Reexamination of Tolman’s law and the Gibbs adsorption equation for curved interfaces

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The influence of the surface curvature $1/R$ on the surface tension $\gamma$ of small droplets in equilibrium with a surrounding vapour, or small bubbles in equilibrium with a surrounding liquid, can be expanded as $\gamma(R) = \gamma_0 + c_1\gamma_0/R + O(1/R^2)$, where $R = R_0$ is the radius of the surface of tension, and $\gamma_0$ is the surface tension of the planar interface corresponding to zero curvature. According to Tolman’s law, the first-order coefficient $c_1 = -2\delta_0$ in this expansion is obtained from the planar limit $\delta_0$ of the Tolman length, i.e., the difference $\delta = R_\rho - R_\gamma$ between the equimolar radius $R_\rho$ and $R_\gamma$. We show here that the deduction of Tolman’s law from interfacial thermodynamics relies on an inaccurate application of the Gibbs adsorption equation to dispersed phases (droplets or bubbles). A revision of the underlying theory reveals that the adsorption equation needs to be employed in an alternative manner to that suggested by Tolman. Accordingly, we develop a generalized Gibbs adsorption equation which consistently takes the size dependence of interfacial properties into account, and show that from this equation, a relation between the size of the dispersed phase on $\gamma$ cannot be deduced, invalidating the argument which was put forward by Tolman [J. Chem. Phys. 17 (1949) 333].

Keywords: Surface tension, nanodroplets, nucleation theory, Tolman length, thermodynamics of small systems

I. INTRODUCTION

The surface tension of small droplets or bubbles at the nanometre length scale has a significant influence on the formation of dispersed phases by homogeneous nucleation. It is also crucial to understand droplet or bubble growth, decay, coalescence, and the coupling between heat and mass transfer at curved interfaces.

The capillarity approximation is commonly employed: The surface tension $\gamma$ of a nanodroplet is assumed to be identical with the value $\gamma_0$ that is attained in the limit of zero curvature, i.e., infinite droplet radius, or for a macroscopic planar interface. This approximation has the advantage that $\gamma_0$ is experimentally measurable, while the actual value of $\gamma$ is unknown for nanodispersed phases.

However, the capillarity approximation leads to a paradox when the Laplace equation

$$p'(\mu, T) - p''(\mu, T) = \frac{2\gamma}{R_\gamma}$$

is applied to extremely small droplets. This equation characterizes the difference between the pressure $p'$ in a dispersed phase (e.g., the droplet) and $p''$ in the surrounding phase (e.g., the vapour) in terms of the Laplace radius $R_\gamma$, which is also referred to as the radius of the surface of tension. In the case of a constant value of $\gamma$, the pressure difference would have to become infinite as $R_\gamma \to 0$.

For molecular fluids, this is unphysical. On extending the equation of state into the metastable region (for the surrounding phase), under the boundary conditions of equal chemical potential $\mu' = \mu''$ and temperature $T' = T''$, a maximum is obtained for the pressure difference that can be established at a curved interface for a given temperature. This maximum pressure difference is reached at the spinodal boundary for the phase that surrounds the nanodispersed phase, as shown in Fig. 1 which contains a $\mu-p$ diagram for the Lennard-Jones truncated and shifted (LJTS) fluid. At the spinodal, corresponding to the circles in Fig. 1, the surrounding phase becomes unstable.

As a consequence, there is either a minimal value for the radius $R_\gamma$ such that no droplets with a smaller radius can form in thermodynamic equilibrium, or the surface tension tends to zero $\gamma \to 0$ (as $R_\gamma \to 0$) in the limit of spinodal conditions for the surrounding phase, such that
the ratio $\gamma / R_\gamma$ remains finite. In some cases, there may be a minimal radius for stable droplets. In general, $\gamma$ depends on $R_\gamma$, and both for droplets and for bubbles it is therefore important to understand the behavior of $\gamma(R_\gamma)$. The consensus seems to be that $\gamma \to 0$ for $R_\gamma \to 0$.\footnote{13} \footnote{14} \footnote{15} 

This was also suggested by Tolman in a posthumous article\footnote{13} submitted for publication by Kirkwood and Buff together with their own comment\footnote{14} on Tolman’s work from the point of view of statistical mechanics, which supported Tolman’s conclusions. The expression\footnote{13} \footnote{14} \footnote{15} is known as Tolman’s law, where the higher-order terms are typically neglected. This relation is frequently employed to describe the influence of the surface curvature on the surface tension. The Tolman length $\delta$ is introduced in Eq. (2) as a characteristic length scale. The value of $\delta$ does not, however, have to be constant; it can depend on the radius itself.\footnote{13} \footnote{14} \footnote{15} \footnote{16} \footnote{17} \footnote{18} \footnote{19} \footnote{20} \footnote{21} The value of $\delta$ to be used in Eq. (2) is that for the planar limit $\delta_0 = \lim_{R_\gamma \to \infty} \delta(R_\gamma)$ of the Tolman length, since the point of reference, around which $\gamma / \gamma_0$ is expanded in Eq. (2), is an interface with zero curvature, i.e., $1/R_\gamma = 0$.

