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Comparison of simple perturbation-theory estimates for the liquid–solid and the liquid–vapor interfacial free energies of Lennard-Jones systems

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The most naive perturbation method to estimate interfacial free energies is based on the assumption that the interface between coexisting phases is infinitely sharp. Although this approximation does not yield particularly accurate estimates for the liquid–vapor surface tension, we find that it works surprisingly well for the interface between a dense liquid and a solid. As an illustration we estimate the liquid–solid interfacial free energy of a Lennard-Jones system with truncated and shifted interactions and compare the results with numerical data that have been reported in the literature. We find that the agreement between theory and simulation is excellent. In contrast, if we apply the same procedure to estimate the variation of the liquid–vapor surface tension, for different variants of the Lennard-Jones potential (truncated/shifted/force-shifted), we find that the agreement with the available simulation data is, at best, fair. The present method makes it possible to obtain quick and easy estimate of the effect on the surface free energy of different potential-truncation schemes used in computer simulations.

Keywords: Surface free energy; Liquid–solid; Tail corrections; Liquid–vapor

1. Introduction

In computer simulations of classical many-body systems, the intermolecular potential is often truncated at a finite distance to reduce the numerical computational cost, which, inevitably, changes the system properties such as energy, pressure, etc.

Standard “tail corrections” exist to compensate for the truncation errors in uniform systems with sufficiently short-ranged potentials (see e.g. Ref. [1]).

In contrast, in inhomogeneous systems, calculations of the tail corrections are not straightforward, and they might not be small compared to the reference values.

In particular, expressions for the tail corrections of the liquid–vapor interfacial free-energy density (γ) in a Lennard-Jones system, were derived using the thermodynamic perturbation theory [2–4]. Chapela *et al.* [5] employed the Kirkwood–Buff–Fowler’s formula to compute the correction to the exact surface tension while postulating a hyperbolic tangent shape for the interfacial profile, and their results were subsequently

refined by Blokhuis *et al.* [6] and Mecke *et al.* [7]. These results were used in Ref. [5–7] to compute the free energy of the liquid–vapor interface in a Lennard-Jones fluids with truncation of the intermolecular potential, adopting the full Lennard-Jones system as a reference.

Interestingly, this approach can also be used for a “rule-of-thumb” estimate of the liquid–solid interfacial free energy, as we show in the present paper. The following assumptions on the interface profile and the reference system seem to be in order in this case. The simplest interfacial profile goes back to Laplace [8], who treated it as a step function in the density. Not surprisingly, it does not yield a particularly good estimate for the liquid–vapor surface tension, where the dividing surface is rough and not well defined, especially close to the critical point. However, one might expect this approximation to be much better for the sharp interface between crystal and dense (and rather incompressible [9]) liquid, where role of fluctuations is much smaller. As a reference system, the hard-sphere model can be exploited by means of the Weeks, Chandler and Andersen’s [10]

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approach. Hard-sphere system exhibits a liquid–solid interface under the appropriate conditions. This again simplifies situation in comparisons with the liquid–vapor interface, where the full Lennard-Jones system needs to be taken as a reference (the hard-sphere do not exhibit a liquid–vapor phase separation).

Thus, we use perturbation theory approach in the present paper to estimate the surface free energy of truncated-force-shifted Lennard-Jones crystals in contact with its melt. For the sake of comparison, we employ the same approach to estimate the difference in the liquid–vapor surface tension of truncated and untruncated LJ models. Although it is not particularly good in the latter case, we include the results for future reference, because the relevant simulation data appeared to be rather scattered in the literature.

2. Method

We aim to estimate the interfacial free energy of particles interacting via a modified [truncated and (force) shifted] Lennard-Jones potential, using either the hard-sphere system (for solid–liquid) or the full Lennard-Jones model (for liquid–vapor) as the reference state.

$$\gamma_{LJ'} = \gamma_{\text{ref}} + \gamma_P. \quad (1)$$

We assume that, γ_{ref} is known. Below, we list the various contributions to the perturbation. In all cases, we make the “Laplacian” assumption that the interface separating the two phases has a step profile. The overall perturbation is additive. We have to consider three possible “perturbation” terms: $v_{P1}(r)$, $v_{P2}(r)$ and $v_{P3}(r)$ contributions to the potential.

