A comparison between simulation methods to compute interfacial tensions discussed at the example of the solid-liquid interface in hard spheres

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We computed the interfacial tension of the solid-liquid interface in the hard-sphere model by means of three simulation methods, which are used frequently to determine interfacial tensions in materials science. We investigate the drawbacks (in theory and practice) of the capillary wave method and conclude that - while it is a useful method for liquid-liquid interfaces - a precise computation of a solid-liquid interfacial tension requires very large computational resources. The interfacial stiffness values we obtained by two versions of the capillary wave method for the (100)-interface are \( \tilde{\gamma} = 0.458(9) k_B \sigma^{-2} \) and \( \tilde{\gamma} = 0.440(5) k_B T \sigma^{-2} \), where \( \sigma \) is the diameter of a sphere. The second method is thermodynamic integration with a specific integration scheme for liquids. We separated the bulk contribution to the total free energy from the interface contribution and obtained for the interfacial tension of the (100)-interface \( \gamma = 0.69(13) k_B T \sigma^{-2} \), \( \gamma = 0.65(10) k_B T \sigma^{-2} \) and \( \gamma = 0.67(5) k_B T \sigma^{-2} \), where the differences are due to details of the numerical integration scheme. We also used the pressure-tensor method, but found it to be too inaccurate for the hard sphere system to present a value for \( \gamma \) here.

I. INTRODUCTION

Monte Carlo simulation is widely used to compute the thermal equilibrium properties of atomistic materials models, such as e.g. the interfacial tension between different phases of a given substance. To compute the interfacial tension between the solid and the liquid phase, various methods have been introduced over the past 50 years. Not all of these methods share the same definition of the term “interfacial tension”, and if they do, then often the systematic errors due to finite size effects differ considerably. Hence the values predicted for a given system differ, even if the simulations have been carried out with high precision. In this article we compare and discuss three common methods to determine the solid-liquid interfacial tension at the example of the hard-sphere system.

Arguably, there are no hard-sphere-like atoms in nature, however the model captures the local ordering of atoms in the dense phases and has therefore been studied quite extensively in theory and colloid experiment. Hard spheres are also interesting as a model system in statistical physics, because their phase behaviour is athermal and the interfacial tension is determined solely by entropy. The hard sphere interfacial tension has been computed by many researchers over the past twenty years, partly producing contradictory results, and a final statement is still missing.

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II. METHODS

A. Thermodynamic Integration

Thermodynamic integration is a method to compute differences in thermodynamic potentials. Consider the case in which we would like to compute the difference in free energy between a system of interest with a Hamiltonian $H_{\text{int}}$ and a reference system with a Hamiltonian $H_{\text{ref}}$, for which we can evaluate the free energy exactly. Further, assume that both Hamiltonians are defined on the same state space. If we blend continuously from one Hamiltonian to the other by means of a combined Hamiltonian $H(\varepsilon) = \varepsilon H_{\text{int}} + (\varepsilon_1 - \varepsilon) H_{\text{ref}}$, where the “switching” parameter $\varepsilon$ is a real number, we obtain

$$F_{\text{int}} - F_{\text{ref}} := \Delta F = \int_0^{\varepsilon_1} d\varepsilon' \left\langle \frac{\partial H}{\partial \varepsilon} \right\rangle_{N,V,T,\varepsilon'}$$

(1)

The angular brackets indicate the average taken with respect to the canonical ensemble for a given value of $\varepsilon$. (We used a linear blending function here for simplicity, but it is straightforward to implement other functional forms of $H(\varepsilon)$ in order to optimize the performance of the method, see e.g. refs. 13,14.) The integrand $\left\langle \frac{\partial H}{\partial \varepsilon} \right\rangle_{N,V,T,\varepsilon'}$ can be computed by means of Monte Carlo sampling.

Thermodynamic integration requires a reference model which can be reached along a path that does not cross a first order phase transition. To construct an analytically solvable reference model for dense, disordered systems, we follow here the method introduced by Schmid and Schilling 15,16: We construct a reference configuration of particles $\{\vec{r}_{\text{ref}}^i | i = 1,\ldots,N\}$ from an arbitrary equilibrated configuration, where $\vec{r}_{\text{ref}}^i$ are the particle coordinates. Analogously to the Einstein crystal method 17, a set of attractive wells $\varphi_i(\vec{r}_i - \vec{r}_{\text{ref}}^i)$, each of which only interacts with one particle $i$, is placed at each coordinate $\vec{r}_{\text{ref}}^i$. Here we will use the same function for all wells and thus drop the index $i$ from $\varphi_i$. As the method is intended to study liquids, we need to take into account the possibility that a particle moves infinitely far away from its reference position. Thus, in contrast to the Einstein crystal method, the potential $\varphi$ needs to be cut off at a finite value to prevent the sampling of a diverging function. We introduce a cutoff radius $r_c$, above which the potential is zero, via $x = |\vec{r}_i - \vec{r}_{\text{ref}}^i|/r_c$.