Tolman\footnote{13} obtained Eq. (2) following a series of arguments based on the Gibbs adsorption equation\footnote{17} \footnote{18} in the form

$$\zeta \, dT + d\gamma = -\Gamma \, d\mu,$$

(3)

which relates a change in the surface tension to the specific surface excess entropy $\zeta$, the adsorption $\Gamma$, and the chemical potential $\mu$ for a pure substance. In general, for a system containing $\nu$ components, $\Gamma \, d\mu$ would have to be replaced by $\Gamma \, d\mu_i$, using vector notation to abbreviate the summation over components.

Tolman pointed out that even for a pure fluid (\nu = 1), an adsorption $\Gamma \neq 0$ can occur if the radius of the surface of tension $R_\gamma$ deviates from the equimolar (Gibbs dividing) radius $R'\rho$, i.e., the radius that is defined from the condition $\Gamma = 0$. In order to quantify the excess of the equimolar radius over the radius of the surface tension, Tolman introduced the quantity\footnote{13} \footnote{14} \footnote{15} \footnote{16}

$$\delta = R_\rho - R_\gamma,$$

(4)

which can be expressed in various ways which are equivalent if the validity of Tolman’s law is assumed.\footnote{19} \footnote{20} \footnote{21} For pure fluids and spherical interfaces, the adsorption $\Gamma$ and the radii $R_\gamma$ and $R_\rho$ are related by\footnote{13} \footnote{14} \footnote{15} \footnote{16}

$$\frac{\Gamma}{\rho' - \rho''} = \delta \left[ 1 + \delta \frac{\delta^2}{3 R_\gamma^2} \right].$$

(5)

Eq. (6) is obtained by integrating over a spherical density profile, where $\rho'$ and $\rho''$ are the densities of the coexisting phases; here and in the following discussion, the phase with the density $\rho'$, the pressure $p'$, etc., is the dispersed phase, and the phase with the density $\rho''$, the pressure $p''$, etc., is the surrounding phase. By combining Eqs. (1), (3), and employing the Gibbs-Duhem equation,

$$(d\mu)_T = \left( \frac{dp'}{\rho'} \right)_T = \left( \frac{dp''}{\rho''} \right)_T = \left( \frac{d[p' - p'']}{\rho' - \rho''} \right)_T,$$

(6)

where the subscript indicates isothermal conditions, Tolman\footnote{13} obtained

$$\left( \frac{\partial \gamma}{\partial R_\gamma} \right)_T = \frac{2 \delta}{R_\gamma^2} \left( 1 + \frac{\delta}{R_\gamma} + \frac{\delta^2}{3 R_\gamma^2} \right)$$

$$\times \left[ 1 + 2 \delta \left( 1 + \frac{\delta}{R_\gamma} + \frac{\delta^2}{3 R_\gamma^2} \right) \right]^{-1},$$

(7)

an integrated version of which is given by Eq. (2). This result can be assessed from both an empirical and a theoretical point of view. Empirically, the size dependence of $\gamma$ can be expressed as an expansion in the inverse radius

$$\frac{\gamma}{\gamma_0} = 1 + \sum_{k=1}^{\infty} \frac{c_k}{R_\gamma^k},$$

(8)
at constant temperature; following Tolman’s law, the Tolman length $\delta$ is seen to characterize the first-order coefficient

$$c_1 = \lim_{R_\gamma \to \infty} \frac{1}{\gamma_0} \left( \frac{\partial \gamma}{\partial (1/R_\gamma)} \right)_T = - \lim_{R_\gamma \to \infty} 2\delta.$$  

(9)

From the empirical point of view, it essentially does not matter how Tolman’s law was derived, whether this derivation correctly reflects the underlying thermodynamics, and how the dependence $\gamma(R_\gamma)$ and the coefficient $c_1$ are related to other properties of the dispersed phase, such as its density profile.

In the recent literature, the first-order expression from Eq. (2) is increasingly regarded as empirically insufficient. It is consistently found that $c_1$ is very small for molecular fluids $^{21-30}$ supporting Tolman $^{13}$ who suggested $\delta \approx 10^{-19}$ m. However, the sign of $c_1$ may be positive, which would contradict Tolman’s expectation $^{13}$ For atomic nuclei, a Tolman length of the order of $\delta \approx 10^{-15}$ m was found $^{31,32}$ In a series of excellent papers, Binder and collaborators $^{33-37}$ have repeatedly shown that the first-order contribution to $\gamma$ in terms of the surface curvature is zero or very small, with the most relevant contribution coming from the second-order term. It has been argued that even if the contribution from $c_1/R_\gamma$ increases $\gamma$ slightly ($c_1 > 0$), it is eventually outweighed by a negative contribution proportional to $1/R_\gamma^2$, following Malijevský and Jackson $^{12}$ or proportional to $1/R_\gamma^2$, following Ghoufi and Malfreyt $^{38}$ from which the trend $\gamma \to 0$ for $R_\gamma \to 0$ is recovered.