$v_{P1}(r)$ is a constant term, that is needed to shift a truncated potential to zero at the cut-off radius r_c :

$$v_{P1}(r) = \begin{cases} -v_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c. \end{cases} \quad (2)$$

It guarantees the continuity of the Lennard-Jones potential (v_{LJ}) at r_c . v_{P1} is positive, as $v_{LJ}(r_c) < 0$. $v_{P2}(r)$ is the perturbation, that removes the long-range part of the LJ potential (for $r \geq r_c$):

$$v_{P2}(r) = \begin{cases} 0 & \text{for } r < r_c \\ -4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & \text{for } r \geq r_c. \end{cases} \quad (3)$$

Finally, only in the truncated and force-shifted potential, we also use $v_{P3}(r)$, a term that ensures the continuity of the first derivative of the potential at r_c

$$v_{P3}(r) = \begin{cases} -(r - r_c)v'_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c, \end{cases} \quad (4)$$

where $v'_{LJ}(r)$ is $(24\epsilon(\sigma^6/r)[(1/r^6) - (2\sigma^6/r^{12})])$. $v_{P3}(r)$ is also positive, as the first derivative is positive for $r > r_c$.

We can now, easily estimate the contributions of these three perturbations to the surface free energy, that follows Rowlinson and Widom’s prescription [2]: the contribution due to $v_{P1}(r)$, is denoted by γ_{P1} and given by:

$$\begin{aligned} \gamma_{P1} &= -\frac{1}{2}(\rho_2 - \rho_1)^2 \int_0^{r_c} dz_1 \int_{z_1}^{r_c} dr (-v_{LJ}(r_c))(2\pi(r^2 - z_1 r)) \\ &= \frac{\pi}{8} v_{LJ}(r_c) r_c^4 (\Delta\rho)^2. \end{aligned} \quad (5)$$

For $r_c = 2.5\sigma$, $v_{LJ}(r_c) \approx -0.0163\epsilon < 0$, and we obtain: $\gamma_{P1} = -0.25(\Delta\rho)^2$, being $\Delta\rho = (\rho_2 - \rho_1)$.

γ_{P2} , the contribution due to $v_{P2}(r)$ is:

$$\begin{aligned} \gamma_{P2} &= -\frac{1}{2}(\rho_2 - \rho_1)^2 \int_0^{r_c} dz_1 \int_{z_1}^{r_c} dr \left\{ -4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \right\} \\ &\quad \times (2\pi(r^2 - z_1 r)) \Theta(r - r_c) \\ &= 2\pi\epsilon \left[\frac{\sigma^{12}}{8r_c^8} - \frac{\sigma^6}{2r_c^2} \right] (\Delta\rho)^2. \end{aligned} \quad (6)$$

For $r_c = 2.5\sigma$, we obtain: $\gamma_{P2} = -0.50(\Delta\rho)^2$.

Finally, γ_{P3} (the contribution due to $v_{P3}(r)$) is:

$$\begin{aligned} \gamma_{P3} &= -\frac{1}{2}(\rho_2 - \rho_1)^2 \int_0^{r_c} dz_1 \int_{z_1}^{r_c} dr [-(r - r_c)v'_{LJ}(r_c)] \\ &\quad \times (2\pi(r^2 - z_1 r)) \\ &= -\frac{\pi}{40} v'_{LJ}(r_c) r_c^5 (\Delta\rho)^2. \end{aligned} \quad (7)$$

For $r_c = 2.5\sigma$, $v'_{LJ}(r_c) \approx 0.039(\epsilon/\sigma) > 0$, and $\gamma_{P3} \approx -0.3(\Delta\rho)^2$.

Thus, by means of $\gamma_{P1} + \gamma_{P2}$ we can compute the corrections needed to a truncated Lennard-Jones potential, by means of $\gamma_{P1} + \gamma_{P2} + \gamma_{P3}$ the corrections for a truncated-force-shifted one.

