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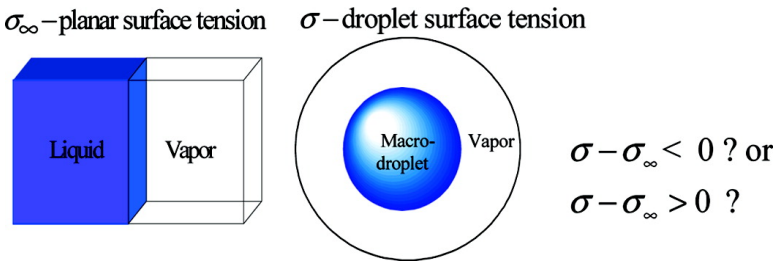

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The Tolman Length: Is It Positive or Negative?

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Liquid—vapor or liquid—solid surface tension is a fundamental property and plays a key role in a variety of interfacial phenomena associated with multiple phases.[1] In general, the interfaces do not assume planar shape but rather exhibit some curvatures, and the magnitude of the surface tension can be affected by interfacial curvature.[2−7] Such a curvature dependence of the surface tension (characterized by the Tolman length[2] defined below) along with the Egelstaff—Widom fundamental lengthscale[8] (defined as the product of the planar surface tension with isothermal compressibility of liquids) have been shown to be related to the free-energy formation of a critical droplet in vapor—liquid nucleation.[9] Garde and co-workers[10] have recently shown that both the Tolman length and the Egelstaff—Widom lengthscale also have direct relevance to the hydrophobic hydration, wherein the hydrophobic solute—water interface has a large curvature. For a spherical droplet, Tolman[2] showed in 1949 that the surface tension (σ) can be written as a simple function of radius of the surface of tension, R_s, i.e.

$$\sigma = \sigma_\infty/(1 + 2\delta/R_s) \tag{1}$$

where σ_∞ denotes the planar surface tension, and δ describes the separation between the equimolar surface, R_e, and the surface of tension R_s, that is, $\delta = R_e - R_s$. The so-called Tolman length, δ_∞, can be defined as the infinitely large drop limit (or planar limit) of δ. To date, however, the sign of the Tolman length is still controversial. For example, for a macrodroplet or gas bubble, whether their surface tension is greater or less than the planar one, is still an open question. For a prototypical simple fluid—the Lennard-Jones (LJ)—classical density-functional theory (DFT) predicts $\delta_\infty < 0$,[11−21] that is, the surface tension of a large droplet is greater than that of the planar one, whereas other theories assumed $\delta_\infty > 0$.[22,23] Prediction of the sign of the Tolman length based on computer simulation has also been inconclusive,[24−29] although the state-of-the-art molecular dynamics simulation[30] showed that the Tolman length is positive over a large temperature range, with magnitude typically on the order of a few tenths of the LJ molecular diameter. In this communication, we report a much larger scale molecular dynamics simulation and show that the Tolman lengths, although positive, are much smaller in magnitude than previously reported. In particular, we found that the range of interparticle interaction can significantly affect the magnitude of the Tolman length. When the range of interaction is longer than five molecular diameters, the Tolman length is on the order of a few hundredths of the molecular diameter, rather than a few tenths known previously.

The molecular dynamics (MD) simulation was performed under a constant-volume and constant-temperature condition. The simulation cell contains a three-dimensional liquid slab in equilibrium with its vapor, as used by many other researchers.[24−27,30] The system itself is enclosed in a cubic box (or a rectangular box) with periodic boundaries in three spatial dimensions. The force field used in the MD simulation is a cutoff and *shifted* LJ potential with a cutoff radius, r_c, i.e.

$$w(r) = \begin{cases} 4\epsilon_{LJ}[(\sigma_{LJ}/r)^{12} - (\sigma_{LJ}/r)^6] - w_{shift}, & r < r_c \\ 0, & r > r_c \end{cases} \tag{2}$$

Here ϵ_{LJ} and σ_{LJ} are the energy and molecular-diameter parameters, and w_{shift} is a constant shift to ensure $w(r_c) = 0$. The system temperature is kept at $T = 0.8\ \epsilon_{LJ}$, far below the critical temperature ($\sim 1.3\ \epsilon_{LJ}$). Hereafter, we will use the reduced units with a setting of $\epsilon_{LJ} = 1$ and $\sigma_{LJ} = 1$ to display numerical results of the density profiles, surface tensions, and Tolman lengths.