From the empirical perspective, the main objection to Tolman’s law essentially concerns the truncation of the infinite power series from Eq. (5) after the $c_1/R_\gamma$ term. This truncation was introduced by Tolman $^{13}$ as an approximation and has therefore always been expected to break down, at least in the limit of extremely small droplets. The theoretical aspect of Tolman’s law, which consists in ascribing a physical meaning to $c_1$, i.e.,

$$c_1 = -2\delta_0 = \lim_{R_\gamma \to \infty} 2(R_\gamma - R_\rho),$$  

(10)

has not come under strict criticism despite the known empirical shortcomings of the Tolman approach.

We show here that the theoretical interpretation of Tolman’s law is not valid, because the derivation of the identity $c_1 = -2\delta_0$ is not consistent with interfacial thermodynamics. The basic reason is that the version of the Gibbs adsorption equation given by Eq. (3), on which Tolman’s approach is based, strictly holds only for transitions which do not alter the surface area. Since changing the radius of a droplet also changes its surface area, it is incorrect to discuss the dependence of $\gamma$ on $R_\gamma$ on the basis of Eq. (3), and the theoretical basis of Tolman’s law is put into question.

II. THEORY

A. Surface tension

A system with $\nu$ components and two coexisting fluid phases in thermodynamic equilibrium is considered here: The dispersed phase has the volume $V'$ and the surrounding phase has the volume $V''$. Different topologies can be considered for the dispersed phase, which can be a spherical droplet (or bubble), i.e., the scenario considered by Tolman, but also, e.g., a planar thin film $^{30,31}$ or a cylinder $^{24,25,31}$ The dispersed phase can be vapour (surrounded by liquid) or liquid (surrounded by vapour or another liquid phase). It is assumed that the topology does not change, i.e., the dispersed phase is either spherical in all cases, cylindrical in all cases, or planar in all cases.

Following the approach of Gibbs $^{22}$ surface excess contributions are ascribed to the interface for all extensive thermodynamic properties. In this way, the Helmholtz free energy $A$ of the system can be decomposed into

$$A = A' + A'' + A^E,$$  

(11)

where $A'$ is the Helmholtz free energy of a homogeneous fluid phase containing $N'$ molecules in a volume $V'$ and at a temperature $T$. Analogously, $A''$ is the free energy of a homogeneous fluid phase characterized by $N''$, $V''$, and $T$. The surface excess term $A^E$ describes the deviation of the Helmholtz free energy of the actual system, containing both phases and the interface, from the sum of the Helmholtz free energies of two homogeneous reference systems. Following Gibbs, the dividing surface is defined as a two-dimensional boundary which does not have a volume. Therefore, the overall volume is always

$$V = V' + V'',$$  

(12)

so that the excess volume is zero, $V^E = 0$.

Thermodynamically, the surface tension $\gamma$ can be defined as the partial derivative of the free energy with respect to the surface area $f$, for a variation that leaves all other thermodynamic properties of the coexisting phases constant, so that only the size of the surface area $f$ changes $^{34}$ In the case of the Helmholtz free energy

$$A = A(N, V', V'', T, f),$$  

(13)
the total differential can be written as

\[ dA = \sum_{i=1}^{\nu} \left( \frac{\partial A}{\partial N_i} \right)_{N_i \neq \nu', \nu'', T, f} dN_i + \left( \frac{\partial A}{\partial V'} \right)_{N, \nu'', T, f} dV' + \left( \frac{\partial A}{\partial V''} \right)_{N, \nu', T, f} dV'' + \left( \frac{\partial A}{\partial T} \right)_{N, \nu', \nu'', f} dT + \left( \frac{\partial A}{\partial f} \right)_{N, \nu', \nu'', T} df. \quad (14) \]

The surface tension corresponds to a variation of the Helmholtz free energy with the surface area at constant number of molecules \( N \) for all components, constant volume \( V' \) and \( V'' \) of the coexisting phases, and constant temperature \( T \):

\[ \gamma = \left( \frac{\partial A}{\partial f} \right)_{N, \nu', \nu'', T}. \quad (15) \]

The other partial derivatives yield the chemical potential of the components \( \partial A/\partial N_i = \mu_i \), the pressure of the coexisting phases \( \partial A/\partial V' = -p', \partial A/\partial V'' = -p'' \), and the entropy \( \partial A/\partial T = -S \), from which Eq. (14) can be expressed as

\[ dA = \mu dN - p' dV' - p'' dV'' - S dT + \gamma df. \quad (16) \]

For discussions of curved interfaces, the radius \( R \) is often included as a variable, contributing to \( dA \) with the term \( C dR \). However, in the case of the radius of tension \( R = R_c \), the identity \( C = 0 \) can be deduced from the Laplace equation, cf. Eq. (1), eliminating this term.\(^{17,43}\) and subsequent equations are valid both for planar and curved interfaces.

This definition of \( \gamma \) is complicated by the fact that a thermodynamic system specified by the boundary conditions \( N, V', V'', T, f \) is actually overspecified, since strictly speaking, these quantities cannot be varied independently from each other. In particular, if \( f(V') \) can be expressed as a function of \( V' \), e.g., for spherical dispersed phases where both \( f \) and \( V' \) are determined by \( R_c \), it is impossible to conduct a variation of \( f \) at constant \( V' \). At thermodynamic equilibrium, for a system containing \( \nu \) components, there are \( \nu + 2 \) thermodynamic degrees of freedom, if extensive properties are counted, assuming that the topology of the system (e.g., containing a spherical droplet) is known. If \( \nu + 2 \) quantities, e.g., \( N, T, \) and \( f \), are specified as boundary conditions, they determine all other properties of the system in thermodynamic equilibrium.

