Interfacial free energy of a hard-sphere fluid in contact with curved hard surfaces

Brian B. Laird, Allie Hunter, and Ruslan L. Davidchack

1Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA
2Department of Mathematics, University of Leicester, Leicester, LE1 7RH, UK

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Using molecular-dynamics simulation, we have calculated the interfacial free energy, \( \gamma \), between a hard-sphere fluid and hard spherical and cylindrical colloidal particles, as functions of the particle radius \( R \) and the fluid packing fraction \( \eta = \rho \sigma^3/6 \), where \( \rho \) and \( \sigma \) are the number density and hard-sphere diameter, respectively. These results verify that Hadwiger’s theorem from integral geometry, which predicts that \( \gamma \) for a fluid at a surface, with certain restrictions, should be a linear combination of the average mean and Gaussian surface curvatures, is valid within the precision of the calculation for spherical and cylindrical surfaces up to \( \eta \approx 0.42 \). In addition, earlier results for \( \gamma \) for this system [Bryk, et al., Phys. Rev. E 68 031602 (2003)] using a geometrically-based classical Density Functional Theory are in excellent agreement with the current simulation results for packing fractions in the range where Hadwiger’s theorem is valid. However, above \( \eta \approx 0.42 \), \( \gamma(R) \) shows significant deviations from the Hadwiger form indicating limitations to its use for high-density hard-sphere fluids. Using the results of this study together with Hadwiger’s theorem allows one, in principle, to determine \( \gamma \) for any sufficiently smooth surface immersed in a hard-sphere fluid.

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The solid-liquid interfacial free energy, \( \gamma \), is a central property governing a wide variety of technologically important phenomena from crystal nucleation and growth to wetting. Because accurate and reliable experimental measurements of \( \gamma \) are rare, much effort has been devoted in recent years to the development of atomistic simulation methods to determine this quantity for interfaces between coexisting solid and fluid phases and for systems in which the solid is modeled by a static wall. These efforts have thus far been primarily restricted to planar interfaces; however, there are many physically relevant systems in which interfacial curvature is relevant, for example, in the formation of critical nuclei in nucleation or the solvation/wetting of hydrophobic nanoscale particles. There have been a number of previous simulation studies that examine the effect of curvature in liquid-vapor interfaces, but direct simulation studies on solid-liquid interfaces are lacking. In this work, we examine the dependence of \( \gamma \) on the surface curvature for a hard-sphere fluid in contact with curved hard surfaces, specifically at spherical and cylindrical colloidal particles.

König, et al. have recently shown that Hadwiger’s theorem from integral geometry puts severe restrictions on the shape (curvature) dependence of the interfacial free energy. In their analysis, the interfacial free energy of an object with a surface \( S \) is given by

\[
\gamma(S) = \gamma_0 + h \bar{H} + \kappa \bar{K}
\]

where \( h \) and \( \kappa \) are constants depending upon the thermodynamic state, but independent of the specific surface \( S \). Here \( \bar{H} \) and \( \bar{K} \) are the averaged mean and Gaussian curvatures of \( S \), defined as

\[
\bar{H} = \frac{1}{2A} \int_S \frac{1}{R_1(\mathbf{q}) + 1/R_2(\mathbf{q})} dS
\]

\[
\bar{K} = \frac{1}{A} \int_S \frac{1}{R_1(\mathbf{q}) \cdot R_2(\mathbf{q})} dS
\]

where \( R_1(\mathbf{q}) \) and \( R_2(\mathbf{q}) \) are the principal curvatures at each point \( \mathbf{q} \) on the surface \( S \), and \( A \) is the surface area. As discussed in Ref. 22, the use of Hadwiger’s theorem to determine the free energy of fluids at bounding surfaces, often referred to as “morphological thermodynamics”, is valid as long as the fluid/surface system satisfies motion invariance, continuity and additivity. These conditions can break down for situations in which the bounding surface is small (i.e. on the order of the fluid particle size), for systems with long-range interactions, or for highly concave surfaces in which the fluid is confined in regions smaller than a few correlation lengths. For a fluid in contact with a spherical convex surface of radius \( R \), \( \bar{H}_s = 1/R \) and \( \bar{K}_s = 1/R^2 \), while for a fluid in contact with at convex cylinder of the same radius, one has \( \bar{H}_c = 1/2R \) and \( \bar{K}_c = 0 \). Much of the previous work on the curvature dependence focused on the first-order curvature correction, referred to as the Tolman length \( \delta \) which, for a convex spherical surface, would be given in terms of \( h \) by \( \delta \gamma_0 = -h/2 \).
The first theoretical treatment for the curvature dependence of \( \gamma \) for a hard-sphere fluid at a hard wall was developed within the so-called Scaled Particle Theory (SPT)\[16, 23, 26\], which is a theory of solvation that is based on an approximate determination of the work required to insert a spherical cavity (or hard-sphere solute) into a fluid. For this system, \( \gamma \) scales trivially with \( T \), that is, \( \gamma(\eta, T) = \gamma^*(\eta)kT/\sigma^2 \), where \( \gamma^* \) is the reduced interfacial free energy, \( k \) is Boltzmann’s constant, \( T \) is temperature and \( \sigma \) is the hard-sphere diameter of the fluid. The SPT result for \( \gamma^* \) for a hard-sphere fluid at a convex spherical surface of radius \( R \) is given by

