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# Semiphenomenological theory of the Tolman length

V. I. Kalikmanov
*Physics Department, Eindhoven University of Technology, W&S, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands*

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A semiphenomenological cluster theory of the curvature correction $\delta_T$ to the surface tension of a spherical liquid drop (known as a ''Tolman length'') is presented. By using the Fisher droplet model of condensation [M. E. Fisher, Physics **3**, 255 (1967)]. we obtain an equation relating $\delta_T$ to the saturation vapor pressure at a given temperature $T$. For low temperatures an analytical solution is obtained. In a general case the equation is solved numerically for various nonpolar substances. Not too close to $T_c$, $\delta_T$ is found to be positive and of the order of $0.2\sigma$, where $\sigma$ is a molecular diameter, in agreement with molecular dynamics simulations. As $T\rightarrow T_c^-$ the Tolman length becomes negative and diverges, as predicted by the density functional analysis. [S1063-651X(97)12502-8]

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## I. INTRODUCTION

In 1949 Tolman [1], on the basis of the Gibbs thermodynamic description of capillarity, predicted that the surface tension of a spherical liquid droplet, defined at the position $R_s$ of a ''surface of tension,'' has a form

$$\gamma[R_s]=\gamma_0\left(1-\frac{2\delta_T}{R_s}\right), \tag{1}$$

where $\gamma_0$ denotes the surface tension of the planar liquid-vapor interface ($R_s\rightarrow\infty$), and $\delta_T$ is the so called ''Tolman length.'' The surface of tension makes the Laplace law exact [2] (thus one can say that the surface tension acts on the surface of tension):

$$p^l-p^v=\frac{2\gamma[R_s]}{R_s}. \tag{2}$$

Here $p^l$ and $p^v$ are the pressures in the bulk liquid within the droplet and the vapor outside it. One can define another dividing surface, called an ''equimolar surface,'' characterized by the zeroth adsorption. If $R_e$ denotes its radius, then by definition

$$\int_0^{R_e}dR\,R^2[\rho(R)-\rho^l]+\int_{R_e}^{\infty}dR\,R^2[\rho(R)-\rho^v]=0,$$

where $\rho(R)$ is the number density at radius $R$, and $\rho^l$ and $\rho^v$ are densities in the bulk liquid and vapor, respectively. The Tolman length in Eq. (1) is defined as a planar limit of the separation between these two surfaces,

$$\delta_T=\lim_{R_e,R_s\rightarrow\infty}(R_e-R_s)=z_e-z_s \tag{3}$$

(the $z$ axis is perpendicular to the interface with positive $z$ directed away from the center of curvature). It is clear that both dividing surfaces are situated in the interfacial zone with a width of the order of the correlation length. Therefore, far from the critical point the Tolman length is expected to be of molecular size. However, the temperature dependence and even the sign of $\delta_T$ remains a matter of controversy.

Recently interest in this problem has been stimulated by the development of semiphenomenological theories of homogeneous nucleation [3–5], where the concept of curvature-dependent surface tension of newly born nuclei plays an important role. As it is known, the rate of homogeneous nucleation $J$ defined as a number of critical nuclei formed per unit volume per unit time is proportional to the Boltzmann factor $J\sim e^{-\Delta G^*/k_BT}$, where $\Delta G^*$ is the Gibbs free energy required to form a critical nucleus. In its simplest form, given by the classical nucleation theory, $\Delta G^*\sim\gamma^3$. Thus $J\sim e^{\gamma^3}$. Critical nuclei are usually very small objects: their size is of the order of 1–10 nm. Therefore even a small correction to surface tension can have a dramatic effect (orders of magnitude) on the nucleation rate.

