho'''(0)$ but they do write down the corresponding expression (their Eq. (5.13)) for $\rho_{2d}(0)$, the coefficient of $R^{-2}$ in the expansion of the density profile of a fluid adsorbed at a hard disk in two dimensions. Their sum rule arguments lead them to conclude that $\rho_{2d}(0)$ must be identically zero. Commenting on this result Stillinger and Cotter write: “The identical vanishing of $\rho_{2d}(0)$ in two dimensions is hardly a transparent property of the complicated $\rho_{2d}(z)$ expression.” This is certainly an understatement. If one glances at their Eq. (5.13) one finds integrals over combinations of one, two and three-body distribution functions of the inhomogeneous fluid evaluated in the planar wall limit and it is not at all obvious why $\rho_{2d}(0)$ should vanish. The corresponding expression for $\rho'''(0)$ in the three dimensional fluid is even more complicated, involving additional four-body distributions. It is remarkable that these complicated expressions should vanish identically but this appears to be a necessary consequence of enforcing consistency with the Maxwell relation.

What then is the status of Stillinger and Cotter’s conclusions regarding the vanishing of $\rho'''(0)$ and $\rho_{2d}(0)$? Their arguments require the existence of the curvature expansion. This is invalid for power-law intermolecular potentials and must fail near the critical point for any type of interaction. We have shown that the expansion can also fail, owing to the onset of drying, for all states sufficiently close to gas-liquid coexistence. Given the existence of these exceptions, one might be concerned that the expressions derived by Stillinger and Cotter for $\rho'''(0)$ and $\rho_{2d}(0)$ in terms of integrals over correlation functions might not necessarily exist for all thermodynamic state points. However, one could restrict attention to states where the bulk correlation length $\xi < R$ and where wetting/drying does not occur or to states where $R > R_c$ if wetting/drying does occur. In fact, this latter restriction is implied in footnote 8 of a slightly later paper by Stillinger another paper remarkable for its allusions to future developments; in particular, Stillinger almost arrives at a modern statement of drying (and hence wetting) transitions (see his Fig. 3 and footnote 5). Under these restrictions the expansions should exist. Do we then accept that the Stillinger-Cotter sum rule, their Eq. (5.13), is ill-defined outside these restrictions? This is feasible because the right-side of their complicated compressibility route sum rule contains integrals over the planar distribution functions alone, which could become very long-ranged in the presence of capillary-wave fluctuations (or bulk critical fluctuations or power-law interactions).

However, provided $\delta \mu > 0$, it is difficult to see why the sum of integrals should vanish for one state and then not exist for another close by. The correlation length for complete wetting diverges only at $\delta \mu = 0$. What is more likely is that the sum of integrals is zero for all state points with $\delta \mu > 0$ but in the non-analytic $R < R_c$ regime, where the power series expansion is not valid, there could be an additional, non-vanishing contribution to the $R^{-3}$ term in that implies a logarithmic term in the free energy.

These matters are not of purely academic interest. There are many practical applications, see e.g. Ref. 34, where it would be beneficial to have a theory that expresses the interfacial free energy and density profiles as power series expansions in the curvature. As mentioned earlier, DFT studies of hard-sphere fluids provide compelling numerical evidence for the vanishing of $\rho'''(0)$. Those studies are based on the Rosenfeld functional which has its basis in scaled particle theory, i.e. it is constructed from a finite number of fundamental (geometric) measures. However, it should not be the particular form of the Rosenfeld functional that dictates $\rho'''(0) = 0$. Any DFT satisfying the sum rules must necessarily yield $\rho'''(0) = 0$ at a hard cavity, provided the curvature expansion exists (in particular, $R > R_c$). If follows that the DFT must yield distribution functions that are consistent with the Stillinger-Cotter sum rule. The behavior of $\rho'''(0)$ defined by our DFT applied to the non-analytic regime $R < R_c$ requires further analysis.

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For a review see R. Evans, in Fundamentals of Inhomogeneous Fluids, edited by D. Henderson (Marcel Dekker, New York, 1992) p. 85.

