

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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Abstract

The most naive perturbation method to estimate interfacial free energies is based on the assumption that the interface 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.

I. INTRODUCTION

In computer simulations of classical many-body systems, the intermolecular potential is often truncated at a finite distance to reduce the computational cost of the simulations. Of course, changing the force between atoms or molecules affects properties such as the energy and the pressure of the system and, for sufficiently short-ranged potentials, there exist standard “tail-corrections” to compensate for the errors caused by truncation (see e.g. [1]). In inhomogeneous systems, the application of tail corrections is not straightforward. In particular, it is well known that the interfacial free-energy density (equivalent to the surface tension, in the case of fluids), is quite sensitive to truncation: the “tail corrections” are not small compared to the reference values. Expressions for these corrections, based on thermodynamic perturbation theory, were already derived by Chapela et al. [3] and subsequently refined by Blokhuis et al. [4] and Mecke et al. [17]. These expressions derived in ref. [4] are particularly useful to compare the free energy of the liquid-vapor interface in rather similar systems (e.g. Lennard-Jones fluids with and without truncation of the intermolecular potential). However, whereas thermodynamic perturbation theory has been very successful in describing the thermodynamic properties of simple liquids, starting from a hard-sphere reference system, the same approach is problematic for the computation of the surface tension, as the reference system (viz. the hard-sphere fluid), does not have a liquid-vapor transition. The approach followed by refs. [3, 4] avoids this problem by simply postulating a shape for the interfacial profile - an approach that had already been used earlier by Fowler [2] and Kirkwood and Buff [5]. The simplest possible interfacial profile that could be assumed is a step function in the density (Laplace already used this picture of the liquid-vapor interface). This simple profile has the advantage that it yields simple analytical expressions for the surface tension. Not surprisingly, the disadvantage is that it does not yield particularly good estimates for the liquid-vapor surface tension.

To our knowledge, much less attention has been paid to possibility to use perturbation theory to estimate the interfacial free energy of the solid-liquid interface. Yet this case seems much more favorable as the reference system (hard spheres) does exhibit a freezing transition. Hence, an interface between the two phases already exists in the reference system. Moreover, the solid-liquid interface is reasonably sharp and density fluctuations in the solid and the dense liquid are small. Hence the chances that a naive perturbation theory will

work are better in this case, in particular in the case of the interface between a crystal and a dense (and rather incompressible) liquid.

In this paper, we use the naive perturbation-theory approach sketched above to estimate the surface free energy of Lennard-Jones crystals in contact with the melt. For the sake of comparison, we use the same approach to estimate the difference in the liquid-vapor surface tension of truncated and untruncated LJ models. Not surprisingly, we find that the naive approach is not particularly good in the latter case. Nevertheless, we include the results for the liquid-vapor interface for future reference, because the relevant simulation data are rather scattered in the literature.

II. RESULTS

A. 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) was reported in 1986 by Broughton and Gilmer [6] and, more recently, by Davidchack and Laird [7]. 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 refs [6, 7] is very nearly equal to that of the hard-sphere system, making the system an ideal target for the naive flat-interface version of the Fowler-Kirkwood-Buff theory.

The TSF-LJ potential has the following form:

$$v_{TSF-LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + c_1 & \text{for } r \leq 2.3\sigma \\ c_2 \left(\frac{\sigma}{r}\right)^{12} + c_3 \left(\frac{\sigma}{r}\right)^6 + c_4 \left(\frac{\sigma}{r}\right)^{-2} + c_5 & \text{for } 2.3\sigma < r \leq 2.5\sigma \\ 0 & \text{for } r > 2.5\sigma \end{cases} \quad (1)$$

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. [6]). The computed values for the interfacial free energies are listed in table I. The same table also contains the values for the solid-liquid interfacial free energy of the hard-sphere system [8]. For the perturbation-theory estimate, we separate the TSF-