For a linear reference potential

$$\varphi(x) = \begin{cases} 0 & \text{for } x \geq 1 \\ x - 1 & \text{for } x < 1 \end{cases}$$

(2)

the Helmholtz free energy can be obtained via integration by parts and using the Stirling approximation.

$$F_{\text{ref}}(\varepsilon_1) \approx N \left[ \ln \left( \frac{N}{V} \right) - \ln \left( 1 + \frac{6V_c}{V} \frac{1}{\varepsilon_1^3} \left( \varepsilon_1^3 - 1 - \varepsilon_1 - \frac{\varepsilon_1^2}{2} - \frac{\varepsilon_1^3}{6} \right) \right) - 1 \right]$$

(3)

where $V_c$ is the volume of a sphere with radius $r_c$.

Table 1 shows a list of other possible functional forms for $\varphi(x)$ and the free energies of the corresponding reference systems. We observed that equilibration times are shortest when using the linear well. However, if one uses molecular dynamics simulations instead of Metropolis Monte Carlo, potentials will be required that are differentiable in every point in space 18. Then the functional forms listed in Table 1 can be useful.

In the liquid-solid coexistence regime, the high density renders equilibration and decorrelation difficult, because particles may be blocked from moving into their wells for many
form of the potential well | free energy of the corresponding $N$-particle system $F(\varepsilon_1)$
---|---
$\varphi(x) = \begin{cases} 0 & \text{for } x \geq 1 \\ x^2 - 1 & \text{for } x < 1 \end{cases}$ | $N \left[ \ln \left( \frac{N}{V} \right) - \ln \left( 1 + \frac{3Vc}{4V} \frac{1}{\sqrt{\varepsilon_1}} \left( \sqrt{\pi} e^{\varepsilon_1} \text{erf}(\sqrt{\pi}) - 2 \sqrt{\varepsilon} - \frac{4}{3} \sqrt{\varepsilon_1^3} \right) \right) \right] - 1$
$\varphi(x) = \begin{cases} 0 & \text{for } x \geq 1 \\ x^3 - 1 & \text{for } x < 1 \end{cases}$ | $N \left[ \ln \left( \frac{N}{V} \right) - \ln \left( 1 + \frac{Vc}{V} \frac{1}{\varepsilon_1} (e^{\varepsilon_1} - 1 - \varepsilon_1)) \right) - 1 \right]$
$\varphi(x) = \begin{cases} 0 & \text{for } x \geq 1 \\ \sqrt{x} - 1 & \text{for } x < 1 \end{cases}$ | $N \left[ \ln \left( \frac{N}{V} \right) - \ln \left( 1 + \frac{720Vc}{V} \frac{1}{\varepsilon_1^7} (e^{\varepsilon_1} - \sum_{k=0}^{\infty} \frac{\varepsilon_1^k}{k!}) \right) - 1 \right]$
$\varphi(x) = \begin{cases} 0 & \text{for } x \geq 1 \\ x^{\frac{2}{n}} - 1 & \text{for } x < 1 \end{cases}$ | $N \left[ \ln \left( \frac{N}{V} \right) - \ln \left( 1 + \frac{n!Vc}{V} \frac{1}{\varepsilon_1^p} \left( \sum_{k=n+1}^{\infty} \frac{\varepsilon_1^k}{k!} \right) \right) - 1 \right]$

TABLE I. Free energy expressions for model systems with different well potentials with finite range in three dimensions. The function erf$(\ldots)$ denotes the error function. The last expression is a generalization of the two expressions preceding it.

Monte Carlo steps. To circumvent this problem we used a swap move as introduced in ref[15,16]

Finally, we need to take into account one specificity of the hard sphere model. As the reference Hamiltonian does not contain pair potentials, pair interactions need to be switched off via $\varepsilon$. To allow for this, we used a finite-valued interaction potential between the spheres - finite, but large enough for small $\varepsilon$ to ensure that the probability of two particles overlapping was negligible

$$V_{\text{sph}}(\mathbf{r}_i, \mathbf{r}_j, \varepsilon) = \begin{cases} A \left( 1 - \frac{\varepsilon}{\varepsilon_1} \right)^B & \text{for } |\mathbf{r}_i - \mathbf{r}_j| < \sigma \\ 0 & \text{for } |\mathbf{r}_i - \mathbf{r}_j| \geq \sigma \end{cases}$$

where $\sigma$ is the diameter of the hard spheres. We set $A = 40 k_B T$. To optimize the equilibration times for all $\varepsilon$, we used a polynomial of order $B = 4$ to switch off this pair potential.