This raises a key question: How can Eqs. (13) to (16), which are based on the \( \nu + 4 \) variables \( N, V', V'', T, \) and \( f \), be given a well-defined meaning thermodynamically?

Various solutions to this problem have been offered. Following Hill, Homman \( ^{44,45} \) and Lau \( ^{46} \) consider the total differential in terms of the variables \( N, T, R_\alpha, R_\beta, \) and \( R_c \), still corresponding \( \nu + 4 \) variables. Two of these variables \( (R_\alpha \) and \( R_\beta) \) are radii far from the interface, inside and outside the droplet, in the case of nano-dispersed phases, however, it is questionable whether there is a position inside the dispersed phase which is sufficiently far away from the interface. For planar interfaces, a notation similar to that of Hill\(^ {44,45} \) is developed by Marmur\(^ 43 \) and Rowlinson and Widom\(^ {48,49} \) use \( R_\alpha \) and \( R_\beta \) as well as a conical angle \( \omega \) to define the system, but subsequently replace these variables by \( f, V', \) and \( V'' \). Lau et al.\(^ {46} \) have recently introduced the concept of a transformation of the spatial metric, on the basis of which the test area method\(^ {43,46} \) was rederived in a mathematically rigorous way. By transforming the spatial metric, i.e., the definition of the intermolecular distances (and the surface area), the area \( f \) can be varied without changing \( N, V', V'', \) or \( T, \) and without departing from thermodynamic equilibrium.\(^ {43} \) Furthermore, there are approaches which effectively assign a volume to the interface and thereby abandon, or generalize, interfacial thermodynamics following Gibbs\(^ {50} \) such that Eq. (12) does not necessarily apply.\( ^{50} \)

A well-defined expression for \( \gamma \) which does not rely on a transformation of the spatial metric, and does not depart from interfacial thermodynamics following Gibbs, can be obtained by subtracting the total differentials for the two bulk phases \((dA' \) and \( dA'') \) from \( dA \).\(^ {18} \) Thereby, the total differential of the surface excess Helmholtz free energy is

\[ dA^E = dA - dA' - dA'' \quad (17) \]

where from Eq. (10)

\[ dA = \mu dN - p' dV' - p'' dV'' - S dT + \gamma df, \]

\[ dA' = \mu dN' - p' dV' - S dT', \]

\[ dA'' = \mu dN'' - p'' dV'' - S'' dT', \]

so that\(^ {18} \)

\[ dA^E = \mu dN^E - S^E dT + \gamma df, \quad (19) \]

wherein \( N^E = \Gamma f \) and \( S^E = S - S' - S'' \). The chemical and thermal equilibrium conditions, \( \mu = \mu' = \mu'' \) and \( T = T' = T'' \), are used here; it is not assumed that the pressure in both phases is equal, which is only the case for planar interfaces. However, \( p' \) and \( p'' \) are not necessarily different, and Eq. (12) is valid for both planar and curved interfaces.

Rowlinson and Widom\(^ {48,49} \) refer to Eq. (19) as the fundamental equation for \( A^E \) in terms of \( N^E, T, \) and \( f \). This is justifed, since an independent variation of these \( \nu + 2 \) quantities is consistently possible. Accordingly, the surface tension is given by

\[ \gamma = \left( \frac{\partial A^E}{\partial f} \right)_{N^E, T}. \quad (20) \]
For a system without an interface \( f = 0 \), there is no surface excess Helmholtz free energy \( \Delta E^E = 0 \) and no adsorption \( N^E = 0 \), for all components \( i \). Hence, by integration at constant temperature, using the system with \( f = 0 \) as a reference state, Eq. (19) uniquely defines
\[
\Delta E^E = \Delta E^E(N^E, T, f) = \gamma f.
\]
The definition of \( \gamma \) from Eq. (20) does not contradict the definition from Eq. (19). As we have shown, one can follow the procedure of Rowlinson and Widom\textsuperscript{55,56} to transform Eq. (19) algebraically to Eq. (20). With this transformation, two thermodynamic degrees of freedom are eliminated, so that only \( \nu + 2 \) independent variables remain.

B. Specific surface excess free energy

The thermodynamic surface tension \( \gamma \) defined by Eq. (20) needs to be distinguished from the specific surface excess free energy \( \bar{\gamma} \), defined here as
\[
A = \mu N - p'V' - p''V'' + \bar{\gamma} f.
\]
For each of the two phases, \( A = G - pV \) and \( G = \mu N \), where \( G \) is the Gibbs free energy, so that the surface excess Helmholtz free energy from Eq. (11) is\textsuperscript{18}
\[
\Delta E^E = A = \mu N - p'V' + \bar{\gamma} f,
\]
assuming that the system is in thermodynamic equilibrium.