LF potential in a repulsive part, as defined by Weeks, Chandler and Andersen [9] and an attractive perturbation term. To map the repulsive LJ system onto a hard-sphere system, we use the Barker-Henderson rule [10] to compute the equivalent hard-sphere radius of continuous repulsive potential:

$$\sigma_{HS} = \int_0^{\infty} [\exp^{-\beta v_R(r)} - 1] dr \quad (2)$$

where σ denotes the effective hard-sphere diameter of particles interacting via the Lennard-Jones potential, and $\beta = \epsilon/(k_B T) = 1/T$ in reduced units. As is obvious from Eq.(2), σ_{HS} is a function of temperature, but not of the density. Solving Eq.(2) at $T^* = 0.617$, the temperature where Broughton and Gilmer computed γ_{LS} , we find that $\sigma_{HS} = 1.032\sigma$. Table I contains the values of the liquid-solid interfacial free energy computed by Davidchack et al. [8] for different crystalline orientations for the hard spheres system (first column: in units of $[k_B T/\sigma_{HS}^2]$, second column: in units of $[\epsilon/\sigma^2]$). In addition, the table contains the estimate for γ based on the perturbation theory, assuming a step profile in the density. The last columns contain the numerical data for the TSF-LJ potential reported by Davidchack and Laird [7] and by Broughton and Gilmer [6].

| | $\gamma_{HS}[k_B T/\sigma_{HS}^2]$ [8] | $\gamma_{HS}[\epsilon/\sigma^2]$ | γ_{LJ} (present work) | γ_{LJ} [7] | γ_{LJ} [6] |
|---------|--|----------------------------------|------------------------------|-------------------|-------------------|
| [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 |

Table I: Values of the liquid-solid interfacial free energy computed at different crystalline orientations for hard spheres by Davidchack et al. [8](second column: in units of $[k_B T/\sigma_{HS}^2]$, third column: in units $[\epsilon/\sigma^2]$). Fourth column: present perturbation-theory our estimate of γ_{TSF-LJ} . Fifth column: estimate of γ_{TSF-LJ} by Davidchack and Laird [7]. Sixth column: estimate of γ_{TSF-LJ} by Broughton and Gilmer [6]. In the bottom line of the table, we compare the corresponding values of γ averaged (without weighting) over the different crystal faces.

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.

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. The various truncation procedures lead to relative minor changes in the potentials, and one might hope that a naive perturbation theory might work well. However, this is not the case.