In summary, the free energy difference between the hard sphere system and the reference system then has the form

$$\Delta F = \int_{\varepsilon'=0}^{\varepsilon' = \varepsilon_1} d\varepsilon' \left\langle - \frac{N_{\text{overlaps}} AB}{\varepsilon_1} \left( 1 - \frac{\varepsilon}{\varepsilon_1} \right)^{B-1} \right. + \sum_{i=1}^{N} \varphi \left( \frac{|\mathbf{r}_i - \mathbf{r}_i^{\text{ref}}|}{r_{\varepsilon}} \right) \right\rangle_{N,V,T,\varepsilon'}$$

We show in detail in section [III.B] how this expression can be used to compute the interfacial tension.

B. Capillary Waves

When two phases are in coexistence, one might assume that the interfacial area between them were kept as small as possible, because enlarging it is related to a free energy cost. However a minimal interface is not favorable in terms of entropy. Hence an interface will fluctuate and have a rough appearance. These fluctuations are called capillary waves.
The interfacial tension $\gamma$ can be inferred from the Fourier transform of the capillary wave height profile. For that purpose, one defines a coarse-grained pseudo-Hamiltonian $H^{19,20}$

$$H = \gamma \int dA ,$$

where the $dA$ is the surface area element and the integration is performed over the entire interface. (In fact, $H$ is a free energy rather than a Hamiltonian, as $\gamma$ is a coarse-grained, thermal quantity.) If the interface does not have overhangs, we can describe it by a height profile $z$ over a projected interfacial plane $(x, y)$. For weakly curved interfaces we rewrite $dA$ such that the Hamiltonian becomes

$$H = \gamma \int \int dx \, dy \left( 1 + \frac{1}{2} \left( \frac{\partial z}{\partial x} \right)^2 + \frac{1}{2} \left( \frac{\partial z}{\partial y} \right)^2 \right) .$$

Furthermore, we can express the interface in terms of its Fourier transform $z(\vec{k})$ with wave vectors $\vec{k} = (k_x, k_y)$. For simplicity, a system with a square interfacial plane $L_z \times L \times L$ is assumed. Using Parceval’s theorem one obtains the following expression$^{19}$.

$$H = \frac{\gamma L^2}{2} \sum_{\vec{k}} \vec{k}^2 \left| z(\vec{k}) \right|^2$$

The canonical partition function of the system described by this “Hamiltonian” takes the form of an integral over Gaussians.

$$Z = \prod_{\vec{k}} \int dz(\vec{k}) \exp \left( -\frac{\gamma L^2}{2k_BT} \sum_{\vec{k}} \vec{k}^2 \left| z(\vec{k}) \right|^2 \right)$$

This makes it straightforward to compute the variance, which leaves us with an expression containing the interfacial tension

$$\langle |z(\vec{k})|^2 \rangle = \frac{k_BT}{\gamma L^2 \vec{k}^2} .$$

(Note that if the normalization factor $1/L^2$ is applied to the forward Fourier transform instead of the inverse Fourier transform, the factor of $L^2$ will occur in the denominator in eqn. (10).)

Thus, in practice the interfacial tension can be obtained by sampling height profiles $z(\vec{r})$, performing a numerical Fourier transform on them and averaging over all obtained $|z(\vec{k})|^2$. This method is suitable for gas-liquid and liquid-liquid interfaces. However, the range of system sizes in which it can be applied is limited. On the one hand, the pseudo-Hamiltonian is coarse-grained, i.e. it requires a sufficiently large system to neglect the atomistic nature of the interface. On the other hand, the system must not be chosen too large, because eqn. (7) is restricted to small fluctuations with no overhangs. In addition, this approach cannot be applied directly to interfaces with a solid constituent, because in solids elasticity plays a major role (see figure 1 for an illustration). In this case, in eqn. (10) the interfacial tension $\gamma$ needs to be replaced by the interfacial stiffness $\tilde{\gamma}$.

One approach to separate the interfacial tension from the interfacial stiffness is to regard $\tilde{\gamma}$ as a sum of $\gamma$ and a curvature term $\gamma''$, the free energy of local elastic deformation.

$$\langle |z(\vec{k})|^2 \rangle = \frac{k_BT}{\gamma L^2 \vec{k}^2} = \frac{k_BT}{(\gamma + \gamma'') L^2 \vec{k}^2}$$
Computational methods to estimate $\gamma''$ are given in refs.\cite{10,21}. As these methods require additional assumptions on the coupling between the different mechanisms of surface deformation, we will here not attempt to separate the contributions from $\gamma$ and $\gamma''$, but we will report values for $\tilde{\gamma}$ instead.