For scaling up from nanodispersed phases to macroscopic systems, it is important that \( A^E \) contains an adsorption contribution \( \mu N^E = \mu \Gamma f \), cf. Rowlinson and Widom\textsuperscript{55,56}. Unless a significant change of \( \mu \) or \( \Gamma \) occurs, this term is roughly proportional to the surface area. It contributes to the surface tension \( \gamma \), following Eq. (20), but not to the specific surface excess free energy \( \bar{\gamma} \), following Eq. (23). This yields a deviation of \( \mu \Gamma \) between the interfacial quantities \( \gamma \) and \( \bar{\gamma} \) which does not disappear even in the case of macroscopic systems; beside, further deviations between \( \gamma \) and \( \bar{\gamma} \) may be present, which are, however, expected to decay in the limit \( f \to \infty \).

Therefore, even for macroscopic interfaces, \( \bar{\gamma} \approx \gamma \) only holds as long as the contribution to the surface excess Helmholtz free energy due to adsorption can be neglected. For planar interfaces, the Gibbs dividing surface can be positioned such that this term vanishes\textsuperscript{55} by imposing the condition \( \mu N^E = 0 \). For spherical interfaces, where the surface of tension is defined by the Laplace equation, cf. Eq (11), \( \mu N^E \neq 0 \) needs to be assumed. However, the surface excess \( \Omega^E = \Omega - \Omega' - \Omega'' \) of the grand potential \( \Omega = A - \mu N \) does not contain a contribution from adsorption, so that \( \Omega^E = \bar{\gamma} f \) remains valid by construction, even if significant adsorption occurs\textsuperscript{18}.

Even though \( \gamma \) and \( \bar{\gamma} \) may be different, they are related quantities which both characterize the contribution of the interface to the Helmholtz free energy of the system. Following Eqs. (20) and (23), the explicit relationship can be expressed as
\[
\gamma = \left( \frac{\partial}{\partial f} \left( \mu N^E + \bar{\gamma} f \right) \right)_{N^E, T} = \mu N^E (0) + \bar{\gamma} f (0) + \bar{\gamma} f (0),
\]
For spherical interfaces, in particular, a second-order curvature contribution to \( \gamma \) (proportional to \( 1/R^2 \) and, hence, to \( 1/f \)) corresponds to a contribution to the free energy which is proportional to \( \ln f \) \( \ln R \gamma \) \( \ln R \gamma \). Accordingly, contributions to surface excess properties which scale with the logarithm of the size have been a recurrent topic of discussion in the literature on nanodispersed phases\textsuperscript{51,53}.

C. Gibbs adsorption equation

Neglecting finite-size effects, the surface excess free energy is approximated by \( \Omega^E \approx \gamma f \), considering the grand potential \( \Omega \), in the derivation of the Gibbs adsorption equation following Rowlinson and Widom\textsuperscript{55} by \( \gamma^E \approx \gamma f \), considering the Gibbs free energy \( G \), as assumed by Alberty\textsuperscript{54} or \( U^E \approx \gamma f \), considering the internal energy \( U \), following Marmur\textsuperscript{55}. On this basis, Eq. (20) can be deduced algebraically\textsuperscript{17,18,41,56,57,58}.

While such a simplification may be justified for macroscopic systems, it is not rigorous for small systems\textsuperscript{56}, where, in general, significant finite-size effects can be present even for planar phase boundaries\textsuperscript{39,41,57,58}. In particular, as discussed above, \( \gamma \) and \( \bar{\gamma} \) cannot be assumed to be identical. It will be shown here that if the distinction between these two quantities is taken into account consistently, a different version of the Gibbs adsorption equation is obtained than the one employed by Tolman\textsuperscript{13}.

The total differential of the Helmholtz free energy is obtained from Eq. (22) as
\[
dA = \mu \, dN + N \, d\mu - p' \, dV' - p'' \, dV'' + \gamma f \, df + f \, d\gamma,
\]
which can be compared with the expression for \( dA \) from Eq. (10): subtracting Eq. (10) from Eq. (25) yields a Gibbs-Duhem like relation
\[
0 = N \, d\mu - V' \, df' - V'' \, df'' + S \, dT + (\gamma - \bar{\gamma}) \, df + f \, d\gamma,
\]
for the whole system, and
\[
0 = N' \, d\mu - V' \, df' + S' \, dT,
\]
\[
0 = N'' \, d\mu - V'' \, df'' + S'' \, dT,
\]
for the two homogeneous reference systems without an interface, where all surface excess terms are absent. By subtracting the reference system contributions, i.e.,
Eq. (27) and Eq. (28), from the expression for the whole system, i.e., Eq. (29), a generalized version of the Gibbs adsorption equation is obtained:

\[ 0 = \mathbf{N}^{E} \mathbf{d} \mu + S^{E} \, dT + (\bar{\gamma} - \gamma) \, df + f \, d\bar{\gamma}. \]  

(29)

Equivalently, in surface specific terms:

\[ \mathbf{\Gamma} \, \mathbf{d} \mu + \zeta \, dT + d\bar{\gamma} = \frac{\gamma - \bar{\gamma}}{f} \, df. \]  

(30)

In particular, these relations between surface excess properties can be applied to dispersed phases at the nanometre length scale. In cases where the approximation \( \bar{\gamma} \approx \gamma \) is legitimate, Eq. (30) reduces to the well-known version of the Gibbs adsorption equation,

\[ \zeta \, dT + d\bar{\gamma} = -\mathbf{\Gamma} \, \mathbf{d} \mu, \]  

(31)

which corresponds to Eq. (31). In the case of variations where the surface area is not altered, corresponding to \( df = 0 \), Eq. (30) simplifies to

\[ \zeta \, dT + d\bar{\gamma} = -\mathbf{\Gamma} \, \mathbf{d} \mu, \]  

(32)

which despite the similar notation is different from Eq. (31), since \( \bar{\gamma} \) is involved instead of \( \gamma \).