3. Results

3.1 Calculation of the liquid–solid interfacial free energy

A numerical calculation of the solid–liquid interfacial free energy of a Lennard-Jones system (more precisely: truncated and force-shifted LJ (TSF)) was reported in 1986 by Broughton and Gilmer [11] and, more recently, by Davidchack and Laird [12]. Both sets of authors considered the [100], [110] and [111] surfaces. In addition, Davidchack and Laird computed the interfacial free energy for the same faces of a hard sphere crystal. It so happens that the reduced density difference between solid and liquid for the TSF-LJ system at the triple-point temperature considered in both Refs [11,12] is very nearly equal to that of the hard-sphere system, making the system an ideal target for the liquid–solid flat-interface version of the Fowler–Kirkwood–Buff theory.

Table 1. Liquid–solid interfacial free energy computed at difference crystalline orientations for hard-sphere [13], present perturbation-theory estimate of $\gamma_{\text{TSF-LJ}}$, estimate of $\gamma_{\text{TSF-LJ}}$ by Davidchack and Laird [12], Broughton and Gilmer [11].

	$\gamma_{\text{HS}}[k_B T/\sigma_{\text{HS}}^2]$ [13]	$\gamma_{\text{HS}}(\epsilon/\sigma^2)$	$\gamma_{\text{TSF-LJ}}$ (present work)	$\gamma_{\text{TSF-LJ}}$ [12]	$\gamma_{\text{TSF-LJ}}$ [11]
[111]	0.546	0.316	0.342	0.347(3)	0.35(2)
[110]	0.557	0.323	0.349	0.360(3)	0.36(2)
[100]	0.574	0.333	0.359	0.371(3)	0.34(2)
Average	0.559	0.324	0.35	0.359	0.35

In the bottom line of the table, we compare the corresponding values of γ averaged (without weighting) over the different crystal faces.

The TSF-LJ potential has the following form:

$V_{\text{TSF-LJ}}(r)$

$$= \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + c_1 & \text{for } r \leq 2.3\sigma \\ c_2 \left(\frac{\sigma}{r} \right)^{12} + c_3 \left(\frac{\sigma}{r} \right)^6 + c_4 \left(\frac{\sigma}{r} \right)^{-2} + c_5 & \text{for } 2.3\sigma < r \leq 2.5\sigma \\ 0 & \text{for } r > 2.5\sigma, \end{cases} \quad (8)$$

where $c_1 = 0.16132\epsilon$, $c_2 = 3.1366 \times 10^3 \epsilon$, $c_3 = -6.8069 \times 10^1 \epsilon$, $c_4 = 0.083312\epsilon$, and $c_5 = 0.74689\epsilon$ (see Ref. [11]). Our computed values for the interfacial free energies of the TSF-LJ are listed in table 1. For the perturbation-theory estimate of the interfacial free energy, we use the full Lennard-Jones as the reference system. To compute its contribution, as suggested by Weeks, Chandler and Andersen [10], we separate the LJ interaction potential in a repulsive term (the hard-sphere, that is ∞ for $r \leq 2^{1/6}\sigma$ and 0 for $r > 2^{1/6}\sigma$) and an attractive perturbation term ($-\epsilon$ for $r \leq 2^{1/6}\sigma$, and $4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ for $r > 2^{1/6}\sigma$).

To map the repulsive LJ system onto a hard-sphere system, we use the Barker–Henderson rule [14] to compute the equivalent hard-sphere radius of continuous repulsive potential:

$$\sigma_{\text{HS}} = \int_0^\infty [\exp^{-\beta v_{\text{R}}(r)} - 1] dr, \quad (9)$$

where σ denotes the effective hard-sphere diameter of particles interacting via the Lennard-Jones potential, and $\beta = \epsilon/(k_B T) = 1/T^*$ assuming ϵ and k_B equal to 1. As is obvious from equation (9), σ_{HS} is a function of temperature, but not of the density. Calculating equation (9) at $T^* = 0.617$, the temperature where Broughton and Gilmer computed γ_{LS} , we find that $\sigma_{\text{HS}} = 1.032\sigma$.

We then compute the LJ liquid–solid interfacial free energy, by adding to the hard-sphere term the perturbation coming from the attractive part of the potential, and estimate the interfacial free energy of the TSF-LJ potential by including the perturbation terms computed according to equation (8).