C. Pressure Tensor

To check whether the simulated system was subject to mechanical stress, we computed the local excess pressure tensor. For hard spheres Allen showed\cite{22} that the following limit holds:

$$\frac{P_{ex}}{k_B T} = \lim_{\xi \to 0} \frac{1}{V \xi} \sum_{i<j}^{N} \phi_{ij} \left( \frac{\mathbf{r}_{ij}}{\mathbf{r}_{ij}} \right) \left( \frac{\mathbf{r}_{ij}}{\mathbf{r}_{ij}} \right)^2 \langle \rangle$$

Hence, to compute the pressure tensor approximately, one increases the hard sphere diameter $\sigma$ by a factor $1+\xi$ with $\xi \ll 1$ and counts the hard sphere overlaps that occur. The double sum is taken over all unique particle pairs. The $\alpha$-th component of the distance vector $\mathbf{r}_{ij}$ between the particle pair $i,j$ is given by $(\mathbf{r}_{ij})_{\alpha}$. $\phi_{ij}$ is a function that is either 1, if the particle pair $i,j$ is overlapping or 0 otherwise. The brackets $\langle \rangle$ denote the thermodynamic ensemble average.

III. SIMULATIONS

A. Setup

We carried out Metropolis Monte Carlo simulations with systems of different geometry and size, in cubic simulation boxes with periodic boundary conditions. The systems consisted of $N = 1.097 \ldots 38.993$ particles. The number density was $\rho = N/V = 0.991 \sigma^{-3}$ (up to single particle accuracy). The geometries of the systems could be divided into two classes. One class contained the systems with constant shorter dimensions $L_x = L_y = 9.3978 \sigma$ and a varying longer dimension $L_z = 12.5304 \sigma \ldots 125.304 \sigma$. The other class contained the systems with constant longer dimension $L_z = 62.652 \sigma$ and varying shorter dimensions $L = 6.2652 \sigma \ldots 25.0608 \sigma$. We chose these geometries such that the $z$-dimension was always significantly larger than the other two. This fixes the solid-liquid interface parallel to the $x$-$y$ plane. Thus its projected area is $L^2$. 

FIG. 1. Microscopic picture of different capillary waves at the liquid-solid interface. Left: fluctuation due to crystallization. Right: fluctuation due to elastic deformation of the crystal.
To obtain well equilibrated systems in coexistence, two smaller systems – one solid, the other liquid – were merged to form a larger system. The solid part was set up as an fcc-crystal with the equilibrium density of the solid at coexistence. The interface orientation of the crystal was (100). The liquid part was set up in a box of the same size, but not in a liquid state. Rather, it was set up in a crystal structure with the equilibrium density of the liquid at coexistence. First, the solid particles were kept fixed in their places and the liquid particles were equilibrated by performing $2N \cdot 10^6$ Monte Carlo (MC) steps. Some of the liquid particles crystallized on the fixed solid interface. Afterwards the whole system was simulated for another $2N \cdot 10^6$ MC steps to reach an equilibrium coexistence state.

To distinguish between solid and liquid particles, we used the bond order parameter described in ref.\textsuperscript{23}.

B. Thermodynamic Integration

The thermodynamic integration procedure was applied to all equilibrated systems in phase coexistence. We used one particle configuration for each system size as a reference configuration, which determined the coordinates of the potential well centers. The total free energy is given by

$$F(\varepsilon_0 = 0) = N \left[ \ln \left( \frac{N}{V} \right) - 1 \right. $$

$$ - \ln \left( 1 + \frac{6Vc}{V_1^\varepsilon_1} \varepsilon_1 \left( \varepsilon_1^3 - 3\varepsilon_1^2 - 3\varepsilon_1 + 1 \right) \right) $$

$$ + \int_{\varepsilon' = \varepsilon_1}^{\varepsilon = \varepsilon_1} \frac{d\varepsilon'}{\varepsilon_1} \left\langle \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1} \right\rangle_{N,V,T,\varepsilon'} $$

$$ + \sum_{i=1}^{N} \varphi \left( \frac{|r_i - r_{i,\text{ref}}|}{r_c} \right) \left( \frac{\varepsilon}{\varepsilon_1} \right)^{B-1},$$

where the ensemble average term in angular brackets needs to be determined by simulation. The parameter $\varepsilon$ that switches between the model system and the hard sphere system Hamiltonian was chosen to be in the range $\varepsilon \in [0, 40] k_BT$. One reason for this choice of the range is that test runs showed that 99% of particles find their respective wells at around $\varepsilon = 12k_BT$, and that on average fewer than 0.1% of all particles are outside of their wells at about $\varepsilon = 30k_BT$. In figure\textsuperscript{2} we show the dependence of the number of particles inside the potential wells on $\varepsilon$ for the system size $L = 25.0608\sigma$, $L_z = 62.652\sigma$, $N = 38,993$. (These numbers change slightly with system size, but they are close enough to allow us to use the same integration interval for all systems.) The integration range was sampled at 161 evenly distributed points (abscissas of the integral) which is, as we will see later, the main source of error of the method. We chose the cutoff radius to be $r_c = 2\sigma$, because the number of sweeps necessary to equilibrate the systems is minimized for this value.