If the surface area is not conserved during the change of Helmholtz free energy of the system, the complete form of the adsorption equation, as given by Eq. (30), must be employed. This includes the problem considered by Tolman and in the present work: The size dependence of the surface tension of nanodispersed phases, such as nanodroplets or nanobubbles.

### D. Tolman’s law

We are now in a position to reexamine Tolman’s law, based on the version of the Gibbs adsorption equation, Eq. (30), which takes into account the possible deviations between the surface tension \( \gamma \) and the specific surface excess free energy \( \bar{\gamma} \). In terms of the set of thermodynamic degrees of freedom introduced for Eq. (13), i.e., \( \mathbf{N}^{E}, T, \) and \( f \), the total differential for \( \bar{\gamma} \) is

\[
\begin{aligned}
d \bar{\gamma} &= \sum_{i=1}^{\nu} \left( \frac{\partial \bar{\gamma}}{\partial N_i^{E}} \right)_{N_j^{E}, T, f} \, dN_i^{E} \\
&\quad + \left( \frac{\partial \bar{\gamma}}{\partial T} \right)_{N_i^{E}, f} \, dT + \left( \frac{\partial \bar{\gamma}}{\partial f} \right)_{N_i^{E}, T} \, df,
\end{aligned}
\]

(33)

where the third term can be obtained from Eqs. (21) and (30) as

\[
\begin{aligned}
\left( \frac{\partial \bar{\gamma}}{\partial f} \right)_{N_i^{E}, T} \, df &= \frac{\gamma - \bar{\gamma}}{f} \, df - \mathbf{\Gamma} \left( \frac{\partial \mu}{\partial f} \right)_{N_i^{E}, T} \, df \\
&= \mathbf{\Gamma} \left[ \mathbf{d} \mu - \left( \frac{\partial \mu}{\partial f} \right)_{N_i^{E}, T} \, df \right] \\
&\quad + d \bar{\gamma} + \zeta \, dT,
\end{aligned}
\]

(34)

and, by developing \( \mathbf{d} \mu \) in \( \mathbf{N}^{E}, T, \) and \( f \),

\[
\begin{aligned}
\mathbf{d} \mu - \left( \frac{\partial \mu}{\partial f} \right)_{N_i^{E}, T} \, dT &= \left( \frac{\partial \mu}{\partial T} \right)_{N_i^{E}, f} \, dT \\
&\quad + \sum_{i=1}^{\nu} \left( \frac{\partial \mu}{\partial N_i^{E}} \right) \, dN_i^{E}.
\end{aligned}
\]

(35)

Eq. (33) can then be expressed as

\[
\begin{aligned}
\sum_{i} \left( \frac{\partial \bar{\gamma}}{\partial N_i^{E}} \right)_{N_j^{E}, T, f} \, dN_i^{E} \\
&\quad + \left[ \left( \frac{\partial \bar{\gamma}}{\partial T} \right)_{N_i^{E}, f} + \zeta \right] \, dT = 0.
\end{aligned}
\]

(36)

All variations of the surface area cancel, and Eq. (36) becomes a statement on changes where \( f \) remains constant. At this point, it becomes impossible to continue, or to rectify, the derivation of Tolman’s law as originally carried out by Tolman.

For a transition with \( df = 0 \), the expression

\[
\begin{aligned}
d \bar{\gamma} + \mathbf{\Gamma} \, \mathbf{d} \mu &= \sum_{i} \left( \frac{\partial \bar{\gamma}}{\partial N_i^{E}} \right)_{N_j^{E}, T, f} \, dN_i^{E} \\
&\quad + \left( \frac{\partial \bar{\gamma}}{\partial T} \right)_{N_i^{E}, f} \, dT \\
&\quad + \left( \frac{\partial \bar{\gamma}}{\partial f} \right)_{N_i^{E}, T} \, df,
\end{aligned}
\]

(37)

in terms of the variables \( \mathbf{N}^{E}, T, \) and \( f \), simplifies to

\[
\begin{aligned}
d \bar{\gamma} + \mathbf{\Gamma} \, \mathbf{d} \mu &= \sum_{i} \left( \frac{\partial \bar{\gamma}}{\partial N_i^{E}} \right)_{N_j^{E}, T, f} \, dN_i^{E} \\
&\quad + \left( \frac{\partial \bar{\gamma}}{\partial T} \right)_{N_i^{E}, f} \, dT,
\end{aligned}
\]

(38)

in terms of the variables \( \mathbf{N}^{E} \) and \( T \). In his original derivation, Tolman applied

\[
(d \bar{\gamma})_{T} = -(\mathbf{\Gamma} \, \mathbf{d} \mu)_{T},
\]