The following table 1 contains the values of the hard-sphere liquid–solid interfacial free energy computed by Davidchack [13] (first column: in units of $[k_B T/\sigma_{\text{HS}}^2]$, second column: in units of $[\epsilon/\sigma^2]$); our estimate for γ based on the perturbation theory, assuming a step profile in

the density; at last, the numerical data for the TSF-LJ potential reported by Davidchack and Laird [12] and by Broughton and Gilmer [11].

As can be seen from the table, the perturbation-theory results are in rather good (2–3%) agreement with the numerical data. Interestingly, the variation of the surface free energy with crystal face appears to be largely due to the corresponding variation in the hard-sphere reference system.

Such an agreement between simple perturbative calculations and simulations might be caused by some cancellation of errors—on one side, an assumption of a infinitely sharp interface (typically, the dividing surface is about one particle diameter thick), and on the other side, the disregard of the dense liquid layering in proximity of the interface with the solid.

Below, we use the same approach to estimate the difference in surface free energy of various Lennard-Jones-like models (untruncated, truncated and shifted, truncated and force-shifted). In this case, we do *not* use a hard-sphere reference system (as this system has no liquid–vapor interface). Rather we use the full (untruncated) LJ system as our reference system.

However, in the liquid–vapor case, the perturbation theory approach with the sharp interface seems to be too simplistic, possibly due to the fact that for liquid and vapor at coexistence, the interface is fairly rough and not well defined, especially close to the critical point.

3.2 Calculation of the liquid–vapor surface tension

According to the expressions given in the method section, the correction to the full Lennard-Jones surface tension due to truncation and shifting of the potential at $r_c = 2.5\sigma$ is of the order of $\gamma_{\text{P1}} + \gamma_{\text{P2}} = -0.75(\Delta\rho)^2$. Considering the full Lennard-Jones as the reference system of our perturbation calculation, we summarize our resulting predictions for the truncated and shifted Lennard-Jones potential in the following tables, where we also show the numerical data, where available.

The data for the full (or “almost full”) Lennard-Jones potential (table 4) were taken from Potoff and Panagiotopoulos [15], Errington [16], Trokhymchuk and Alejandre [17] (truncated Lennard-Jones with $r_c = 5.5\sigma$), Holcomb, Clancy and Zollweg [18] (truncated Lennard-Jones with $r_c = 6.3\sigma$), Mecke, Winkelmann and Fischer [7] (truncated Lennard-Jones with $r_c = 6.5\sigma$), and Nijmeijer, Bakker and Bruin [19] (truncated Lennard-Jones with

Table 2. Comparison with literature data for the surface tension of various Lennard-Jones models for $0.42 \leq T^* \leq 0.62$. $\Delta\rho$ (in reduced units) is the density difference between ρ_l (liquid) and ρ_v (vapor).

$\Delta\rho$	ρ_l	ρ_v	T	γ_{LJ}	γ_{TS-LJ}	Source
0.46 ± 0.02	0.5794	0.1030	1.0	—	0.082 ± 0.008	[17]
0.46 ± 0.02	0.5694	0.0987	1.0	—	0.076 ± 0.002	[20]
0.46 ± 0.02	0.565	0.103	1.0	—	0.088 ± 0.007	[19]
0.46 ± 0.02	0.580	0.100	1.0	0.124 ± 0.001^a	-0.004^d	
0.55 ± 0.02	0.6213	0.0068	0.95	—	0.154 ± 0.003	[20]
0.55 ± 0.02	0.618	0.0068	0.95	0.224 ± 0.001^b	-0.003^d	
0.59 ± 0.01	0.6505	0.0518	0.92	—	0.197 ± 0.016	[17]
0.59 ± 0.01	0.645	0.055	0.94	0.343 ± 0.002^c	0.08^d	
0.62 ± 0.02	0.6619	0.0454	0.90	—	0.223 ± 0.003	[20]
0.62 ± 0.02	0.662	0.0439	0.90	—	0.224 ± 0.009	[19]
0.62 ± 0.02	0.671	0.040	0.90	—	0.23 ± 0.02	[21]
0.62 ± 0.02	0.6644	0.0444	0.90	—	0.227 ± 0.016	[17]
0.62 ± 0.02	0.666	0.046	0.90	0.46 ± 0.03^a	0.17^d	

T is the temperature for each $\Delta\rho$. $\gamma_{TS-LJ} = \gamma_{LJ} + \gamma_{P1} + \gamma_{P2}$. The numerical data for γ_{LJ} of the full Lennard-Jones potential come from Refs.[15] (superscript a) [17] (superscript b) and [16] (superscript c). Our data are indicated by in superscript d.

