# Thermodynamic theory of the Tolman's length*

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There still exists controversy on the sign and magnitude of the Tolman's length and the Tolman's gap. Further experimental, computational and theoretical investigations on them are needed to solve this problem. In 2006, Blokhuis and Kuipers obtained a rigorous relationship between the Tolman's length and other thermodynamic quantities for the single-component liquid–vapour system. In the present paper, we derive two general relationships between the Tolman's length and other thermodynamic quantities for the single-component liquid–vapour system. The relationship derived by Blokhuis and Kuipers and an earlier result turn out to be two special cases of our results.

**Keywords:** surface tension, Tolmans length, thermodynamics

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## 1. Introduction

The liquid–vapour interface is a transition zone between the liquid phase and the vapour phase. The density, pressure and other thermodynamic quantities in the transition zone vary continuously. The surface tension of the liquid–vapour interface is one of the most interesting physical properties of fluids. It is related to a great number of natural phenomena as well as to numerous industrial applications, for instance, nucleation, wetting, adhesives, emulsions, foams, dispersions, adsorption-based separations, lubricants, capillary penetration into porous media and floatation.[1−6] Therefore, surface tension is an important topic in chemical physics.[1−4] Surface tension phenomena was studied theoretically by mechanics, thermodynamics, quasi-thermodynamic and statistical mechanics. The interest here is the thermodynamic theory of surface tension.

Gibbs developed a rigorous theory of the phenomena of surface tension by the methods of thermodynamics.[1,7,8] In Gibbs's thermodynamical theory of capillary phenomena, the transition zone is modeled as a geometrical surface of zero thickness called dividing surface. The dividing surface can be any one of the equidensity surfaces, so it is not unique. For a spherical droplet, a dividing surface is a closed spherical surface with its centre located at the centre of the droplet. Different dividing surfaces have different surface tension and different extensive quantities, for instance, the molecule number of the liquid–vapour interface. A dividing surface with radius $R_{\rm s}$ is called the surface of tension if the Laplace's equation

$$p_{\rm l} - p_{\rm v} = \frac{2\sigma(R_{\rm s})}{R_{\rm s}} \tag{1}$$

is valid at it. Here $p_{\rm l}$ and $p_{\rm v}$ are the bulk pressures of liquid phase and vapour phase respectively, $\sigma$ is the surface tension of the liquid–gas interface. The surface tension of the surface of tension is denoted by $\sigma_{\rm s}$ below. A dividing surface with the number of molecules being zero called equimolecular dividing surface and its radius is denoted by $R_{\rm e}$.

The definition of the Tolman's gap is

$$\delta_{\rm G} = R_{\rm e} - R_{\rm s}. \tag{2}$$

The Tolman's gap is a function of $R_{\rm s}$ and temperature. The definition of the Tolman's length is

$$\delta_{\rm L} \equiv \lim_{R_{\rm s}\to\infty} \delta_{\rm G} \equiv \lim_{R_{\rm s}\to\infty} (R_{\rm e} - R_{\rm s}). \tag{3}$$

The Tolman's gap $\delta_{\rm G}$ and the Tolman's length $\delta_{\rm L}$ are of nanoscale and are typical nano-concepts.

Based on thermodynamics, Gibbs found that the surface tension of the liquid–gas interface was related to the radius of the surface of tension and later the following differential equation, i.e., the famous Gibbs-Tolman–Koening–Buff equation[1,6−12] was es-

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$$\frac{1}{\sigma_{\rm s}}\frac{{\rm d}\sigma_{\rm s}}{{\rm d}R_{\rm s}}=\frac{\dfrac{2\delta_{\rm G}}{R_{\rm s}^2}\left[1+\dfrac{\delta_{\rm G}}{R_{\rm s}}+\dfrac{1}{3}\left(\dfrac{\delta_{\rm G}}{R_{\rm s}}\right)^2\right]}{1+\dfrac{2\delta_{\rm G}}{R_{\rm s}}\left[1+\dfrac{\delta_{\rm G}}{R_{\rm s}}+\dfrac{1}{3}\left(\dfrac{\delta_{\rm G}}{R_{\rm s}}\right)^2\right]}. \tag{4}$$

The Gibbs–Tolman–Koening–Buff equation is valid for single-component liquids as well as multi-components liquids. For the latter the meaning of the symbol $R_{\rm e}$ in Eq. (2) must be renewed. But we restrict ourselves here only in single-component liquids.

