Tolman’s law and the adsorption equation for nanodispersed phases

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Nucleation and atmospheric aerosols

aerosols in the atmosphere\(^1\) … in Budapest, December 21, 2014

Most widespread approach: Classical nucleation theory (CNT).

Nucleation is often inaccurately described by CNT which assumes \(\gamma = \gamma_0\).

How does the surface tension \(\gamma\) of dispersed phases depend on their size?

Tolman’s law

Surface tension of nanodispersed phases in equilibrium:\(^1\)

\[
\frac{d \ln R_L}{d \ln \gamma} = 1 + \frac{1}{2} \left( \frac{\delta}{R_L} + \left[ \frac{\delta}{R_L} \right]^2 + \frac{1}{3} \left[ \frac{\delta}{R_L} \right]^3 \right)
\]

\[
\frac{\gamma_0}{\gamma} = 1 + \frac{2 \delta}{R_L} + O \left( \left[ \frac{\delta}{R_L} \right]^2 \right)
\]

Estimate by Tolman:\(^1\) \(\delta = +1 \text{ Å}\).

(surface tension \(\gamma\), Laplace radius \(R_L = 2\gamma/\Delta \rho\), at constant temperature \(T\))

Therein, the Tolman length \(\delta\) is given by\(^1\)

\[
\delta = R_e - R_L.
\]

Tolman’s law: A critical reexamination

The relation obtained by Tolman\(^1\) for the surface tension of droplets ...

\[
\frac{d \ln R_L}{d \ln \gamma} = 1 + \frac{1}{2} \left( \frac{\delta}{R_L} + \left[ \frac{\delta}{R_L} \right]^2 + \frac{1}{3} \left[ \frac{\delta}{R_L} \right]^3 \right) \]

\[
\frac{\gamma_0}{\gamma} = 1 + \frac{2 \delta}{R_L} + O\left(\left[ \frac{\delta}{R_L} \right]^2 \right)
\]

- … accounts for an influence of the radius on the surface tension, but not for curvature independent effects (by construction),
- … is often linearized; at least, it is assumed that the dependence of \(\gamma\) on curvature is monotonous (otherwise, the behavior of \(\delta\) itself is complex),
- … is derived from a thermodynamic approach based on the adsorption equation, in the particular version given by \(d\gamma = -\Gamma \, d\mu\), at constant \(T\).

Curvature-independent non-linear effects\textsuperscript{1, 2}

Surface tension of thin films\textsuperscript{1}

Relation with $\gamma(R)$ for droplets\textsuperscript{1, 2}

Malijevský & Jackson (2012):

\[ \delta_0 = -0.07 \sigma \]

“an additional curvature dependence of the $1/R^3$ form is required …”\textsuperscript{2}

Correlation:

\[ \frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3} \]

\textsuperscript{1}Werth \textit{et al.}, Physica A 392, 2359, 2013.

\textsuperscript{2}Malijevský, Jackson, J. Phys.: Cond. Mat. 24, 464121, 2012.
Differential and absolute quantities

„There is no fate that cannot be surmounted by scorn. […] The absurd man says yes, and his efforts will then be unceasing. […]

The struggle itself toward the heights is enough to fill a man's heart. One must imagine Sisyphus happy.”

Camus, *The Myth of Sisyphus*

(Note that the work is not necessarily a first-order homogeneous function in terms of the way gone.)
Differential and absolute quantities

Example: Excess grand potential $\Omega^E$ of an interface with the area $f$

- Macroscale:
  - Surface area $f$
  - $d\Omega^E = \gamma df$
  - $\Omega^E = \gamma f$

- Nanoscale:
  - Surface area $f$
  - $d\Omega^E = \gamma df$
  - $\gamma$ may depend on $f$ significantly!
Differential and absolute quantities

Example: Excess grand potential $\Omega^E$ of an interface with the area $f$

$\Omega^E = \gamma f$

$d\Omega^E = \gamma df$

$\int \gamma df = \overline{\gamma} f$
Dividing surface: Arbitrary position

Two-phase system: total differential for the Helmholtz free energy

\[ dA = \mu \, dN - p^I \, dV^I - p^{II} \, dV^{II} - S \, dT + \gamma \, df + C \, dR \]

„take some point […] and imagine a geometrical surface to pass through this point and all other points which are similarly situated […] called the dividing surface“.