B. Calculation of the liquid-vapor surface tension

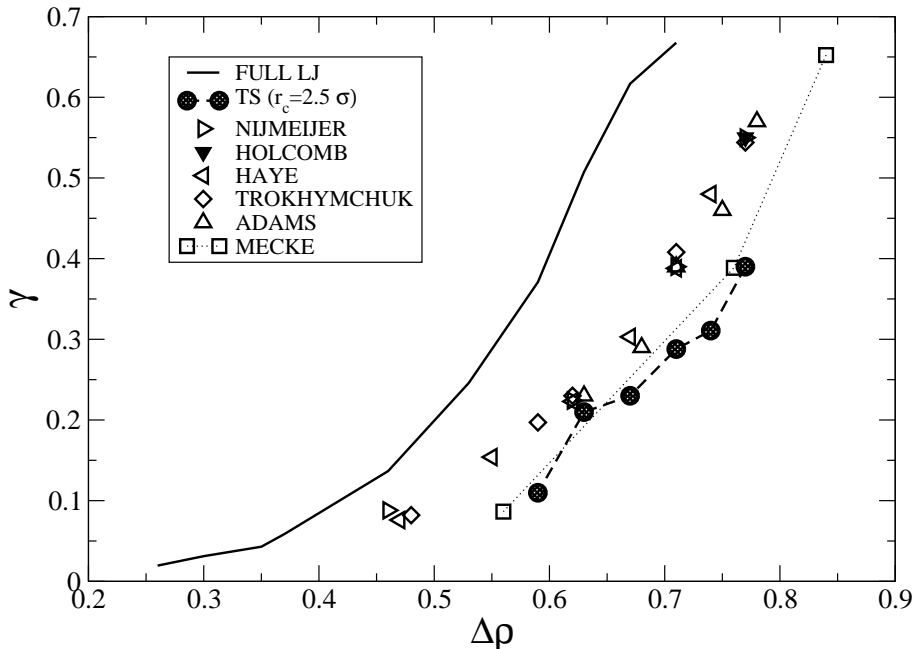


Figure 1: Surface tension as a function of the liquid-vapor density difference for a truncated and shifted Lennard Jones at $r_c = 2.5\sigma$. The perturbation-theory estimates for the TS-LJ model are represented by filled circles. The simulation data are represented as follows: ref. [19] (\triangleleft), ref. [12] (∇), ref. [11] (\triangleright), ref. [15] (\diamond), and ref. [20] (\triangle).

According to the expressions given in the Appendix, the correction to the surface tension of the full Lennard-Jones surface tension due to truncation and shifting is of the order of $\gamma_{P1} + \gamma_{P2} = -0.75(\Delta\rho)^2$. For the TSF-LJ potential, the correction is $\gamma_{P1} + \gamma_{P2} + \gamma_{P3} = -1.05(\Delta\rho)^2$. The resulting predictions are summarized in tables(II) for low temperatures

and table (III) for higher temperatures. In these tables we also show the numerical data, where available.

| $\Delta\rho$ | ρ_l | ρ_v | T | γ_{LJ} | γ_{TS} | Source |
|--------------|----------|----------|------|--------------------------|---------------------|--------|
| 0.46±0.02 | 0.5794 | 0.1030 | 1.0 | - | 0.082±0.008 | [15] |
| 0.46±0.02 | 0.5694 | 0.0987 | 1.0 | - | 0.076±0.002 | [19] |
| 0.46±0.02 | 0.565 | 0.103 | 1.0 | - | 0.088±0.007 | [11] |
| 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 | [19] |
| 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 | [15] |
| 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 | [19] |
| 0.62±0.02 | 0.662 | 0.0439 | 0.90 | - | 0.224±0.009 | [11] |
| 0.62±0.02 | 0.671 | 0.040 | 0.90 | - | 0.23±0.02 | [20] |
| 0.62±0.02 | 0.6644 | 0.0444 | 0.90 | - | 0.227±0.016 | [15] |
| 0.62±0.02 | 0.666 | 0.046 | 0.90 | 0.46±0.03 ^a | 0.17 ^d | |

Table II: 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). T is the temperature for each $\Delta\rho$. $\gamma_{TS} = \gamma_{LJ} + \gamma_{LR1} + \gamma_{LR2}$. The numerical data for γ_{LV} of the full Lennard-Jones potential come from ref.[14] (superscript *a*) ref.[15] (superscript *b*), and ?? (superscript *c*). Our data are indicated by in superscript *d*.

The data for the full (or “almost full”) Lennard-Jones potential (table IV) were taken from Potoff and Panagiotopoulos [14], Errington [16], Trokhymchuk and Alejandre [15] (truncated Lennard-Jones with $r_c = 5.5\sigma$), Holcomb, Clancy and Zollweg [12](truncated Lennard-Jones with $r_c = 6.3\sigma$), Mecke, Winkelmann and Fischer [17](truncated Lennard-Jones with $r_c = 6.5\sigma$), and Nijmeijer, Bakker and Bruin [11] (truncated Lennard-Jones with $r_c = 7.33\sigma$). These data are all considered to be un-truncated, 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