Tolman[9] pointed out that for sufficiently large droplets, neglecting high terms and treating $\delta_{\rm G}$ as a constant $\delta_{\rm L}$, Eq. (4) can be solved. The result is

$$\frac{\sigma_{\rm s}}{\sigma_\infty}=\frac{1}{1+\dfrac{2\delta_{\rm L}}{R_{\rm s}}}+\ldots=1-\frac{2\delta_{\rm L}}{R_{\rm s}}+\ldots. \tag{5}$$

Fisher and Israelachvili's experimental results confirmed that the surface tension of the liquid–gas interface is curvature-dependent.[13]

It is obvious that in Eq. (4), the surface tension $\sigma_{\rm s}$ and the Tolman's gap $\delta_{\rm G}$ are two unknown functions, therefore given either of them, we can obtain the other by solving this equation. Thus, the surface tension $\sigma_{\rm s}$ and the Tolman's gap $\delta_{\rm G}$ are both important in chemical physics and are both difficult to study. These two functions are both attractive for researchers. Since the Tolman's length $\delta_{\rm L}$ is the limiting value of the Tolman's gap $\delta_{\rm G}$ at infinite large $R_{\rm s}$, the Tolman's length $\delta_{\rm L}$ is also an attractive problem.

For simple liquids, the Tolman's length obtained by density functional theory is negative.[14–23] Molecular dynamics simulations for a Lennard–Jones system showed that the Tolman's length is positive.[24–26] In 2006, Lei *et al.*[27] reported a larger scale molecular dynamics simulation and showed that the Tolman's lengths, although positive, are much smaller in magnitude than previously reported. In particular, they found that the cut-length of interparticle interaction can significantly affect the magnitude of the Tolman's length.

Thus we see that there still exists controversy on the sign and magnitude of the Tolman's length or the Tolman gap. Therefore further experimental, computational and theoretical investigations on the Tolman's length and the Tolman gap are needed to solve this problem.

The purpose of this paper is to study the Tolman's length by methods of thermodynamics. In this respect Fisher *et al.*[28–30] derived the following explicit relationship between the Tolman's length and other thermodynamic quantities for single-component liquid–vapour system by methods of thermodynamics

$$\delta_{\rm L}=-\frac{(\rho_{\rm l1e}-\rho_{\rm v1e})}{2(\rho_{\rm l0}-\rho_{\rm v0})}-\frac{\mu_{2\rm e}(\rho_{\rm l0}-\rho_{\rm v0})}{2\sigma_\infty}, \tag{6}$$

where $\mu$ is the chemical potential of the system, $\rho_{\rm l0}$ and $\rho_{\rm v0}$ are the number densities of the liquid phase and the vapour phase of the planar-interface liquid–vapour system respectively, $\rho_{\rm l1e}$ and $\rho_{\rm v1e}$ are the isothermal partial derivatives of number densities of the liquid phase and the vapour phase with respect to the curvature of the equimolecular dividing surface at the zero curvature respectively, $\mu_{2\rm e}$ is the second-order isothermal partial derivative of the chemical potential with respect to the curvature of the equimolecular dividing surface at the zero curvature, $\sigma_\infty$ is the surface tension of the planar-interface liquid–vapour system.

In 2006, Blokhuis and Kuipers[14] transfer Eq. (6) into a more useful relationship between the Tolman's length and the isothermal compressibility of the liquid and the vapour

$$\begin{aligned}\delta_{\rm L}=&-\frac{\sigma_\infty}{(\rho_{\rm l0}-\rho_{\rm v0})^2}(\rho_{\rm l0}^2\kappa_{\rm l}-\rho_{\rm v0}^2\kappa_{\rm v})\\&-\frac{\mu_{2\rm e}(\rho_{\rm l0}-\rho_{\rm v0})}{2\sigma_\infty},\end{aligned} \tag{7}$$

where $\kappa_{\rm l}$ and $\kappa_{\rm v}$ are the isothermal compressibility of the liquid phase and the vapour phase at zero curvature respectively.

Our aim is to derive two explicit relations between the Tolman's length and other thermodynamic quantities for the single-component liquid–vapour system in terms of any dividing surface, which will contain Eqs. (6) and (7) as special cases.