To compute the integral in eqn. (13), for every abscissa an average value of $\partial H/\partial \varepsilon$ is required. Hence, after an equilibration period of $3N \cdot 10^5$ Monte Carlo steps, between $1 \cdot 10^5$ and $2 \cdot 10^4$ samples of this quantity were recorded (depending on the system size) with $200N$ decorrelation steps between each pair of samples. This is done separately for each abscissa. As the quantity $\langle \partial H/\partial \varepsilon \rangle$ is only obtained at a finite number of abscissas with a finite accuracy, the integral needs to be estimated numerically.

We used three different quadrature rules to approximate the integral: the trapezoidal rule, Simpson’s rule and Romberg-integration with Richardson-extrapolation. The error of the integral due to the uncertainty of the data points $\langle \partial H/\partial \varepsilon \rangle$ was estimated with a parametric bootstrapping method. For that we assumed that every data point stems from a Gaussian distribution. From these distributions random numbers were generated that were then used as artificial data sets for the integration scheme instead of the real data. From the obtained integral values of the artificial data sets one can then estimate an error for the
integral, and hence, for the free energy. However, the errors of this kind produce a relatively small error in the free energy (about $3 \cdot 10^{-3}\%$) and they will therefore be neglected. The numerical error due to the finite number of 161 abscissas is the major contribution to the total error.

Fig. 3 shows a thermodynamic integration curve for a system of size $L = 9.3978\sigma$, $L_z = 62.652\sigma$. The error bars are not visible, because they are smaller than the center dots of the diamonds. (Note that in the graph, $(\partial H/\partial \varepsilon)$ has been divided by the number of particles to allow for comparison with other systems.)

The free energy per particle $f \equiv F/N$ as a function of the system size and integration scheme is shown in figure 4 for varying $L_z$ and in figure 5 for varying $L$. The error of the free energies $s_{F/N} = 0.003k_B T$ was estimated by using 401 abscissas for the three smallest systems and comparing the results to the free energies obtained with 161 abscissas.

For an infinitely long system $L_z \to \infty$ the contribution to the free energy of the two interfaces $f_{\text{interface}}$ which are not varying in size $L$ vanishes. The remaining free energy per particle should thus be equal to the average bulk free energy per particle $f_{\text{bulk}}$. Moreover the interfacial contribution to the free energy per particle should be proportional to the inverse length of the system $1/L_z$. The proportionality hence contains $\gamma$ as follows

$$
\frac{F(L_z)}{N(L_z)} = f_{\text{bulk}} + f_{\text{interface}}(L_z)
= f_{\text{bulk}} + \frac{2\gamma L^2}{N(L_z)}
= f_{\text{bulk}} + \frac{2\gamma}{\rho L_z}
$$

(14)

This expression can be fitted to the free energies per particle obtained from systems with the same $L$ and varying $L_z$. For the fitting, we used the Levenberg-Marquardt algorithm provided by the R-package 'minpack.lm' to find the minimum of the sum of weighted least squares in parameter space. The fit curves are also shown fig. 4. The resulting interfacial tension values are

![Graph showing phase diagram](image.png)

**FIG. 2.** Ratio of particles $N_{\text{in}}/N$ that are in the attraction range of their respective potential wells for the system of size $L = 25.0608\sigma$, $L_z = 62.652\sigma$, $N = 38,993$. Note that the graph on the right-hand side is a enlarged version of the graph on the left-hand side and it shows all $\varepsilon$-values for which the ratio is close to 1.
FIG. 3. Integrand used for thermodynamic integration of a system of size $L = 9.3978\sigma$, $L_z = 62.652\sigma$, $N = 5483$. $\langle \partial H/\partial \varepsilon \rangle$ has been divided by the number of particles, to allow for comparison with other systems. Each data point is an average over 9000 independent samples. The error bars cannot be seen, because they are smaller than the center dots of the symbols.

$\gamma = 0.69(13)k_BT\sigma^2$, $\gamma = 0.65(10)k_BT\sigma^2$, $\gamma = 0.67(5)k_BT\sigma^2$ (15)

The three different values $\gamma_{\text{trap}}, \gamma_{\text{simp}}, \gamma_{\text{romb}}$ stem from the different integration methods.
FIG. 5. Free energy per particle as a function of the interfacial edge length \( L \) for different integration schemes. The longer dimension \( L_z \) is the same for all systems (\( L_z = 62.652\sigma \)).

used to perform the free energy calculation. The relative errors are quite large, but they can be reduced by improving the accuracy of the numerical quadrature and the number of simulated systems.

Since this method of calculating the free energy uses a wide range of system sizes, finite size effects on the interfacial tension are expected. Schmitz et al. identified three finite-size contributions by phenomenological considerations:

\[
\gamma = \gamma_\infty - P \frac{\ln(L_z)}{L^2} + Q \frac{\ln(L)}{L^2} + R \frac{1}{L^2}
\]

(16)

where \( P \geq 0, Q \geq 0 \) and \( R \) are constants. \( \gamma_\infty \) is the interfacial tension for the system with infinite size. \( P \) and \( Q \) only depend on the dimension of the system, on the statistical ensemble and on whether or not periodic boundary conditions are employed. In our case the constants are \( P = 3/4 \) and \( Q = 1/2 \) (3 dimensions, periodic boundary conditions, canonical ensemble). The constant \( R \) needs to be estimated. These corrections to the interfacial tension make up about 1% of the total free energy. As the relative errors of our interfacial tension values are quite large, we can neglect these corrections for now, however for more precise measurements taken with the method presented here, they need to be added to the fit function, eqn. (14).