\[
\gamma^*_\text{SPT}(\eta) = \frac{3\eta(2 + \eta)}{2\pi(1 - \eta)^2} + \frac{3\eta}{2\pi(1 - \eta)}R + \frac{\ln(1 - \eta)}{4\pi} \frac{1}{R^2} \tag{4}
\]

where \( \eta \) is the packing fraction, defined in terms of the single particle density \( \rho \) as \( \eta = \pi \rho \sigma^3 / 6 \). (For simplicity in what follows we measure distance in units of \( \sigma \) and energy in units of \( kT \) and drop the * superscript for reduced units.) The SPT treatment is consistent with the Hadwiger form of \( \gamma \) (Eq. 1) with \( h \) and \( \kappa \) equal to the coefficients of \( 1/R \) and \( 1/R^2 \) in Eq. 4 respectively. Note that, the value of the interfacial free energy between a fluid and a wall depends upon the precise definition of the dividing surface that determines the volume of the bounding wall. In this work, we define the dividing surface to be coincident with the wall surface.

Using classical density functional theory (DFT), Bryk, et al.\[25\], have examined the scaling of the interfacial free energy and the excess interfacial adsorption for hard-sphere fluid at both spherical and cylindrical hard surfaces. This work, which utilized the Fundamental Measure Theory (FMT) version of DFT proposed by Rosenfeld\[28\], determined \( \gamma \) for this system as a function of packing fraction and curvature with \( 1/R \) in Eq. 4 respectively. Note that, the value of the interfacial free energy between a fluid and a wall depends upon the precise definition of the dividing surface that determines the volume of the bounding wall. In this work, we define the dividing surface to be coincident with the wall surface.

In this work, we make use of an adsorption equation derived using Cahn’s extension\[29\] of the surface thermodynamics of Gibbs\[31\], namely,

\[
\left( \frac{\partial \gamma}{\partial P} \right)_T = v_N \tag{5}
\]

where the excess interfacial volume per unit area, \( v_N \), is defined by

\[
v_N = \frac{1}{AN_f} \left| \frac{V}{N_f} \right| = \frac{1}{A} \left( V - V_f N/N_f \right) \tag{6}
\]

where \( A \) is the interfacial area, \( V \) and \( N \) are the volume and number of particles, respectively, of a region containing the interface and \( V_f \) and \( N_f \) are the corresponding quantities for a region entirely within the bulk fluid.[11] This adsorption equation can be shown to be equivalent through a change of variables and Maxwell relations to the usual Gibbs adsorption equation

\[
\left( \frac{\partial \mu}{\partial P} \right)_T = \Gamma_N \tag{7}
\]

where \( \Gamma_N \) is the excess interfacial number of particles per unit area at the interface. Eq. 5 can be integrated with respect to pressure to give

\[
\gamma(P) = \gamma_{P=0} + \int_0^P v_N(P) dP \tag{8}
\]

where \( P \) is the pressure. For the hard-sphere/hard-wall case, \( \gamma_{P=0} = 0 \). Eq. 7 was recently used to determine \( \gamma \) for a hard-sphere fluid at a flat wall[11]. The excess interfacial volume can be related to the density profile \( \rho(r) \) by

\[
v_N = \frac{1}{\sigma^2} \int_0^\infty \left[ 1 - \frac{\rho(r)}{\rho_f} \right] r^i dr \tag{9}
\]

where \( i = 1 \) and 2 for the cylindrical and spherical geometries, respectively.