Unfortunately there are no reliable experimental data on the Tolman length. However, during the last decade several analytical and simulation results were obtained. Fisher and Wortis [6], on the basis of density functional considerations, showed that when the two coexisting phases are symmetric, $\delta_T$ vanishes exactly at all temperatures. The same result was obtained by Blokhuis and Bedeaux [7] on the basis of the Irwing-Kirkwood expression for the pressure tensor in an inhomogeneous fluid. In the presence of *asymmetry* (which is always the case for real fluids) this conclusion does not hold. Nijmeijer *et al.* [8] performed molecular dynamics (MD) simulations of liquid droplets with molecules interacting via the Lennard-Jones potential. Simulations made for one particular temperature $T/T_c\approx0.83$ gave the estimate $|\delta_T|<0.7\sigma$, where $\sigma$ is the hard-core molecular diameter. Haye and Bruin [9] recently evaluated the temperature dependence of the Tolman length for a Lennard-Jones fluid from MD simulations of a *planar* interface using the relations proposed in [7]. Their data, characterized by much higher accuracy than the estimate of [8] (though not in conflict with the latter), show that within the range $0.69\leqslant T/T_c\leqslant0.92$, $\delta_T$ is positive and small. However, at high temperatures, $T/T_c\geqslant0.87$, simulation results exhibited large fluctuations.

Fisher and Wortis studied the critical behavior of $\delta_T$, and found that within the Landau theory $\delta_T(T)$ approaches a constant value (of the order of molecular size) as $T\rightarrow T_c^-$ and its sign is determined solely by the coefficient of the fifth-order term in the free energy expansion. Furthermore, within van der Waals theory this limiting value is negative. Near the critical point fluctuations become extremely important, and one has to go beyond the Landau theory. The scaling hypothesis and renormalization group analysis [6] predict the divergence of $\delta_T$ at $T_c$ (for asymmetric phase transitions). In this paper, we present a semiphenomenological cluster theory of the Tolman length based on the Fisher cluster model of condensation and discuss its behavior in a wide temperature range.

## II. MODEL

Our starting point is Fisher's cluster model of condensation [10]. Let us consider a real gas and, following Fisher, assume that it can be regarded as a collection of noninteracting spherical clusters (intracluster interactions are important). Clusters of different sizes are in mutual statistical equilibrium, associating and dissociating. An $n$ cluster can be viewed as a microscopic liquid droplet containing $n$ molecules in the surrounding vapor. The grand partition function of the gas can then be written in an exponential form,

$$\Xi = \exp\left[\sum_{n=1}^{\infty} q_n z^n\right], \tag{4}$$

where $q_n$ is the configuration integral for the $n$-cluster in a domain of volume $V$ [11], $z \equiv e^{\beta\mu}/\Lambda^3$ is the fugacity, $\beta = 1/k_BT$, $\mu$ the chemical potential, and $\Lambda$ the de Broglie wavelength of a molecule. As a result the pressure equation of state, $pV = k_BT\ln\Xi$, which we apply at the coexistence (saturation) line, reads

$$\frac{p_{\rm sat}}{k_BT} = \sum_{n=1}^{\infty} \rho_{n,\rm sat}, \tag{5}$$

where

$$\rho_{n,\rm sat} = \frac{1}{V} q_n z_{\rm sat}^n \tag{6}$$

is the number density of $n$-clusters at coexistence and $p_{\rm sat}(T)$ and $z_{\rm sat}(T)$ are coexistence values of the pressure and fugacity. The configuration integral has the form [10]

$$q_n = q_0 V \Lambda^{3n} \exp[-n\beta\mu_{\rm sat} - \beta\gamma_{\rm micro} s_1 n^{2/3} - \tau \ln n]. \tag{7}$$

The terms in the argument of the exponential refer to the bulk energy, surface energy and entropic contributions, respectively; $\mu_{\rm sat}(T)$ is the chemical potential at coexistence, $s_1 n^{2/3}$ is the surface area of an $n$ cluster, $s_1 = 4\pi r_1^2$, and

$$r_1 = \left[\frac{3}{4\pi}\frac{1}{\rho^l}\right]^{1/3}, \tag{8}$$

where $\rho^l(T)$ is the liquid number density at coexistence. The important feature of Eq. (7) is that the surface energy of the $n$ cluster contains a "microscopic surface tension" $\gamma_{\rm micro}$ which is not identical to its macroscopic counterpart $\gamma_0$. The term with $\ln n$ takes into account contributions from various degrees of freedom of a cluster, and from configurational effects. Pursuing the consequences of the model in the critical region, Fisher found that the parameter $\tau$ has a universal nature, and can be expressed in terms of the critical exponent $\delta$ describing the shape of the critical isotherm ($\delta \approx 4.81$ [2])