As we expect a constant relation between the interfacial area \( L^2 \) and the free energy per particle, it is not possible to extract the interfacial tension from fig. 5 directly. However, if one knows the free energy of the solid and liquid bulk phases at their respective coexistence densities this is still possible. We determined the densities far away from the interface and set up separate simulations to determine the bulk free energies at these densities.

\[
\rho_{\text{coex}}^{\text{liquid}} = 0.9391(10) \frac{1}{\sigma^3}
\]

\[
\rho_{\text{coex}}^{\text{solid}} = 1.0410(10) \frac{1}{\sigma^3}
\]

\[
\frac{F_{\text{liquid}}}{N} = 3.745(3) k_B T
\]

\[
\frac{F_{\text{solid}}}{N} = 4.953(3) k_B T
\]

(17)
The strategy is then to subtract the bulk free energies $F_{\text{liquid}}$ and $F_{\text{solid}}$ weighted by the particle number in the respective phase from the free energy of the systems in coexistence to be left with the total interfacial free energy. (This approach is similar to interfacial tension calculations at hard walls, where the free energy difference between a system with and without hard walls is calculated\cite{26}.) However, the bond order parameter analysis did not allow for a sufficiently precise determination of the particle numbers in the two phases to produce a value for $\gamma$ that is as accurate as eqns. 15.

C. Pressure Tensor Analysis

In those systems which contain two phases at coexistence, we expect the pressure to be homogeneous in the $x$- and $y$-direction parallel to the interface and inhomogeneous in the $z$-direction normal to the interface. Thus computing the spatial profile of the pressure tensor in the $z$-direction can be helpful in detecting systems that are out of thermal equilibrium. Due to the periodic boundary conditions, the system as a whole can shift freely in the box without a free energy cost. Using the bond-order parameter, we map every particle to a phase. We then compute the centers of mass of the phases and translate every particle by an amount that puts the center of mass of the solid phase into the center of the box.

The pressure tensor was computed for all systems in coexistence. The bin width was chosen to be as small as possible, without making the statistical error too large to conclude whether the systems was free of stresses ($\Delta z = 0.25 \sigma$). Fig. 6 shows the pressure tensor for the system with $L = 9.3978 \sigma$, $L_z = 62.652 \sigma$. The scaling factor was chosen close enough to $\xi = 0$ such that the systematic effects only play a minor role, but large enough that statistics allow to resolve potential stresses ($\xi = 3 \cdot 10^{-4}$). The measured values are an average over $2 \cdot 10^5 \ldots 7 \cdot 10^6$ samples (depending on the system size) with 200 sweeps between each sample.

None of the systems showed any unusual behavior in the pressure tensor, thus they are stress-free and in equilibrium. All off-diagonal elements are compatible with zero within their margin of error. Far from the interface one should recover bulk system behavior. Thus, the diagonal elements should approach the same value there, which they do (as can be seen in the lower panel of figure 6 for one example).

With eqn. \cite{12} we can also compute the coexistence pressure of the systems by averaging

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pressure_tensor.png}
\caption{Pressure tensor profile for $L_z = 62.652 \sigma$ and $L^2 = (9.3978 \sigma)^2$.}
\end{figure}
the diagonal elements $P_{\text{coex}} = (P_{xx} + P_{yy} + P_{zz})/3$. Using a finite $\xi$ leads to a variance-bias trade-off problem. For smaller values of $\xi$ the probability that two spheres overlap is relatively small which leads to bigger statistical fluctuations. However, increasing $\xi$ to reduce the statistical error leads to a systematic error, because the assumptions that were made to derive eqn. (12) do not hold anymore. To obtain the best possible value, we performed the calculations for different $\xi = 1 \cdot 10^{-2}, 2 \cdot 10^{-3}, 4 \cdot 10^{-4}, 8 \cdot 10^{-5}$. With these data it is possible to extrapolate to $\xi = 0$ by means of linear regression. Thus, we can obtain a fairly good approximation of the coexistence pressure. (Note that the ideal gas pressure ($P_{\text{id}} = \rho k_B T$) was added to all measured pressure values to obtain the total pressure.)