To determine \( \gamma \) for this system using Eq. 7 we use molecular-dynamics (MD) simulation to calculate \( v_N \) as a function of bulk packing fraction \( \eta = \rho \sigma^3 / 6 \) for a hard-sphere fluid in contact with spherical and cylindrical colloidal particles of radius \( R \) varying from 10 down to 0.5, over a range of \( \eta \) from 0.03 to 0.49, the upper limit being the fluid packing fraction at freezing. For the simulations, we use the algorithm of Rapaport[31] and use...
Eq. 9 directly to determine \( v_N \) in the simulations. For additional simulation details and plots of \( v(\eta; R) \) see the Supplemental Information.\(^{32}\)

Because we find \( v_N \) as a function of the packing fraction, not the pressure, we transform Eq. 6 to give

\[
\gamma(\eta) = \int_0^\eta v_N(\eta') \left( \frac{\partial P}{\partial \eta} \right)_T d\eta' \tag{9}
\]

To obtain the derivative of \( P \) with respect to \( \eta \) we use the KLM-low equation of state (EOS).\(^{33}\) This EOS has been shown to give five decimal place accuracy in the pressure even at high density when compared to high-quality simulations,\(^{34}\) so any errors introduced by its use are much smaller than the statistical error in the simulation data. To reduce the numerical integration error in evaluating Eq. 9 we subtract from the integrand the corresponding value obtained from the SPT (Eq. 4) - the corresponding SPT expression for the cylindrical surface is obtained from Eq. 4 by setting the coefficient of the \( 1/R^2 \) term to zero and dividing the coefficient of the \( 1/R \) term by two. Accurate calculation of the excess interfacial volume \( v \) at very low densities is difficult because of sampling issues; however, this quantity can be calculated exactly in the limit \( \rho \rightarrow 0 \). In this limit, we have

\[
\lim_{\rho \rightarrow 0} v_N(R) = \frac{1}{2} + \frac{a_1}{R} + \frac{a_2}{R^2} \tag{10}
\]

where \( a_1 \) and \( a_2 \) are constants equal to \( 1/4 \) (1/8) and 1/24 (0), respectively, for the spherical (cylindrical) wall.

For small values of \( R \), the statistical errors in \( v_N \) are larger for similar simulation lengths because the number of particles near the wall is relatively small. For the special case of \( R = 0.5 \) where the spherical surface is identical in size to the fluid particles, high precision results can be generated by recognizing that the density profile \( \rho(r) \) is equivalent to \( \rho_f g(r) \), where \( g(r) \) is the radial distribution in the bulk hard sphere fluid. For this value of \( R \), we use an MD simulation for a bulk hard-sphere fluid to calculate \( g(r) \) from which \( v_N \) can be determined with high precision. Alternatively, by replacing \( \rho(r) \) with \( \rho_f g(r) \) for \( R = 0.5 \), we have from Eq. 8 that

\[
v_N(R = 0.5) = 4 \int_{1/2}^\infty r^2 [1 - g(r)] dr \tag{11}
\]

\[
= -\frac{1}{\pi} \int_0^\infty 4\pi r^2 [g(r) - 1] dr - 1/6
\]

Using the compressibility equation from liquid state physics,\(^{35}\) the integral in the previous equation can be replaced with a term dependent upon the isothermal compressibility \( \kappa_T = \rho^{-1}(\partial \rho/\partial P)_T \) to yield

\[
v_N(\rho; R_s = 1/2) = -\frac{1}{\pi} (k T \kappa_T - \rho^{-1}) - 1/6 \tag{12}
\]

Using an equation of state, the isothermal compressibility \( \kappa_T \) can be determined analytically as a function of \( \eta \) allowing for an analytical calculation of \( v_N \), and thus \( \gamma \) for \( R = 1/2 \).

The calculated values of \( \gamma \) from our simulations for the spherical and cylindrical walls are plotted as functions of \( \eta \) in Fig. 1 for values of \( R \) ranging from the planar wall (\( R = \infty \)) to 0.5. At all densities, these figures show that at fixed \( \eta \), the interfacial free energy \( \gamma \) is a monotonically increasing function of \( 1/R \).

![FIG. 1. Color online. Top panel: Interfacial free energy between a hard-sphere fluid and a hard cylindrical colloidal particle as a function of \( \eta \) for several values of the radius, \( R \). Bottom panel: Same as the top panel except for the spherical surface. The inset shows the value of the excess volume, \( v_N \), for the spherical surface as a function of packing fraction for \( R = \infty \), 5 and 0.5. The symbols in this panel and in the inset are as indicated in the top panel legend.](image-url)