$$\tau = 2 + \frac{1}{\delta} \approx 2.2.$$

Kiang [12] showed (see also [5]) that $\tau$ can be related to the critical state parameters

$$\frac{p_c}{\rho_c k_B T_c} = \frac{\zeta(\tau)}{\zeta(\tau-1)}, \tag{9}$$

where $\zeta(u) = \Sigma_{n=1}^{\infty} n^{-u}$ is the Riemann zeta function, and $p_c$ and $\rho_c$ are the critical pressure and the critical number density, respectively. The values of $\tau$ obtained from Eq. (9) for various substances are close to Fisher's original universal number. The other parameter $q_0$ is related to $\tau$ by

$$q_0 = \rho_c/\zeta(\tau-1). \tag{10}$$

The microscopic surface tension remains undetermined in Fisher's model. We will associate $\gamma_{\rm micro}$ with the surface tension of a spherical surface of an $n$ cluster with the radius $r_n = r_1 n^{1/3}$:

$$\gamma_{\rm micro}(n) = \gamma_0\left(1 - \frac{2\delta_T}{r_n}\right). \tag{11}$$

This Tolman-like ansatz is consistent with a conceptual view on the cluster as being a microscopic liquid droplet. It proved to be quite successful in quantitative predictions of the nucleation behavior of complex substances [5]. From Eqs. (5)–(7), we find

$$\rho_{n,\rm sat} = q_0 \exp[-\beta\gamma_{\rm micro} s_1 n^{2/3} - \tau \ln n]. \tag{12}$$

Combining ansatz (11) with Eqs. (5) and (12), we obtain

$$\frac{p_{\rm sat}}{q_0 k_B T} = \sum_{n=1}^{\infty} n^{-\tau} \exp[-\theta_0(1 + \alpha_\gamma n^{-1/3}) n^{2/3}], \tag{13}$$

where

$$\theta_0 \equiv \frac{\gamma_0 s_1}{k_B T} \tag{14}$$

is a dimensionless macroscopic surface tension. For convenience we have introduced an unknown $\alpha_\gamma$, related to $\delta_T$ as

$$\alpha_\gamma \equiv -\frac{2\delta_T}{r_1}. \tag{15}$$

Equation (13) is the central point of the proposed theory. It relates a Tolman length to the known macroscopic quantities.

The saturation pressure and liquid density are empirically well defined and tabulated for various substances for a wide temperature range up to $T_c$ [13]. There also exist several empirical correlations for the macroscopic surface tension based on the law of corresponding states. Empirical correlations for $p_{\rm sat}$, $\rho^l$, and $\gamma_0$ are discussed in the Appendix. Equation (13) is highly nonlinear, its right-hand side

$$R \equiv \sum_{n=1}^{\infty} n^{-\tau} \exp[-\theta_0(1+\alpha_\gamma n^{-1/3})n^{2/3}] \qquad (16)$$

is a positively termed series containing the unknown quantity $\alpha_\gamma$ in the argument of the exponential function. For each $T$ we are searching for the root in the interval $-1 \leqslant \alpha_\gamma < \infty$ ($\alpha_\gamma \geqslant -1$ implies that the microsopic surface tension for all clusters is positive). The derivative $(\partial R/\partial \alpha_\gamma)_T$ is negative for all temperatures, which means that $R$ is a monotonically decreasing function of $\alpha_\gamma$, yielding the uniqueness of the root of Eq. (13).

For *low* temperatures the surface tension is large ($\theta_0 > 1$), and the Tolman length is expected to be small ($|\alpha_\gamma| \ll 1$). With a high degree of accuracy we can in this case truncate the series at $n=1$, which results in the analytical solution

$$\alpha_\gamma = -\frac{1}{\theta_0} \ln\left[\frac{p_{\mathrm{sat}}}{q_0 k_B T}\right] - 1, \quad |\alpha_\gamma| \ll 1 \qquad (17)$$