The extrapolations for different system sizes are shown in figure 7. For small systems one can see that there are finite size effects lowering the pressure. Thus, we excluded these values from the computation of the average pressure value. Depending on the system size the pressure was computed between $4 \cdot 10^4$ and $3 \cdot 10^6$ times with 200 sweeps between each pair of samples. The error is estimated based on the variance of the fit parameters. In conclusion we obtain

$$P_{\text{coex}} = 11.582(10) \frac{k_B T}{\sigma^3}$$

(18)

This result agrees with many previous studies, but is is slightly larger – however statistically more accurate – than most of them (e.g. $P_{\text{coex}} = 11.5727(10) \frac{k_B T}{\sigma^3}^{[44]}$ with umbrella sampling, or $P_{\text{coex}} = 11.57(10) \frac{k_B T}{\sigma^3}^{[27]}$.

One can see that on approach of $\xi = 0$ the pressure value might increase more slowly than linearly, but the error bars are too big to be certain. Thus, our pressure value for the coexistence might by systematically slightly larger than the true value.
FIG. 8. Sketch of a solid-liquid (orange-blue online) interface. The vertical black lines mark the borders of the bins. The (green) dots show the two separate interface estimates per bin that emerge from the method described in the text. The horizontal (green) line denote the average of the two interface estimates.

D. Capillary Wave Analysis

To obtain the interfacial tension $\gamma$ from the shape of the interface, we carry out an analysis of the capillary wave spectrum. First, we need to define the height profile $z(x, y)$. There are many methods to define an interface in general and they usually involve parameter fine tuning. However, certain scientific questions already exclude certain methods. Capillary wave theory only holds for small wave vectors (large wave lengths), thus a fairly low resolution of the interface is sufficient. But no smoothing or interpolation method should be used (as e.g. Shepard interpolation\textsuperscript{10}), because this might alter the Fourier components corresponding to a given interface.

We used the following procedure: We divided the interface into bins of quadratic shape with edge length $l \approx 0.7\sigma$. (The edge length $l$ varied slightly to fit an integer number of bins into the interface, e.g. $L = 11\sigma \Rightarrow l = 0.6875\sigma, N\text{bins} = 16$). For every bin we then detected all particles that intersect the line that is perpendicular to the planar (projected) interface through the center of a bin (see figure 8 for a sketch). The detected particles were then separated according to their phases and for each phase the particle that was the farthest away from the bulk was taken as the interface particle. As a result there are always two interface particles for every bin. We then added a correction term $\Delta l$ to the $z$-coordinate of the interface particles to take their diameter into account. This correction term prevents neighboring bins from having the same height value due to sharing the same interface particle. The final height of the interface in a given bin then reads

$$z(x_m, y_n) = \frac{1}{2} (z_{mn,s} + \Delta l_s + z_{mn,l} - \Delta l_l) \quad (19)$$
FIG. 9. Height profiles of a system with size $L = 25.0608 \sigma$, $L_z = 62.652 \sigma$, $N = 38993$ for different simulation snapshots.

\[
\Delta l_\alpha = \sqrt{\left(\frac{\sigma}{2}\right)^2 - (x_m - x_{mn,\alpha})^2 - (y_n - y_{mn,\alpha})^2}.
\]  

(20)

where the coordinates $(x_m, y_n)$ mark the center of each bin, $z_{mn,\alpha}$ is the z-coordinate of the corresponding interface particle in the solid phase $(z_{mn,1}$ respectively in the liquid), and the other two coordinates of the interface particles are given by $x_{mn,\alpha}$ and $y_{mn,\alpha}$, $\alpha = s, l$. To center the fluctuations around $z = 0$ we subtracted a constant value from all height values $z(x_m, y_n)$. Thus, the $\vec{k} = 0$ mode of the Fourier transform vanishes. On rare occasions particles far from the interface were recognized falsely as the opposite phase. The algorithm would then recognize these particles as interface particles. However, they could easily be detected by regarding the sign and absolute value of the difference between the $z$-coordinates of the interface particles. We replaced these particles by the next particle that was considered belonging to the interface.

After obtaining the height profile, the Fourier transform was carried out. In fig. 9 and 10 the height profiles in real and in reciprocal space are shown for a system with size $L = 25.0608 \sigma$, $L_z = 62.652 \sigma$, $N = 38993$. We obtained the interfacial stiffness in two different ways: One method uses the relation between $\langle |z(\vec{k})| \rangle$ and $1/\vec{k}^2$ (see fig. 11 for $L = 25.0608 \sigma$, $L_z = 62.652 \sigma$, $N = 38993$.) According to eqn. (11), we expect to find a linear relation for small wave vectors. Knowing the interfacial area $L^2$, the interfacial stiffness can be computed from the slope given by a linear regression of the data. However, even for small wave vectors we obtained data that is not even close to matching the linear regression line within the margin of error. This problem becomes even more apparent, when plotting the interfacial stiffness values directly obtained from the data via

\[
\tilde{\gamma} = \frac{k_BT}{\langle |z(\vec{k})|^2 \rangle L^2 \vec{k}^2}.
\]

(21)
which should remain constant with respect to varying \( \vec{k} \). Fig. 12 shows this relation for a system with size \( L = 25.0608\sigma, L_z = 62.652\sigma, N = 38993 \).