To test the validity of Hadwiger’s theorem for this sys-
tem, we fit the data shown in Fig. 1 to Eq. 1 to determine the constants $h$ and $\kappa$ for each $\eta$. The fit was performed using standard weighted quadratic (for the spherical case where $\bar{H} = 1/R$ and $\bar{K} = 1/R^2$) and linear (for the cylindrical case where $\bar{H} = 1/2R$ and $\bar{K} = 0$) least-squares regression. The weights in the regression were equal to the inverse of the statistical variance of the data points. The results of these fits are shown in Fig. 2 for packing fractions up to 0.42. A table of the fitted values for $\gamma_0$, $h$ and $\kappa$ is included in the Supplemental Information.\[32\] Also, shown in Fig. 2 are the results for $h$ and $\kappa$ from the SPT expression \[34\] and from the Rosenfeld DFT.\[27\] The DFT results agree remarkably well with the simulation results for the values of $\eta$ shown in Fig. 2. Most notable in these results is the fact that the estimates for $h$ for the spherical and cylindrical geometries shown in Fig. 2 are in excellent agreement, as predicted by Hadwiger’s theorem. The SPT prediction agrees well with the simulation results at low packing fractions, but underestimates $h$ and slightly overestimates $\kappa$ at packing fractions above about 0.25. Note that, as mentioned earlier, the value of $\gamma$ and, by extension, the Hadwiger coefficients $\gamma_0$, $h$ and $\kappa$ will depend upon the choice of dividing surface; however, the Hadwiger form (Eq. 1) is remains valid, albeit with modified coefficients.\[10\]

Above $\eta = 0.42$, however, significant deviations from the Hadwiger form were found. To quantify this deviation, we performed a cubic and quadratic weighted least-square regression with respect to $1/R$ on the sphere and cylinder data, respectively. The results of these calculation are plotted in Fig. 3. At packing fractions below 0.42, the cubic coefficient ($a_3$) for the spherical surface is zero within the estimated statistical error, consistent with Hadwiger’s theorem, but this coefficient diverges quickly from zero at packing fractions above 0.42, indicating a significant breakdown of the Hadwiger form at packing fractions approaching the freezing density ($\eta = 0.492$). The situation is similar for the quadratic coefficient ($a_2$) for the cylindrical case (Fig. 3 top panel): there is one value of $a_2$ at $\eta = 0.25$ that is marginally different from zero outside the error bars, but given its marginality and the small value of the coefficient, we do not view this deviation as significant. The origin of the divergence of the non-Hadwiger coefficients at high packing fraction can be seen in the inset in Fig. 1 in which the excess volume, $v_N$, is plotted for the spherical surface as a function of $\eta$ for $R/\sigma = \infty$, 5, 1 and 0.5. At high $\eta$, the excess volume $v_N$ for the planar wall ($R = \infty$) exhibits a downward curvature that is not present in the other values of $R$, making it impossible to fit $v_N(R)$ purely as a quadratic polynomial in $1/R$. It is possible that this anomalous decrease in $v_N$ for the planar wall is connected to the prefreezing transition that has been observed for the hard-sphere fluid at a hard planar wall at high packing fraction\[10, 36, 37\], and further analysis is underway. These results also indicate that the errors in the SPT at the intermediate packing fractions are not likely to be due to the omission of higher-order terms (beyond the quadratic for the sphere) in $1/R$, as has been proposed (see Ref. 38 for a review). The results here put severe upper bounds on the magnitude of any such higher-order terms. As an example, our calculated value for $\gamma$ at $\eta = 0.25265$ and $R = 1.0$ is 0.6595(6). The corresponding SPT value from Eq. 1 is 0.6711 - a difference of 0.0116(6), which is more than an order of magnitude larger than the estimated upper bound to the contribu-
FIG. 3. Bottom panel: Plot of the first non-Hadwiger coefficient (cubic, $a_3$) of $1/R$ in the curvature expansion of $\gamma$ for the hard-sphere fluid at a spherical colloidal particle as a function of packing fraction $\eta$. For clarity, the inset shows the data for $\eta < 0.42$ on a smaller scale. Top panel: Same as bottom panel, but for the cylindrical surface.

In summary, we have calculated the curvature dependence of the interfacial free energy between hard-sphere fluid and hard spherical and cylindrical colloidal particles of varying radius, $R$. These calculations have important applications in determining the solvation free energy of nanoscale objects. From our simulation results, we have verified that the predictions of Hadwiger’s theorem, which predicts that $\gamma$ for fluids at a bounding surface, under certain restrictions, is completely described by a linear combination of the average mean and Gaussian curvatures, are valid for the systems studied at low to moderate fluid packing fractions ($\eta < 0.42$) and have calculated the coefficients of this linear combination ($h$ and $\kappa$) as functions $\eta$. For these packing fractions, the Hadwiger form for $\gamma$ (Eq. 11) is shown to be valid for both convex spherical and cylindrical surfaces even down to $R = 0.5\sigma$, where the radius of the bounding surface is equal to that of the fluid particles. In addition, earlier DFT results based on Rosenfeld’s fundamental measure theory are found to be in excellent agreement with the results of the current simulations. At higher packing fractions ($\eta > 0.42$), however, significant deviations from the Hadwiger form are observed. The results of these simulations can serve as a useful reference model to determine the thermodynamics of the hydrophobic solvation of nanoscale particles.

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* Author to whom correspondence should be addressed; blaird@ku.edu

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