For *high* temperatures the surface tension becomes small, and truncation of (16) at the first term is impossible. In a general case Eq. (13) has to be solved by iteration. The fast (exponential) convergence of (16) at each iteration step $k$ is provided by the terms with large absolute values of the argument of the exponential. Therefore we can truncate the series at $n = N^{(k)}$, satisfying

$$\theta_0 (N^{(k)})^{2/3} + \theta_0 \alpha_\gamma^{(k)} (N^{(k)})^{1/3} = G, \qquad (18)$$

where $\alpha_\gamma^{(k)}$ is the value of $\alpha_\gamma$ at the $k$th iteration step, and $G \gg 1$ is a large number (in our numerical procedure we have chosen $G = 100$). For each iteration step the truncation limit is given by

$$N^{(k)}(\theta_0; \alpha_\gamma^{(k)}) = \frac{1}{8}\left[-\alpha_\gamma^{(k)} + \left((\alpha_\gamma^{(k)})^2 + \frac{4G}{\theta_0}\right)^{1/2}\right]^3. \qquad (19)$$

Figure 1 shows the behavior of the reduced Tolman length

$$\delta_T^* \equiv \frac{\delta_T}{\sigma} = -\frac{\alpha_\gamma}{2} \frac{r_1}{\sigma}$$

for three nonpolar substances—argon, benzene, and $n$-nonane—as a function of the reduced temperature

$$t = \frac{T - T_c}{T_c}. \qquad (20)$$

The values of the molecular diameter $\sigma$ are given in Table I.

Comparison of theoretical predictions with MD simulations of [8] and [9] shows a good agreement in a temperature domain where reliable simulations were performed—except for one point all theoretical curves lie within the error bars of MD simulations. Not too close to $T_c$, the Tolman length for all substances is positive, and is about $0.2\sigma$. For small $|t|$ ($|t| \lesssim 2\times10^{-2}$) it changes sign at a certain temperature $T_\delta$ and becomes negative. At $T_\delta$ the surface tension of a droplet is equal to that of the flat surface. Finally, there is an indication that $\delta_T$ diverges when the critical point is approached as predicted by the density functional analysis of Fisher and Wortis. For this reason the numerical procedure fails near $T_c$. According to the thermodynamic definition (3), a negative Tolman length means that the surface of tension is situated on the gas side of the equimolar surface. Our results suggest that at $T > T_\delta$ the microscopic surface tension increases with increasing curvature, the effect being larger the larger the temperature. This trend is opposite to the usually discussed one taking place far from $T_c$. Note that a possibility of negative $\delta_T$ for the model system of penetrable spheres was pointed out by Hemingway, Henderson, and Rowlinson [14]. Figure 1 also shows the analytical solution (17) for argon. For $|t| > 0.3$ it appears to be a good approximation to the ''exact'' numerical solution but closer to the critical region it is essentially in error.

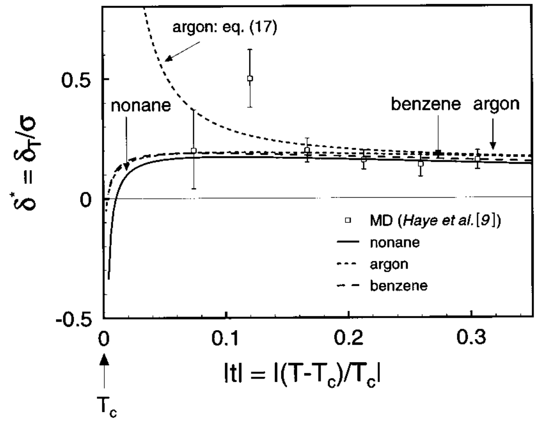

FIG. 1. Temperature dependence of the Tolman length. $\delta_T^* = \delta_T/\sigma$, $\sigma$ is a hard-core molecular diameter; $t = (T-T_c)/T_c$ is the reduced temperature. Lines, theoretical predictions [solution of Eq. (13)] for argon, benzene, and nonane. Squares, MD results of Haye and Bruin [9]. The MD estimate of Nijmeijer *et al.* [8] is $|\delta_T^*(|t|=0.17)| < 0.7$. Also shown is the approximate analytical solution (17) for argon, which is suitable in a low-temperature region but fails at high absolute temperatures (see the text).