\footnote{J. W. Gibbs, Transact. CT Acad. Arts Sci. 3, 343 – 524, 1878.}

Thermodynamic **excess quantities** are ascribed to this dividing surface:

\[ \chi^\text{System} = \chi^I + \chi^{II} + \chi^E. \]

Notation: \( \mu, N, \) etc., are vectors, e.g., \( N = (N_1, \ldots, N_\nu) \), for \( \nu \) components. Accordingly, e.g., \( \mu \, dN = \sum_{1 \leq i \leq \nu} \mu_i \, dN_i \). However, the focus here is on single-component systems, where \( \mu, N, \) etc., are scalars.
Dividing surface: Laplace radius

Two-phase system: total differential for the Helmholtz free energy

\[ dA = \mu \, dN - p' \, dV' - p'' \, dV'' - S \, dT + \gamma \, df + C \, dR_L \]  
(\text{where } C = 0 \text{ for } R = R_L)

\[ p' - p'' = 2\gamma / R_L \]

Laplace radius \( R_L \) chosen as dividing surface\(^1\text{-}^3\)

Coefficient \( C \) vanishes only for the choice \( R = R_L \).\(^3\text{-}^4\)

\(^1\) J. W. Gibbs, Transact. CT Acad. Arts Sci. 3, 343 – 524, 1878.

Notation: \( \mu, N, \text{ etc.} \), are vectors, e.g., \( N = (N_1, \ldots, N_\nu) \), for \( \nu \) components. Accordingly, e.g., \( \mu \, dN = \sum_{1 \leq i \leq \nu} \mu_i \, dN_i \). However, the focus here is on single-component systems, where \( \mu, N, \text{ etc.} \), are scalars.
Adsorption equation for macrosystems

A comparison of the total differential for the Helmholtz free energy

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

(where \( C = 0 \) for \( R = R_L \))

with the absolute quantity \( A = \mu N - p'V' - p''V'' + \gamma f \) yields:

\[ dA = \mu \, dN - p' \, dV' - p'' \, dV'' - S \, dT + \gamma \, df \]
\[ dA = \mu \, dN + N \, d\mu - p' \, dV' - V' \, dp' - p'' \, dV'' - V'' \, dp'' + \gamma \, df + f \, d\gamma \]

\[ 0 = -N \, d\mu + V' \, dp' + V'' \, dp'' - S \, dT - f \, d\gamma \]

Notation: \( \mu, N, \text{ etc.}, \) are vectors, e.g., \( N = (N_1, \ldots, N_\nu), \) for \( \nu \) components. Accordingly, e.g., \( \mu \, dN = \sum_{1 \leq i \leq \nu} \mu_i \, dN_i \). However, the focus here is on single-component systems, where \( \mu, N, \text{ etc.}, \) are scalars.
Adsorption equation for macrosystems

A comparison of the total differential for the Helmholtz free energy

\[ dA = \mu \, dN - p' \, dV' - p'' \, dV'' - S \, dT + \gamma \, df + \nabla \cdot \mathbf{R} \]

\( (d\Omega^E = \gamma \, df) \)

with the absolute quantity

\[ A = \mu N - p' V' - p'' V'' + \gamma f \]

yields:

\[ f \, dy = -N \, d\mu + V' \, dp' + V'' \, dp'' - S \, dT \]

\[ 0 = -N' \, d\mu + V' \, dp' - S' \, dT \]

\[ 0 = -N'' \, d\mu + V'' \, dp'' - S'' \, dT \]

\[ f \, dy = -N^E \, d\mu - S^E \, dT \]

(with \( N^E \) given by \( N - N' - N'' \), etc.)

For isothermal transitions \((dT = 0)\) it follows with \( N^E = \Gamma f \) that

\[ dy = -\Gamma \, d\mu. \]
Adsorption equation for nanosystems

A comparison of the total differential

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

with the absolute quantity \( A = \mu N - p' V' - p'' V'' + \bar{\gamma} f \) yields:

\[
\begin{align*}
\int \bar{\gamma} \; df + (\bar{\gamma} - \gamma) \; df &= -N \; d\mu + V' \; dp' + V'' \; dp'' - S \; dT \\
0 &= -N' \; d\mu + V' \; dp' - S' \; dT \\
0 &= -N'' \; d\mu + V'' \; dp'' - S'' \; dT \\
\int \bar{\gamma} \; df + (\bar{\gamma} - \gamma) \; df &= -N^E \; d\mu - S^E \; dT
\end{align*}
\]

For isothermal transitions \((dT = 0)\) it follows with \( N^E = \Gamma f \) that

\[
d\bar{\gamma} + (\bar{\gamma} - \gamma) \; d\ln f = -\Gamma \; d\mu.
\]
Tolman’s law: Theoretical derivation

Adsorption equation for macrosystems

\[ d\gamma = -\Gamma \, d\mu - \zeta \, dT \]

Laplace radius chosen as dividing surface\(^1,\,2\)

\[ p' - p'' = 2\gamma / R_L \]

The coefficient \( C \) vanishes only for \( R = R_L \)\(^1\).