| $\Delta\rho$ | ρ_l | ρ_v | $T/T_c(T)$ | γ_{LJ} | γ_{TS} | Source |
|--------------|----------|----------|-------------|--------------------------|-------------------|--------|
| 0.67±0.03 | 0.6973 | 0.0307 | 0.85 | - | 0.303±0.003 | [19] |
| 0.67±0.03 | 0.706 | 0.027 | 0.85 | - | 0.29±0.07 | [20] |
| 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 | [15] |
| 0.71±0.01 | 0.7315 | 0.195 | 0.80 | - | 0.39 ±0.01 | [11] |
| 0.71±0.01 | 0.731 | 0.02 | 0.80 | - | 0.39 ±0.07 | [20] |
| 0.71±0.01 | 0.7287 | 0.02 | 0.80 | - | 0.388 ±0.04 | [19] |
| 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 | [19] |
| 0.74±0.01 | 0.761 | 0.014 | 0.75 | - | 0.46±0.05 | [20] |
| 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 | [15] |
| 0.77±0.01 | 0.777 | 0.009 | 0.72 | - | 0.55 | [12] |
| 0.77±0.01 | 0.7764 | 0.0093 | 0.72 | - | 0.55 ±0.01 | [11] |
| 0.77±0.01 | 0.787 | 0.006 | 0.72 | - | 0.57 ±0.04 | [20] |
| 0.77±0.01 | 0.777 | 0.007 | 0.72 | 0.837±0.002 ^c | 0.39 ^d | |

Table III: Same as in table(II)

and Bruin [19], Holcomb, Clancy and Zollweg [12], Nijmeijer, Bakker and Bruin[11], Trokhymchuk and Alejandre [15], Adams and Henderson [20] and Mecke et al. [17]. It is evident that the naive perturbation-theory estimate that works well for the TSF-LJ solid-liquid interface, fails rather badly in the case of the liquid-vapor interface. Although the latter observation is not new, we have included tables II-IV, as they contain data that are rather scattered in the literature.

The data of tables(II) and (III) have been plotted in fig.1, where the full Lennard-Jones data from table(IV) 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 much so that for small $\Delta\rho$, γ_{PT} would become negative. However, there is also considerable spread between the various numerical data. It

| $\Delta\rho$ | 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 | [14] | 0.586 | 0.6410 | 0.05485 | 1.100 | 0.343 | [16] |
| 0.187 | 0.412 | 0.225 | 1.305 | 0.0019575 | [14] | 0.587 | 0.642 | 0.055 | 1.110 | 0.33855 | [14] |
| 0.211 | 0.424 | 0.213 | 1.300 | 0.00429 | [14] | 0.6316 | 0.672 | 0.0404 | 1.050 | 0.462 | [14] |
| 0.217 | 0.4271 | 0.2096 | 1.300 | 0.005 | [16] | 0.6631 | 0.694 | .0309 | 1.000 | 0.45 | [15] |
| 0.234 | 0.436 | 0.202 | 1.295 | 0.0068635 | [14] | 0.6716 | 0.701 | 0.0294 | 1.000 | 0.56 | [14] |
| 0.256 | 0.447 | 0.191 | 1.290 | 0.009933 | [14] | 0.709 | 0.730 | 0.0210 | 0.950 | 0.608 | [14] |
| 0.276 | 0.458 | 0.182 | 1.285 | 0.0132355 | [14] | 0.715 | 0.7358 | 0.0208 | 0.920 | 0.629 | [15] |
| 0.295 | 0.468 | 0.173 | 1.280 | 0.017408 | [14] | 0.721 | 0.739 | 0.018 | 0.920 | 0.61 | [12] |
| 0.31 | 0.476 | 0.166 | 1.275 | 0.019635 | [14] | 0.722 | 0.740 | 0.018 | 0.920 | 0.63 | [11] |
| 0.323 | 0.483 | 0.160 | 1.270 | 0.024638 | [14] | 0.7311 | 0.7458 | 0.0147 | 0.900 | 0.679 | [15] |
| 0.334 | 0.488 | 0.154 | 1.265 | 0.03036 | [14] | 0.7608 | 0.7698 | 0.009 | 0.850 | 0.7527 | [17] |
| 0.348 | 0.497 | 0.149 | 1.260 | 0.036288 | [14] | 0.7664 | 0.776 | 0.009611 | 0.850 | 0.837 | [16] |
| 0.368 | 0.509 | 0.141 | 1.250 | 0.04875 | [14] | 0.7875 | 0.7927 | 0.0052 | 0.800 | 0.854 | [15] |
| 0.4644 | 0.564 | 0.0996 | 1.200 | 0.1236 | [14] | 0.8235 | 0.8254 | 0.0019 | 0.720 | 1.042 | [15] |
| 0.5311 | 0.605 | 0.0739 | 1.150 | 0.21965 | [14] | 0.8355 | 0.8375 | 0.002 | 0.700 | 1.075 | [17] |
| 0.5484 | 0.6147 | 0.0663 | 1.127 | 0.224 | [15] | 0.84 | 0.8424 | 0.001992 | 0.700 | 1.182 | [16] |
| 0.5646 | 0.6236 | 0.059 | 1.100 | 0.2853 | [17] | | | | | | |