Table 3. Continuation of table 2.

$\Delta\rho$	ρ_l	ρ_v	$T/T_c(T)$	γ_{LJ}	γ_{TS-LJ}	Source
0.67 ± 0.03	0.6973	0.0307	0.85	—	0.303 ± 0.003	[20]
0.67 ± 0.03	0.706	0.027	0.85	—	0.29 ± 0.07	[21]
0.67 ± 0.03	0.699	0.029	0.745	0.56 ± 0.02^a	0.22^d	
0.71 ± 0.01	0.7306	0.0196	0.80	—	0.408 ± 0.018	[17]
0.71 ± 0.01	0.7315	0.195	0.80	—	0.39 ± 0.01	[19]
0.71 ± 0.01	0.731	0.02	0.80	—	0.39 ± 0.07	[21]
0.71 ± 0.01	0.7287	0.02	0.80	—	0.388 ± 0.04	[20]
0.71 ± 0.01	0.730	0.020	0.75(0.705)	0.61 ± 0.01^a	0.23^d	
0.74 ± 0.01	0.7580	0.0132	0.75	—	0.480 ± 0.003	[20]
0.74 ± 0.01	0.761	0.014	0.75	—	0.46 ± 0.05	[21]
0.74 ± 0.01	0.754	0.0142	0.75	0.679^b	0.27^d	
0.77 ± 0.01	0.7749	0.0088	0.72	—	0.544 ± 0.018	[17]
0.77 ± 0.01	0.777	0.009	0.72	—	0.55	[18]
0.77 ± 0.01	0.7764	0.0093	0.72	—	0.55 ± 0.01	[19]
0.77 ± 0.01	0.787	0.006	0.72	—	0.57 ± 0.04	[21]
0.77 ± 0.01	0.777	0.007	0.72	0.837 ± 0.002^c	0.39^d	

$r_c = 7.33\sigma$). These data are all considered to be untruncated, as the effect of truncation for these large values of r_c is negligible.

The data for the truncated and shifted Lennard-Jones potentials were taken from Haye and Bruin [20], Holcomb, Clancy and Zollweg [18], Nijmeijer, Bakker and Bruin[19], Trokhymchuk and Alexandre [17], Adams and Henderson [21] and Mecke *et al.* [7]. It is evident that the perturbation-theory with the sharp dividing surface estimate that works well for the TSF-LJ solid-liquid interface, fails rather badly in the case of the TS-LJ liquid-vapor interface. Although, the latter observation is not new, we have included tables 2–4, as they contain data that are rather scattered in the literature.

The data of tables 2 and 3 have been plotted in figure 1, where the full Lennard-Jones data from table 4 are fitted to a polynomial function. The figure clearly shows that, the step-profile perturbation theory estimate is not

particularly accurate and gets worse as we approach the critical temperature: so that for small $\Delta\rho$, γ_{PT} would become negative. However, there is also considerable spread between the various numerical data. It has been noted before (already in Ref. [22]) that the discrepancy between the discontinuous-interface approximation and the simulation results is due to the fact that the L-V interface gets more and more diffuse as T_c is approached. The step-profile approximation is then not justified (see Ref. [6]).

We estimate the surface tension as a function of $\Delta\rho = \rho_L - \rho_v$ (figure1) for the full Lennard-Jones potential ($T_c = 1.312$ Ref.[23]), and for the truncated and shifted LJ potential (TS-LJ) ($T_c = 0.935$ Ref. [24]). In view of the rather poor performance of the perturbation-theory estimate for the liquid-vapor interface, the success in the case of the solid-liquid interface is encouraging and, in fact, somewhat surprising.

Table 4. Liquid–vapor surface tension in reduced units as a function of temperature and reduced density difference for the full Lennard-Jones ($T_c = 1.312$ [23]).