We should note that the sum rule (9) also pertains to fluid adsorbed inside the cavity. Note also that (9) is a close analog of the Maxwell relation

valid for a fluid confined by two parallel, planar hard walls separated by a distance L. \( \Gamma(L, \mu) \) is the Gibbs adsorption per unit area and \( f_s(L, \mu) \) is the so-called solvation force (or disjoining pressure), i.e. the excess pressure arising from confinement. One can obtain the adsorption by integrating \( k_BT \frac{\partial}{\partial \mu} [\rho_w(L, \mu) - \rho_w(\infty, \mu)] \) w.r.t. L just as one can obtain \( \Gamma(R, \mu) \) by integrating the r.h.s. of \( (34) \) w.r.t. R.
In the case of a hard cylinder of radius $R$ the term in question is known to be $\xi_\infty / (k_B T R^2)$, for $R < R_c$, which is certainly non-vanishing - see Eq. (8) of Ref. 12. This does not, of course, prove that the right-side of Stillinger and Cotter’s sum rule Eq. (5.13) remains well-defined. Note that for the sphere a $R^{-3}$ term in the expansion of $\rho_w(R)$ implies a contribution proportional to $\ln R$ in $\Omega_{eq}$. This would be weaker than the $R \ln R$ contribution associated with complete drying - see present Eq. (13).
FIG. 1: The difference in adsorption $\Gamma(R, \mu) - \Gamma_{wg}(R, \mu)$, divided by $4\pi R^2$, for a square-well fluid in the liquid and gas phases versus $x = -\xi^2\Delta\rho\ln\{k_B T \sigma^{-3}/(2\gamma_0^\infty(R^{-1} + R_c^{-1}))\}$ for fixed temperature $k_B T / \varepsilon = 1$ and fixed $R_c \equiv 2\gamma_0^\infty / (\Delta\rho\delta\mu) = 5000\sigma$, a value typical for water. The results of the DFT calculation (symbols and line) are for sphere radii ranging between $R = 5 \cdot 10^5 \sigma$ (bottom) and $R = 295\sigma$ (top). The line has gradient unity consistent with the prediction of Eq. (19). For this temperature $\Delta\rho\sigma^3 = 0.54542$, $\gamma_0^\infty \sigma^2 / k_B T = 0.19327$ and the correlation length of the coexisting gas phase $\xi = 0.48962\sigma$.

FIG. 2: As in Fig. 1 but now for fixed $R_c = 250\sigma$. The sphere radii range between $R = 5 \cdot 10^5 \sigma$ (bottom) and $R = 295\sigma$ (top). Small deviations from a straight line with gradient unity can be ascertained at small values of $R$ (large $x$).

FIG. 3: Difference between the contact density at the spherical cavity and that at a planar wall, $\rho_w(R, \mu) - \rho_w(\infty, \mu)$, versus $\sigma/R$ for a fixed $R_c = 250\sigma$ and $k_B T / \varepsilon = 1$. The solid line denotes the DFT results. For $R \gtrsim R_c$ these lie on the straight (dotted) line whose slope is given by the planar tension $2\gamma_0^\infty(\infty, \mu)\sigma^2 / k_B T$, as predicted by Eq. (17).
\[ \frac{(\Gamma(R, \mu)_R - \Gamma_{wg}(R, \mu))s^2}{4 \pi R^2} \]

\[ R_s = 5000 \sigma \]

R. Evans, J.R. Henderson, and R. Roth, Fig. 11
\[
\frac{\Gamma(R,\mu) - \Gamma_{wg}(R,\mu)\sigma^2}{(4\pi R^2)} = \frac{R_s}{250}\sigma.
\]

R. Evans, J.R. Henderson, and R. Roth, Fig. 2
\[ \frac{\sigma}{R} \]

\[ \rho_w(R, \mu) - \rho_w(\infty, \mu) \]

\[ \sigma^3 \]

\[ R_s = 250 \sigma \]

R. Evans, J.R. Henderson, and R. Roth, Fig. 3