## 2. Two general thermodynamic formulae of the Tolman's length for single-component liquid–vapour system in terms of arbitrary dividing surface

For an arbitrary dividing surface with radius $R_\varepsilon$, we introduce the following notation

$$R_\varepsilon=R_{\rm e}-\varepsilon\delta_{\rm G}, \tag{8}$$

where $\varepsilon$ is a real number. For $\varepsilon=0$ and $\varepsilon=1$, Eq. (8) gives

$$R_\varepsilon|_{\varepsilon=0}=R_{\rm e}, \tag{9}$$

$$R_\varepsilon|_{\varepsilon=1} = R_{\rm e} - \delta_{\rm G} = R_{\rm s}. \tag{10}$$

Using Eqs. (10) and (5), Eq. (1) becomes

$$\begin{aligned} p_{\rm l} - p_{\rm v} &= \frac{2\sigma_\infty\left(1 - \dfrac{2\delta_{\rm L}}{R_{\rm s}} + \ldots\right)}{R_{\rm e}\left(1 - \dfrac{\delta_{\rm G}}{R_{\rm e}}\right)} \\ &= \frac{2\sigma_\infty}{R_{\rm e}}\left(1 - \frac{2\delta_{\rm L}}{R_{\rm e}} + \frac{\delta_{\rm G}}{R_{\rm e}} + \ldots\right). \end{aligned} \tag{11}$$

We have the following Tayler's expansion

$$\delta_{\rm G} = \delta_{\rm L} + \delta_{G1\varepsilon}\frac{1}{R_\varepsilon} + \ldots\,, \tag{12}$$

where

$$\delta_{\rm G1\varepsilon} = \left.\frac{\partial\delta_{\rm G}}{\partial(1/R_\varepsilon)}\right|_{1/R_\varepsilon=0}. \tag{13}$$

Using Eqs. (12) and (8), Eq. (11) becomes

$$p_{\rm l} - p_{\rm v} = \frac{2\sigma_\infty}{R_\varepsilon}\left[1 - \frac{\delta_{\rm L}}{R_\varepsilon}(1+\varepsilon)\right] + \ldots\,. \tag{14}$$

For isothermal processes, we have

$$\mathrm{d}p_{\rm l} = \rho_{\rm l}\mathrm{d}\mu\,, \tag{15}$$

$$\mathrm{d}p_{\rm v} = \rho_{\rm v}\mathrm{d}\mu\,, \tag{16}$$

which give

$$\mathrm{d}(p_{\rm l} - p_{\rm v}) = (\rho_{\rm l} - \rho_{\rm v})\mathrm{d}\mu. \tag{17}$$

For the number densities of the liquid phase and the vapour phase of single-component spherical droplets, we have the following Tayler's expansions with respect to the curvature of any dividing surface $1/R_\varepsilon$, respectively

$$\rho_{\rm l} = \rho_{l0} + \frac{\rho_{\rm l1\varepsilon}}{R_\varepsilon} + \ldots\,, \tag{18}$$

$$\rho_{\rm v} = \rho_{v0} + \frac{\rho_{\rm v1\varepsilon}}{R_\varepsilon} + \ldots\,, \tag{19}$$

where

$$\begin{aligned} \rho_{\rm l1\varepsilon} &= \left.\frac{\partial\rho_{\rm l}}{\partial(1/R_\varepsilon)}\right|_{1/R_\varepsilon=0}, \\ \rho_{\rm v1\varepsilon} &= \left.\frac{\partial\rho_{\rm v}}{\partial(1/R_\varepsilon)}\right|_{1/R_\varepsilon=0}. \end{aligned} \tag{20}$$

From Eqs. (18) and (19), we have

$$\rho_{\rm l} - \rho_{\rm v} = (\rho_{\rm l0} - \rho_{\rm v0}) + \frac{(\rho_{\rm l1\varepsilon} - \rho_{\rm v1\varepsilon})}{R_\varepsilon} + \ldots\,. \tag{21}$$