$\Delta\rho$	ρ_l	ρ_v	T	γ_{LJ}	Source	$\Delta\rho$	ρ_l	ρ_v	T	γ_{LJ}	Source
0.165	0.401	0.236	1.310	0.0000786	[15]	0.586	0.6410	0.05485	1.100	0.343	[16]
0.187	0.412	0.225	1.305	0.0019575	[15]	0.587	0.642	0.055	1.110	0.33855	[15]
0.211	0.424	0.213	1.300	0.00429	[15]	0.6316	0.672	0.0404	1.050	0.462	[15]
0.217	0.4271	0.2096	1.300	0.005	[16]	0.6631	0.694	0.0309	1.000	0.45	[17]
0.234	0.436	0.202	1.295	0.0068635	[16]	0.6716	0.701	0.0294	1.000	0.56	[15]
0.256	0.447	0.191	1.290	0.009933	[15]	0.709	0.730	0.0210	0.950	0.608	[15]
0.276	0.458	0.182	1.285	0.0132355	[15]	0.715	0.7358	0.0208	0.920	0.629	[17]
0.295	0.468	0.173	1.280	0.017408	[15]	0.721	0.739	0.018	0.920	0.61	[18]
0.31	0.476	0.166	1.275	0.019635	[15]	0.722	0.740	0.018	0.920	0.63	[19]
0.323	0.483	0.160	1.270	0.024638	[15]	0.7311	0.7458	0.0147	0.900	0.679	[17]
0.334	0.488	0.154	1.265	0.03036	[15]	0.7608	0.7698	0.009	0.850	0.7527	[7]
0.348	0.497	0.149	1.260	0.036288	[15]	0.7664	0.776	0.009611	0.850	0.837	[16]
0.368	0.509	0.141	1.250	0.04875	[15]	0.7875	0.7927	0.0052	0.800	0.854	[17]
0.4644	0.564	0.0996	1.200	0.1236	[15]	0.8235	0.8254	0.0019	0.720	1.042	[17]
0.5311	0.605	0.0739	1.150	0.21965	[15]	0.8355	0.8375	0.002	0.700	1.075	[7]
0.5484	0.6147	0.0663	1.127	0.224	[17]	0.84	0.8424	0.001992	0.700	1.182	[16]
0.5646	0.6236	0.059	1.100	0.2853	[7]						

The data are taken from: Potoff and Panagiotopoulos [15] (here we express the surface tension in reduced units), Holcomb, Clancy and Zollweg [18] (truncated Lennard-Jones with $r_c = 6.3\sigma$), Nijmeijer, Bakker and Bruin [19] (truncated Lennard-Jones with $r_c = 7.33\sigma$), Trokhymchuk and Alejandre [17] (truncated Lennard-Jones with $r_c = 5.5\sigma$), Errington [16] and Mecke, Winkelmann and Fischer [7] (truncated Lennard-Jones with $r_c = 6.5\sigma$).

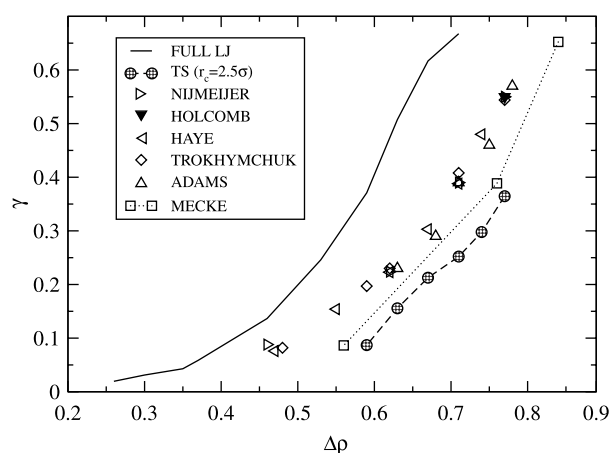


Figure 1. Surface tension as a function of the liquid–vapor density difference for a truncated and shifted Lennard-Jones at $r_c = 2.5\sigma$. The perturbation-theory estimates for the TS-LJ model are represented by filled circles, and obtained considering the full Lennard-Jones as the reference system. The simulation data are represented as follows: Refs. [20] (\circ), [18] (∇), [19] (\triangleright), [17] (\diamond) and [21] (Δ).

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