(39)

while we find

\[
(d \bar{\gamma} + \mathbf{\Gamma} \, \mathbf{d} \mu + \zeta \, dT)_{f} = 0,
\]

(40)

which is obtained by combining Eqs. (33) and (38), and hence

\[
(d \bar{\gamma})_{T, f} = -(\mathbf{\Gamma} \, \mathbf{d} \mu)_{T, f}.
\]

(41)

The subscripts \( T \) and \( f \) indicate that the identity in Eq. (41) only holds for changes that do not modify the temperature and the surface area. However, transitions with a constant value of \( f \) are not of interest for the problem considered by Tolman: For a droplet or a bubble, a constant surface area requires a constant radius, corresponding to a constant curvature of the interface and a constant volume of the dispersed phase.
By comparing Eqs. (39) and (41) it is apparent that the argument put forward by Tolman is invalid. According to Eq. (39), the adsorption isotherm $d\gamma = -\Gamma d\mu$ can be applied to changes where $f$ is modified, e.g., by varying the size of a nanodispersed droplet; this is the fundamental feature on which Tolman’s deduction is based. However, Eq. (39) is incomplete. The isotherm $d\gamma = -\Gamma d\mu$ applies to interfaces of pure fluids only as long as the surface area is constant, as in the case of a planar interface under appropriate boundary conditions. An assessment of the curvature dependence of the surface tension cannot be obtained from an analysis of the adsorption $\Gamma$ or, equivalently, from the Tolman length $\delta = R_\rho - R_\gamma$ of nanodispersed phases.

III. DISCUSSION

As shown in the previous section, Tolman’s law, stating that the curvature dependence of the surface tension is related to the difference between the Laplace radius and the equimolar radius, cf. Eqs. (4) and (9),

$$\lim_{R_\gamma \to \infty} \frac{1}{2\gamma_0} \left( \frac{\partial \gamma}{\partial (1/R_\gamma)} \right)_T = \lim_{R_\gamma \to \infty} (R_\gamma - R_\rho),$$

(42)
is not rigorously valid. Therefore, the first-order coefficient

$$c_1 = \lim_{R_\gamma \to \infty} \frac{1}{\gamma_0} \left( \frac{\partial \gamma}{\partial (1/R_\gamma)} \right)_T,$$

(43)

should be treated as a quantity which is unrelated to the planar limit of the Tolman length

$$\delta_0 = \lim_{R_\gamma \to \infty} \delta = \lim_{R_\gamma \to \infty} (R_\rho - R_\gamma).$$

(44)

Selected recent values obtained for $c_1$ are given in Tab. I for Lennard-Jones (LJ) and similar models. In Tab. II recent findings for $\delta$ are shown for LJ or similar nanodispersed phases. From these values it can be seen that both $c_1$ and $\delta$ are very small, of the order of 0.1 to 0.5 $\sigma$ or even smaller, where $\sigma$ is the size parameter of the corresponding model. For most models of low-molecular fluids, $\sigma$ is of the order of 3 to 4 Å.

Most recent studies report a positive coefficient $c_1 \approx 0.2 \sigma$, cf. Tab. I and the corresponding literature sources. This suggests that the first-order curvature correction increases the surface tension. It also suggests that this contribution is not very strong, and that it may be neglected except for very small droplets: Based on this effect only, a droplet with a radius of 20 $\sigma$ (i.e., typically, 7 to 8 nm) would have a surface tension which is 1% greater than that of the planar limit ($\gamma = 1.01 \gamma_0$). For larger droplets, the deviation from $\gamma_0$ would be smaller than 1%.

Tolman was aware of this, but he nonetheless proposed a truncation of the curvature expansion of $\gamma$ after the first-order term. However, it is plausible that at this

| $T/T_\sigma$ | $c_1^\ast$ | model | method | source |
|------------|-----------|-------|--------|-------|
| 0.27       | 0.36 LJ   | MD (cavitation) | [23, 26] |
| 0.46       | 0.2 LJ    | MD (cavitation) | [23, 26] |
| 0.6        | 0.2 VdW EOS | compressibility | [63] |
| 0.61       | 0.18 LJ   | MD (cavitation) | [23, 26] |
| 0.74       | 0.3 LJ + shielding DFT | | [20] |
| 0.83       | 0.2 LJTS | MD | [20] |
| 0.9        | 0.3 VdW EOS | compressibility | [63] |
| ≤ 0.92     | 0.16 LJTS | SGT | [28] |
| ≤ 0.92     | 0.2 LJ    | SGT | [28] |
| $T \to T_\sigma$ | 0.4 LJ | SGT | [22] |
| $T \to T_\sigma$ | 0.3 LJTS | SGT | [22] |

Table I. Literature values reported for the first-order coefficient in the curvature expansion of the surface tension, cf. Eq. (43), for the LJ fluid, the fluid described by the van der Waals equation of state (VdW EOS), the LJ fluid with a hard core (shielding), and the LJTS fluid with a cutoff radius of $r_c = 2.5 \sigma$, using molecular dynamics (MD) simulation, a thermodynamic approach based on the compressibility, density functional theory (DFT), and square gradient theory (SGT). The asterisk in $c_1^\ast$ indicates normalization by the characteristic length scale of the corresponding molecular model, such as the LJ size parameter $\sigma$; cf. the cited references for details. The temperature is normalized by the critical temperature $T_\sigma$ of the molecular model.