Note finally that it would be desirable to derive a critical exponent for the Tolman length on the basis of the proposed semiphenomenological theory, and compare it with the density functional analysis of Fisher and Wortis [6]. However, at the present stage this does not seem to be plausible. The reason is that the Fisher droplet model [10] yielding Eq. (13) ignores cluster-cluster interactions (excluded volume effects), which become important in the critical region. Therefore in this region our theory is suggestive, but it cannot be taken literally for a calculation of a critical exponent. Taking into account intercluster interactions could be a direction for future development of the theory.

### III. CONCLUSIONS

We have formulated a semiphenomenological cluster theory of the Tolman length based on the Fisher cluster model of condensation combined with a Tolman-like ansatz for the microscopic surface tension of a cluster. Calculations performed for several nonpolar substances show that not too close to $T_c$ the Tolman length is positive and is about $0.2\sigma$; theoretical predictions are in good agreement with available MD simulation data. Near $T_c$, $\delta_T$ changes sign and diverges.

TABLE I. Thermophysical properties of argon, benzene, and nonane [13]. $p_c$, critical pressure in bar; $T_c$, critical temperature in K; $\rho_c$, critical number density in mol/cm$^3$; $T_b$, normal boiling point in K, $\sigma$, molecular diameter in Å, $a$, $b$, $c$, and $d$ are parameters of the saturation vapor pressure (A1).

| | $p_c$ | $T_c$ | $\rho_c^{-1}$ | $T_b$ | $\sigma$ | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|---|---|---|---|---|
| argon | 48.7 | 150.8 | 74.9 | 87.3 | 3.542 | −5.905 01 | 1.126 27 | −0.767 87 | −1.627 21 |
| benzene | 48.9 | 562.2 | 259 | 353.2 | 5.349 | −6.982 73 | 1.332 13 | −2.628 63 | −3.333 99 |
| nonane | 22.9 | 594.6 | 548 | 424 | 6.567 | −8.244 80 | 1.578 85 | −4.381 55 | −4.044 12 |

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## APPENDIX: EMPIRICAL CORRELATIONS FOR MACROSCOPIC PROPERTIES

In this appendix we present empirical correlations for $p_{\mathrm{sat}}$, $\rho^l$, and $\gamma_0$ for argon, benzene, and nonane used in calculations of the Tolman length from Eq. (13). The saturation vapor pressure $p_{\mathrm{sat}}$ for all of these substances has the form [13]

$$\ln\frac{p_{\mathrm{sat}}}{p_c}=(1-|t|)^{-1}[a|t|+b|t|^{1.5}+c|t|^3+d|t|^4], \quad \text{(A1)}$$

with the values of parameters $a$, $b$, $c$, and $d$ given in Table I.

The liquid mass densities $\rho_m^l$ (g/cm$^3$) of the compounds read as follows. Argon [15]: $\rho_m^l=1.37396[1-4.65\times10^{-3}(t_{\mathrm{Cels}}+183.15)]$. Benzene [15]: $\rho_m^l=0.90005-1.0636\times10^{-3}t_{\mathrm{Cels}}-0.0376\times10^{-6}t_{\mathrm{Cels}}^2-2.213\times10^{-9}t_{\mathrm{Cels}}^3$ Nonane [16]: $\rho_m^l=0.733503-7.87562\times10^{-4}t_{\mathrm{Cels}}-9.68937\times10^{-8}t_{\mathrm{Cels}}^2-1.29616\times10^{-9}t_{\mathrm{Cels}}^3$, $t_{\mathrm{Cels}}$ is the Celsius temperature. The liquid number density is given by

$$\rho^l=\frac{\rho_m^l N_A}{M},$$

where $M$ is a molar mass and $N_A$ the Avogadro number.

The widely used correlation for the macroscopic surface tension, $\gamma_0$, of nonpolar fluids reads [13]

$$\gamma_0(t)=A_\gamma|t|^{1.26}, \quad \text{(A2)}$$

$$A_\gamma=p_c^{2/3}T_c^{1/3}Q,$$
$$Q=0.1196\left[1+\frac{T_{br}\ln(p_c/1.01325)}{1-T_{br}}\right]-0.279. \quad \text{(A3)}$$

Here $A_\gamma$ is in dyn/cm, $p_{\mathrm{sat}}$ and $p_c$ are in bars, $T_{br}=T_b/T_c$, $T_b$ is a normal boiling point in K. Values of $T_c$, $T_b$, and $p_c$ are given in Table I.

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