We have the following Tayler's expansion of the chemical potential with respect to the curvature of any dividing surface $1/R_\varepsilon$

$$\mu = \mu_0 + \frac{\mu_{1\varepsilon}}{R_\varepsilon} + \frac{\mu_{2\varepsilon}}{R_\varepsilon^2} + \ldots\,, \tag{22}$$

where

$$\begin{aligned} \mu_{1\varepsilon} &= \left.\frac{\partial\mu}{\partial(1/R_\varepsilon)}\right|_{1/R_\varepsilon=0}, \\ \mu_{2\varepsilon} &= \left.\frac{\partial^2\mu}{2\partial(1/R_\varepsilon)^2}\right|_{1/R_\varepsilon=0}. \end{aligned} \tag{23}$$

Putting Eqs. (14), (21), and (22) into Eq. (17), we have

$$\begin{aligned} &\mathrm{d}\left[\frac{2\sigma_\infty}{R_\varepsilon}(1 - \frac{(1+\varepsilon)\delta_{\rm L}}{R_\varepsilon} + \ldots)\right] \\ &= \left[(\rho_{\rm l0} - \rho_{\rm v0}) + \frac{(\rho_{\rm l1\varepsilon} - \rho_{\rm v1\varepsilon})}{R_\varepsilon} + \ldots\right] \\ &\quad\times \mathrm{d}\left(\mu_0 + \frac{\mu_{1\varepsilon}}{R_\varepsilon} + \frac{\mu_{2\varepsilon}}{R_\varepsilon^2} + \ldots\right). \end{aligned} \tag{24}$$

Comparing the two main terms on the two sides of Eq. (24), we obtain

$$\mu_{1\varepsilon} = \frac{2\sigma_\infty}{\rho_{\rm l0} - \rho_{\rm v0}}, \tag{25}$$

$$\mu_{2\varepsilon} = -\frac{2(1+\varepsilon)\delta_{\rm L}\sigma_\infty}{\rho_{\rm l0} - \rho_{\rm v0}} - \frac{\sigma_\infty(\rho_{\rm l1\varepsilon} - \rho_{\rm v1\varepsilon})}{(\rho_{\rm l0} - \rho_{\rm v0})^2}. \tag{26}$$

From Eqs. (25) and (26), we obtain the first general thermodynamic formula of the Tolman's length of single-component liquid–vapour system in terms of arbitrary dividing surface

$$\delta_{\rm L} = -\frac{(\rho_{\rm l1\varepsilon} - \rho_{\rm v1\varepsilon})}{2(1+\varepsilon)(\rho_{\rm l0} - \rho_{\rm v0})} - \frac{\mu_{2\varepsilon}(\rho_{\rm l0} - \rho_{\rm v0})}{2(1+\varepsilon)\sigma_\infty}. \tag{27}$$

The definition of isothermal compressibility $\kappa_{\rm T}$ of bulk fluid is

$$\kappa_{\rm T} = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_{\rm T} = \frac{1}{\rho^2}\left(\frac{\partial\rho}{\partial\mu}\right)_{\rm T}. \tag{28}$$

From Eqs. (28) and (25), we obtain

$$\kappa_{\rm l} = \frac{1}{\rho_{\rm l0}^2}\left(\frac{\partial\rho_{\rm l}}{\partial\mu}\right)_{\rm T} = \frac{\rho_{\rm l1\varepsilon}}{\rho_{\rm l0}^2\mu_{1\varepsilon}} = \frac{\rho_{\rm l1\varepsilon}(\rho_{\rm l0} - \rho_{\rm v0})}{2\sigma_\infty\rho_{\rm l0}^2}, \tag{29}$$

$$\kappa_{\rm v} = \frac{1}{\rho_{\rm v0}^2}\left(\frac{\partial\rho_{\rm v}}{\partial\mu}\right)_{\rm T} = \frac{\rho_{\rm v1\varepsilon}}{\rho_{\rm v0}^2\mu_{1\varepsilon}} = \frac{\rho_{\rm v1\varepsilon}(\rho_{\rm l0} - \rho_{\rm v0})}{2\sigma_\infty\rho_{\rm v0}^2}, \tag{30}$$

where $\kappa_{\rm l}$ and $\kappa_{\rm v}$ are the isothermal compressibilities of the liquid phase and the vapour phase respectively.