In the second method the average and the variance of the “direct” interfacial stiffness values are computed. The wave vector above which eqn. 21 is expected to fail is approximately \( |\vec{k}| = 1.0\sigma^{-1} \). However, below this value \( \tilde{\gamma} \) still shows large deviations (up to 20\%) from a constant within the margins of error (as estimated based on the variance). This effect has also been observed in other studies\(^8\). The source of the discrepancy is that fluctuations with large wave lengths need more Monte Carlo steps to be decorrelated than fluctuations on shorter wave length (which is equally true for MD simulations). Hence, the large deviations at small \( |\vec{k}| \) are due to under-sampling and the estimate of the error-bars is wrong as it ignores correlations between samples. Unfortunately, the computational time

\[ \langle |z(\vec{k})|^2 \rangle / \sigma^2 \]

FIG. 10. \( |z(\vec{k})|^2 \) averaged over \( 2 \cdot 10^4 \) samples.

\[ \langle |z(\vec{k})|^2 \rangle / \sigma^2 \]

FIG. 11. \( \langle |z(\vec{k})| \rangle \) as a function of \( 1/|\vec{k}|^2 \) for a system of size \( L = 25.0608\sigma, L_z = 62.652\sigma, N = 38993 \). The grey (orange online) diamonds indicate the data used to compute the interfacial stiffness. The error bars are barely visible in the data points.
\[ \tilde{\gamma} = 0.45(33) k_B T \sigma^2 \]

FIG. 12. Interfacial stiffness for \( L = 25.0608 \sigma \), \( L_z = 62.652 \sigma \), \( N = 38993 \) as a function of \( |\vec{k}| \), which should be constant for small \( |\vec{k}| \). The grey (orange online) diamonds indicate the data used to compute the interfacial stiffness.

FIG. 13. Height profile in real space for a system of size \( L = 25.0608 \sigma \), \( L_z = 62.652 \sigma \), \( N = 38993 \) averaged over the entire simulation run.

required to decorrelate the height profile for large wave lengths might not even be accessible with current computational resources. (We used 50 000 CPU hours for the capillary wave analysis presented here.) (This problem also interferes with the interest in increasing the system size to approach smaller \( |\vec{k}| \), because even larger wave lengths will take even longer to decorrelate.)

To visualize the effect of under-sampling at large wave lengths, the average of all height profile samples of the system with size \( L = 25.0608 \sigma \), \( L_z = 62.652 \sigma \), \( N = 38993 \) is shown
in figure 13. The small wave length fluctuations are completely averaged out, but the large wave length fluctuations are clearly visible.

In fig. 14 we show $\tilde{\gamma}$ for different choices of the bin width. This analysis was performed for the system with size $L = 25.0608\sigma$, $L_z = 62.652\sigma$, $N = 38993$. The linear regression method seems to be stable, because it yields similar results for all three values of the bin width. The direct method, however, seems to be very unreliable in that respect. It yields $\tilde{\gamma} = 0.413(69) k_B T/\sigma^2$ for the bin width $l = 0.353\sigma$, $\tilde{\gamma} = 0.450(33) k_B T/\sigma^2$ for the bin width $l = 0.716\sigma$ and $\tilde{\gamma} = 0.464(72) k_B T/\sigma^2$ for the bin width $l = 1.474\sigma$. For systems with small interfaces the number of data points which can be used for capillary wave analysis is very limited. Thus, we left them out of the calculation of the average value of the interfacial stiffness.

In summary, with the linear regression method we obtained an average stiffness of

$$\tilde{\gamma} = 0.440(5) \frac{k_B T}{\sigma^2} .$$

(22)

With the direct approach we obtained an average stiffness of

$$\tilde{\gamma} = 0.458(9) \frac{k_B T}{\sigma^2} .$$

(23)

IV. CONCLUSION AND DISCUSSION

We have compared several methods to compute the solid-liquid interfacial tension in hard spheres. Our results for the interfacial tension of the (100)-interface are $\gamma = 0.69(13) k_B T \sigma^{-2}$, $\gamma = 0.65(10) k_B T \sigma^{-2}$ and $\gamma = 0.67(5) k_B T \sigma^{-2}$, depending on the integration scheme. These values agree with predictions by density functional theory,
e.g. $\gamma = 0.664(2) k_B T \sigma^{-2}$, as well as with simulation results obtained with the cleaving method, e.g. $\gamma = 0.62(2) k_B T \sigma^{-2}$. However one of the more recent studies using the cleaving method produced a slightly lower value of $\gamma = 0.596(2) k_B T \sigma^{-2}$, and capillary wave analysis yielded even lower values, e.g. $\gamma = 0.56(2) k_B T \sigma^{-2}$ from. Thus the problem is not solved. We have discussed the advantages and disadvantages of the capillary wave method and the method via thermodynamic integration, which are computationally equally expensive, but subject to different sources of finite-size effects and numerical errors.

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