The Tolman length can be computed straightforwardly on the basis of a rigorous statistical-mechanics formula.[27,30]

$$\delta_\infty = -\delta_1 - \delta_2 = -\frac{1}{\sigma_\infty}\int_{z_l}^{z_v} dz(z - z_e)f_1(z) - \frac{1}{\sigma_\infty}\int_{z_l}^{z_v} dz f_2(z) \tag{3}$$

where z_l and z_v denote z-coordinates of two points deep inside the liquid and vapor phase, respectively; z_e is the position of the equimolar surface, and the functions, f_1 and f_2, are given in the Supporting Information. Here, we fix $z_v = L_z$ (where L_z is the dimension of the simulation cell in the z direction), while we allow z_l to change. The smallest value for z_l is $L_z/2$. In the first MD simulation, we attempted to reproduce previous simulation results of van Giessen and Blokhuis[30] (who used a particle number $N = 7100$ and a number of time step $N_t = 4\,000\,000$), but with a particle number 2 orders of magnitude larger ($N = 768\,000$) and a total number of time step 2.5 times larger ($N_t = 10\,000\,000$). The same cutoff radius, $r_c = 2.5$, was used. As shown in Figure 1a, the calculated equilibrium liquid and vapor densities (ρ_l and ρ_v) as well as the planar surface tension ($\sigma_\infty = 0.396$) are in excellent agreement with previous results[27] ($\rho_l = 0.729$ and $\rho_v = 0.020$, and $\sigma_\infty = 0.391$).

However, the calculated Tolman length ($\delta_\infty = 0.11$) is notably smaller than the previous result ($\delta_\infty = 0.169$) at $T = 0.8$. Similar conclusions can be drawn for two other state points examined ($T = 0.75$ and 0.85). An explanation for the numerical difference in δ_∞ is that the Tolman length is the first-order correction to the surface tension and thus can be very sensitive to small numerical fluctuation in the MD simulation. A larger system size and longer simulation time improve the statistics and numerical accuracy of the averaged Tolman length. However, even with 10 million time steps, the $\delta_1(z_l)$ profile (Figure 1b) at the liquid side is still not a perfectly smooth line but entails discernible fluctuation. This fluctuation is the main source of the error of Tolman length, which amounts to about 10% even with 10 million steps at $z_l = L_z/2$. Next, we carried out two additional MD simulations with two larger cutoff radii, $r_c = 5.0$ and 7.5. Note that the use of these larger cutoff radii significantly increases the cost of computation. Consequently, a relatively smaller particle number ($N = 240\,000$) and number of time step ($N_t = 2\,000\,000$) were used.

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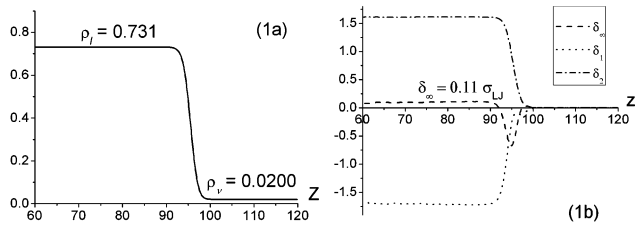

Figure 1. (a) Interfacial density profile. (b) Tolman length δ_∞, δ_1, and δ_2 as a function of lower limit of the integrand z_l in eq 3. The dimension of the system ($L_x \times L_y \times L_z$) is 120 × 120 × 120; the time step is 0.0435; the cutoff radius is $r_c = 2.5$. The calculated planar surface tension is $\sigma_\infty = 0.396$.