| $R_\gamma^\ast$ | $R_\rho^\ast$ | $\delta^\ast$ | $T/T_\sigma$ | model | method | source |
|----------------|-------------|-------------|-----------|-------|--------|-------|
| ≈ 3            | ≈ 3.7       | 0.7        | 0.78      | LJTS-27/6 | MC | [37] |
| ≈ 3.5          | ≈ 4.2       | 0.7        | 0.78      | LJTS-27/6 | MC | [37] |
| ≈ 4.5          | ≈ 5.1       | 0.6        | 0.78      | LJTS-27/6 | MC | [37] |
| 4.52           | 3.96        | -0.56      | 0.74      | LJTS   | MC   | [25] |
| ≈ 5            | ≈ 5.5       | 0.5        | 0.78      | LJTS-27/6 | MC | [37] |
| 7.11           | 6.60        | -0.51      | 0.74      | LJTS   | MC   | [25] |
| 16.32          | 16.22       | -0.10      | 0.74      | LJTS   | MC   | [25] |
| $\infty$       | $\infty$    | -0.04      | 0.74      | LJTS   | MC   | [25] |
| $\infty$       | $\infty$    | -0.13      | 0.6 - 0.9 | LJ      | SGT  | [64] |
| $\infty$       | $\infty$    | -0.13      | 0.78      | LJTS-27/6 | DFT | [37] |

Table II. Literature values reported for the Tolman length of the LJ fluid as well as the LJTS fluid with a cutoff radius of $r_c = 2.5 \sigma$ (denoted by LJTS in the table) and $r_c = 27/6 \sigma$ (LJTS-27/6), using Monte Carlo (MC) simulation, square gradient theory (SGT), and density functional theory (DFT). The asterisks in $R_\gamma^\ast$, $R_\rho^\ast$, and $\delta^\ast$ indicate normalization by the LJ size parameter $\sigma$. The temperature is normalized by the critical temperature $T_\sigma$ of the molecular model.

length scale, higher-order contributions to $\gamma$, e.g., proportional to $1/R_\gamma^2$ or $1/R_\rho^2$, are already at least as significant as the first-order contribution. It is therefore important to take such terms into account; otherwise it is impossible to assess whether $\gamma \to 0$ holds in the limit $R_\gamma \to 0$. Baidakov and Bobrov and Wilhelmsen et al.
advocate the use of the Helfrich expansion,
\[ \gamma = \gamma_0 + \frac{c_1 \gamma_0}{R_\gamma} + \frac{2\kappa + \tilde{\kappa}}{R^2_\gamma} + O\left(\frac{1}{R^3_\gamma}\right), \] (45)
where \( \kappa \) is the bending rigidity and \( \tilde{\kappa} \) is the rigidity with respect to the Gaussian surface curvature \( 1/R^2_\gamma \). A truncation of this expression, or equivalently of Eq. (5), after the second-order term has been proposed on the basis of the Hadwiger theorem which can be understood to imply the absence of a bending rigidity and of higher-order terms.\(^{67}\)

\[ \gamma = \gamma_0 + \frac{c_1 \gamma_0}{R_\gamma} + \frac{\tilde{\kappa}}{R^2_\gamma}. \] (46)

However, results on the hard-sphere fluid indicate that at least at high packing fractions, this interpretation of the Hadwiger theorem constitutes an oversimplification.\(^{68–71}\)

IV. CONCLUSION

Care must be taken when concepts from macroscopic equilibrium thermodynamics are applied to small systems.\(^{66,72,73}\) This also holds for relations which are well established, such as the Gibbs adsorption equation. It was discussed here how a deviation between the surface tension \( \gamma \) and the specific surface excess free energy \( \bar{\gamma} \) affects this equation. A generalized Gibbs adsorption equation was derived which takes these effects consistently into account.

On this basis, for expansions of the type \( \gamma/\gamma_0 = 1 + \sum_k c_k R^{-k}_\gamma \), we have shown that the coefficient \( c_1 \), which characterizes the influence of the surface curvature on the surface tension to first order in \( 1/R_\gamma \), cannot be determined from the Tolman length \( \delta \). As a consequence, the leading-order coefficient cannot be computed, e.g., by molecular simulation, comparing the equinor radius \( R_\rho \) and the Laplace radius \( R_\gamma \). This does not imply that the only way to obtain \( c_1 \) is from an analysis of numerical data for \( \gamma(R_\gamma) \). Thermodynamic approaches can be employed to determine the coefficient from the compressibility of the fluid phases at equilibrium or from other related properties.\(^{63,72,73}\)

However, since recent findings indicate that \( c_1 \) is very small or zero, and that the contribution to \( \gamma \) which is proportional to \( 1/R_\gamma \) is very small (and could even be entirely absent), such approaches will probably fail to capture \( \gamma(R_\gamma) \) correctly. The challenge of developing rigorous thermodynamic approaches and simulation methods to quantify the higher-order curvature contributions to the surface tension of small bubbles and droplets therefore remains an important area of investigation.

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