From Eqs. (29) and (30), we obtain

$$\rho_{\rm l1\varepsilon} - \rho_{\rm v1\varepsilon} = \frac{2\sigma_\infty}{(\rho_{\rm l0} - \rho_{\rm v0})}(\rho_{\rm l0}^2\kappa_{\rm l} - \rho_{\rm v0}^2\kappa_{\rm v}). \tag{31}$$

Putting Eq. (31) into Eq. (27), we obtain the second general thermodynamic formula of the Tolman's length of single-component liquid–vapour system in terms of arbitrary dividing surface and the isothermal compressibilities

$$\begin{aligned} \delta_{\rm L} &= -\frac{\sigma_\infty}{(1+\varepsilon)(\rho_{\rm l0} - \rho_{\rm v0})^2}(\rho_{\rm l0}^2\kappa_{\rm l} - \rho_{\rm v0}^2\kappa_{\rm v}) \\ &\quad - \frac{\mu_{2\varepsilon}(\rho_{\rm l0} - \rho_{\rm v0})}{2(1+\varepsilon)\sigma_\infty}. \end{aligned} \tag{32}$$

## 3. Comparison between our general thermodynamic formulae of the Tolman's length and the previous formulae

The two general thermodynamic formulae (27) and (32) of the Tolman's length contain a parameter $\varepsilon$, the values of which cover all the dividing surface. Therefore, formulae (27) and (32) can be applied to any dividing surface. For example, letting $\varepsilon = 1$ in formulae (27) and (32), we obtain the following two explicit thermodynamic formulae of the Tolman's length in terms of the surface of tension

$$\delta_{\rm L} = -\frac{(\rho_{\rm l1s} - \rho_{\rm v1s})}{4(\rho_{\rm l0} - \rho_{\rm v0})} - \frac{\mu_{\rm 2s}(\rho_{\rm l0} - \rho_{\rm v0})}{4\sigma_\infty}, \quad (33)$$

$$\delta_{\rm L} = -\frac{\sigma_\infty}{2(\rho_{\rm l0} - \rho_{\rm v0})^2}(\rho_{\rm l0}^2\kappa_{\rm l} - \rho_{\rm v0}^2\kappa_{\rm v}) - \frac{\mu_{\rm 2s}(\rho_{\rm l0} - \rho_{\rm v0})}{4\sigma_\infty}, \quad (34)$$

where

$$\rho_{\rm l1s} = \rho_{\rm l1\varepsilon}\big|_{\varepsilon=1}, \rho_{\rm v1s} = \rho_{\rm v1\varepsilon}\big|_{\varepsilon=1}, \quad \mu_{\rm 2s} = \mu_{2\varepsilon}\big|_{\varepsilon=1}.$$

Letting $\varepsilon = 0$ in formulae (27) and (32), we obtain the following two explicit thermodynamic formulas of the Tolman's length in terms of the equimolecular dividing surface

$$\delta_{\rm L} = -\frac{(\rho_{\rm l1e} - \rho_{\rm v1e})}{2(\rho_{\rm l0} - \rho_{\rm v0})} - \frac{\mu_{\rm 2e}(\rho_{\rm l0} - \rho_{\rm v0})}{2\sigma_\infty}, \quad (35)$$

$$\delta_{\rm L} = -\frac{\sigma_\infty}{(\rho_{\rm l0} - \rho_{\rm v0})^2}(\rho_{\rm l0}^2\kappa_{\rm l} - \rho_{\rm v0}^2\kappa_{\rm v}) - \frac{\mu_{\rm 2e}(\rho_{\rm l0} - \rho_{\rm v0})}{2\sigma_\infty}, \quad (36)$$

where

$$\rho_{\rm l1e} = \rho_{\rm l1\varepsilon}\big|_{\varepsilon=0}, \quad \rho_{\rm v1e} = \rho_{\rm v1\varepsilon}\big|_{\varepsilon=0}, \quad \mu_{\rm 2e} = \mu_{2\varepsilon}\big|_{\varepsilon=0}.$$

Equations (35) and (36) are the same as Eqs. (2.14) and (3.4) in Ref. [14] given by Blokhuis and Kuipers, which illustrate that the latter two formulae are the special cases of our results Eqs. (27) and (32).

## 4. Conclusion

There still exists controversy on the sign and magnitude of the Tolman's length and the Tolman's gap. Further experimental, computational and theoretical investigations on them are needed to solve this problem. We have derived two general relationships between the Tolman's length and other thermodynamic quantities for single-component liquid–vapour system by method of thermodynamics. The relationship of Blokhuis and Kuipers in Ref. [14] and an early result turn out to be two special cases of our results.

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