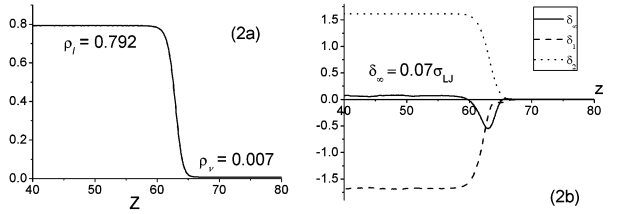

Figure 2. The same as Figure 1, but the dimension of the system ($L_x \times L_y \times L_z$) is 80 × 80 × 80; the time step is 0.0438; the cutoff radius is $r_c = 5.0$. The calculated planar surface tension is $\sigma_\infty = 0.804$.

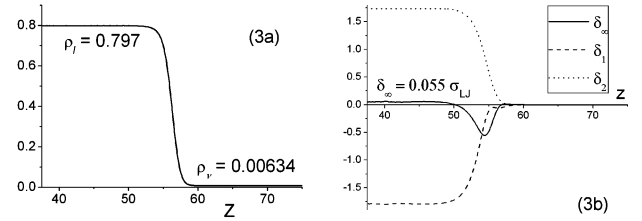

Figure 3. The same as Figure 1, but the dimension of the system ($L_x \times L_y \times L_z$) is 90 × 90 × 75; the time step is 0.0438; the cutoff radius is $r_c = 7.5$. The calculated planar surface tension is $\sigma_\infty = 0.876$.

Simulation results are given in Figures 2 and 3. As expected, with the increased ranges of interaction, the equilibrium liquid density is slightly enhanced and the equilibrium vapor density is reduced, whereas the planar surface tension is more than doubled. More surprisingly, we found that the Tolman length is significantly reduced with increasing the range of interaction. In fact, both simulations indicate that the Tolman length is on the order of a few hundredths of molecular diameter σ_{LJ} rather than a few tenths. To our knowledge, this is the first computer simulation evidence of interaction-range dependence of the Tolman length.

The simulation results have several implications to the sign and trend of the Tolman length in the large droplet limit. First, it is known that in *realistic* nonpolar inert-gas liquids (such as liquid argon, whose equilibrium and transport properties can be well described by the LJ potential[31]) the van der Waals (vdW) interaction entails a long attractive tail; thus, the larger cutoff ($r_c = 7.5$) should be a much better approximation than the shorter one ($r_c = 2.5$) to describe the long-ranged tail attraction. Hence, our results suggest that in true LJ systems with a r^{-6} attractive tail at long distance, the Tolman length can be further reduced at temperatures below the critical point. Second, our results suggest that a simulation with much larger numbers of particles and longer cutoff radii (e.g., $r_c = 10$) is needed to see whether the rate of δ_∞ reduction has leveled off at $r_c = 7.5$, and if not, to what extent δ_∞ can be further reduced. Such a MD simulation may be feasible in the near future in the researchers' laboratory with a larger computer cluster. The conclusion we can draw from the present study is that, for simple nonpolar fluids with midrange interactions, the Tolman length is positive but very small. We note that in the scaling theory of McGraw and Laaksonen[9a] the Tolman length is assumed to be zero, while curvature dependence to the surface tension is still permitted. Our large-scale simulation supports that, at least for the LJ system, their zero-Tolman-length assumption is very reasonable.

On the other hand, from theoretical perspective, we have pointed out that DFT generally predicts negative Tolman lengths for large *droplets* (with a magnitude still on the order of a few tenths of molecular diameter)[11−17] and positive Tolman lengths for large *bubbles*.[16] Note that most DFT calculations employed the local-density approximation.[11−18] Recently, we applied a simple form of nonlocal density approximation (i.e., weighted-density approximation of Tarazona[32]) and found that Tolman lengths can be reduced by about 5% in magnitude over a large temperature range.[21] Another approximation commonly used in previous DFTs is the so-called random-phase approximation, which can be viewed as a first-order approximation to the correlation function of fluids. By introducing a second-order approximation, we showed that Tolman lengths can be also reduced by about 5−10% in magnitude over a large temperature range.[19] In summary, it appears that any improved theoretical approximations tend to give smaller Tolman lengths in magnitude. In this regard, the improved DFT is consistent with the present large-scale MD simulation in that the more accurately calculated Tolman lengths are closer to zero.