Table IV: Liquid-vapor surface tension in reduced units as a function of temperature and reduced density difference for the full Lennard-Jones ($T_c = 1.312$ [18]). The data are taken from: Potoff and Panagiotopoulos [14] (here expressing the surface tension in reduced units), Holcomb, Clancy and Zollweg [12] (truncated Lennard-Jones with $r_c = 6.3\sigma$), Nijmeijer, Bakker and Bruin,[11] (truncated Lennard-Jones with $r_c = 7.33\sigma$), Trokhymchuk and Alejandre [15] (truncated Lennard-Jones with $r_c = 5.5\sigma$), Errington [16] and Mecke, Winkelmann and Fischer [17] (truncated Lennard-Jones with $r_c = 6.5\sigma$).

has been noted before (already in ref. [21]) 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. [4]).

We estimate the surface tension as a function of $\Delta\rho = \rho_L - \rho_V$ (fig.1) for the full Lennard-Jones potential ($T_c = 1.312$ ref.[18]), and for the truncated and shifted LJ potential ($T_c = 0.935$ [22]). 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.

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III. APPENDIX

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.

$$\gamma_{LJ} = \gamma_{ref} + \gamma_P \quad (3)$$

We assume that γ_{ref} is known. Below, we list the various contributions to the perturbation. In all cases we make the naive (“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 :

$$v_{P1}(r) = \begin{cases} -v_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases} \quad (4)$$

It guarantees the continuity of the potential 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 $r \geq r_c$):

$$v_{P2}(r) = \begin{cases} 0 & r < r_c \\ -4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] & r \geq r_c \end{cases} \quad (5)$$

Finally, 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

$$v_{P3}(r) = \begin{cases} -(r - r_c)v'_{LJ}(r_c) & \text{for } r \leq r_c \\ 0 & \text{for } r > r_c \end{cases} \quad (6)$$

where $v'_{LJ}(r)$ is $\left(24\epsilon\frac{\sigma^6}{r} \left[\frac{1}{r^6} - \frac{2\sigma^6}{r^{12}}\right]\right)$. $v_{P3}(r)$ 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:

The contribution due to $v_{P1}(r)$, is denoted by γ_{P1} and is given by:

$$\begin{aligned} \gamma_{P1} &= -\frac{1}{2}(\rho_2 - \rho_1)^2 \int_0^{r_c} dz_1 \int_{z_1}^{r_c} dr (-v_{LJ}(r_c)) (2\pi(r^2 - z_1 r)) \\ &= \frac{\pi}{8} v_{LJ}(r_c) r_c^4 (\Delta\rho)^2 \end{aligned} \quad (7)$$

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

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

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

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:

$$\begin{aligned}\gamma_{P3} &= -\frac{1}{2}(\rho_2 - \rho_1)^2 \int_0^{r_c} dz_1 \int_{z_1}^{r_c} dr \left[-(r - r_c) v'_{LJ}(r_c) \right] (2\pi(r^2 - z_1 r)) \\ &= -\frac{\pi}{40} v'_{LJ}(r_c) r_c^5 (\Delta\rho)^2\end{aligned}\quad (9)$$

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

With these three terms we can easily convert between different reference systems and models with truncated and (force) shifted potentials.

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