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Supporting Information Available: Equations for f_1 and f_2 are collected. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Interscience: New York, 1997.
(2) Tolman, R. C. *J. Chem. Phys.* **1949**, *17*, 333.
(3) Choi, D. S.; Jhon, M. S.; Eyring, H. *J. Chem. Phys.* **1970**, *53*, 2608.
(4) Mandell, M. J.; Reiss, H. *J. Stat. Phys.* **1975**, *13*, 107.
(5) Falls, A. H.; Scriven, L. E.; Davis, H. T. *J. Chem. Phys.* **1981**, *75*, 3986.
(6) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Oxford University Press: New York, 1982.
(7) Guermeur, R.; Biquard, F.; Jacolin, C. *J. Chem. Phys.* **1985**, *82*, 2040.
(8) Egelstaff, P. A., Widom, B. *J. Chem. Phys.* **1970**, *53*, 2667.
(9) (a) McGraw, R.; Laaksonen, A. *Phys. Rev. Lett.* **1996**, *76*, 2754. (b) Koga, K.; Zeng, X. C. *J. Chem. Phys.* **1999**, *110*, 3466.
(10) Rajamani, S.; Truskett, T. M.; Garde, S. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 9475.
(11) Iwamatsu, M. *J. Phys.: Condens. Matter* **1993**, *5*, 7537.
(12) Talanquer, V.; Oxtoby, D. W. *J. Chem. Phys.* **1995**, *99*, 2865.
(13) van Giessen, A. E.; Blokhuis, E. M.; Bukman, D. J. *J. Chem. Phys.* **1998**, *108*, 1148.
(14) Koga, K.; Zeng, X. C.; Shchekin, A. K. *J. Chem. Phys.* **1998**, *109*, 4063.
(15) Granasy, L. *J. Chem. Phys.* **1998**, *109*, 9660.
(16) Bykov, T. V.; Zeng, X. C. *J. Chem. Phys.* **1999**, *111*, 3705.
(17) Barrett, J. *J. Chem. Phys.* **1999**, *111*, 5938.
(18) Baidakov, V. G.; Boltachev, G. Sh. *Phys. Rev. E* **1999**, *59*, 469.
(19) Bykov, T. V.; Zeng, X. C. *J. Phys. Chem. B* **2001**, *105*, 11586.
(20) Bartell, L. S. *J. Phys. Chem. B* **2001**, *105*, 11615.
(21) Bykov, T. V.; Zeng, X. C. *J. Chem. Phys.* **2002**, *117*, 1851.
(22) Schmelzer, J. W. P.; Gutzow, I.; Schmelzer, J., Jr. *J. Colloid Interface Sci.* **1996**, *178*, 657.
(23) Kashchiev, D. *J. Chem. Phys.* **2003**, *118*, 9081.
(24) Rusanov, A. I.; Brodskaya, E. N. *J. Colloid Interface Sci.* **1977**, *62*, 542.
(25) Thompson, S. M.; Gubbins, K. E.; Walton, J. P. R. B.; Chantry, R. A. R.; Rowlinson, J. S. *J. Chem. Phys.* **1984**, *81*, 530.
(26) Nijmeijer, M. J.; Bruin, C.; van Woerkom, A. B.; Bakker, A. F. *J. Chem. Phys.* **1992**, *92*, 565.
(27) Haye, M. J.; Bruin, C. *J. Chem. Phys.* **1994**, *100*, 556.
(28) Ten Wolde, P. R.; Frenkel, D. *J. Chem. Phys.* **1998**, *109*, 9901.
(29) Moody, M. P.; Attard, P. *J. Chem. Phys.* **2001**, *115*, 8967.
(30) van Giessen, A. E.; Blokhuis, E. M. *J. Chem. Phys.* **2002**, *116*, 302.
(31) (a) Verlet, L. *Phys. Rev.* **1967**, *159*, 98. (b) Vogelsang, R.; Hoheisel, C.; Ciccotti, G. *J. Chem. Phys.* **1987**, *86*, 6371.
(32) Tarazona, P. *Phys. Rev. A* **1985**, *31*, 2672.

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