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Tolman’s law: Theoretical derivation

Adsorption equation for macrosystems

\[ d\gamma = -\Gamma d\mu - \zeta dT \]

Laplace radius chosen as dividing surface \(^1\)

\[ \rho^I - \rho^II = 2\gamma / R_L \]

single component, isothermal

\[ dy = -\Gamma d\mu \]

The adsorption is \( \Gamma \neq 0 \), whenever:

Dividing surface \( R_L \neq \) equimolar surface \( R_e \)

\[
\frac{\Gamma}{\rho^I - \rho^II} = \delta \left( 1 + \frac{\delta}{R_L} + \frac{1}{3} \left( \frac{\delta}{R_L} \right)^2 \right)
\]

\[ \delta = R_e - R_L. \]

Tolman’s law: Theoretical derivation

**Adsorption equation for macrosystems**

\[ d\gamma = -\Gamma d\mu - \zeta dT \]

- single component, isothermal

\[ d\gamma = -\Gamma d\mu \]

**Tolman’s law:** \[ \frac{\gamma_0}{\gamma} = 1 + \frac{2\delta}{R_L} + \ldots \]

\[ \Gamma (\rho' - \rho'')^{-1} \text{ expressed in terms of } \delta \]

\[ \rho' d\mu = dp' \]

\[ \rho'' d\mu = dp'' \]

\[ (\rho' - \rho'') d\mu = d(\rho' - \rho'') \]

**Gibbs-Duhem equation**

\[ N \, d\mu = V \, dp - S \, dT \]

- single component, isothermal
Tolman’s law: Reexamination

Adsorption equation for nanosystems

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

single component, isothermal

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

\[ f \, d\gamma + (\bar{\gamma} - \gamma) \, df = -N^E \left(\rho' - \rho''\right)^{-1} \, d(\rho' - \rho'') \]

f \, d\gamma + (\bar{\gamma} - \gamma) \, df = d\mu

Gibbs-Duhem equation

\[ N \, d\mu = V \, dp - S \, dT \]

single component, isothermal

\[ \rho \, d\mu = dp \]

\[ \mu = \mu' = \mu'' \]

\[ \rho' \, d\mu = dp' \]

\[ \rho'' \, d\mu = dp'' \]

\[ (\rho' - \rho'') \, d\mu = d(\rho' - \rho'') \]
Tolman’s law: Reexamination

\[ f \, d\gamma + (\bar{\gamma} - \gamma) \, df = -N^E (\rho' - \rho'')^{-1} \, d(\rho' - \rho'') \]

(Gibbs adsorption equation + Gibbs-Duhem equation)

Surface tension, i.e., a differential excess quantity:

\[ \gamma = (\partial A / \partial f)_{N, V', V'', T} = (\partial A^E / \partial f)_{N^E, T} \]

Surface free energy, an absolute excess quantity:

\[ A^E = \Omega^E + \mu N^E = \bar{\gamma} f + \mu N^E \]

Dependence \( \gamma(R_L), \bar{\gamma}(R_L), \) and \( \mu(R_L) \) at constant \( T \)?
Tolman’s law: Reexamination

\( f \, d\gamma + (\gamma - \gamma) \, df = -N^E \left( \rho' - \rho'' \right)^{-1} \, d(\rho' - \rho'') \)

(Gibbs adsorption equation + Gibbs-Duhem equation)

Surface tension, i.e., a differential excess quantity:
\[ \gamma = \left( \partial A / \partial f \right)_N, V', V'', T = \left( \partial A^E / \partial f \right)_{N^E, T} \]

Surface free energy \( A^E(N^E, T, f) \), partial derivative:
\[ \left( \partial A^E / \partial f \right)_{N^E, T} = \gamma + f \left( \partial \gamma / \partial f \right)_{N^E, T} + N^E \left( \partial \mu / \partial f \right)_{N^E, T} \]

For \( \gamma(f) \), \( \bar{\gamma}(f) \), and \( \mu(f) \), at constant \( T \), as \( f \) varies:
\[ f \, d\bar{\gamma} + (\bar{\gamma} - \gamma) \, df = -N^E d\mu \quad \text{(... by definition!)} \]

\(-N^E d\mu = -N^E d\mu\)
Conclusion

The capillarity approximation fails for nanoscale bubbles and droplets, as is known from a variety of nucleation processes which are inadequately described by the classical nucleation theory.

The dependence $\gamma(R)$ needs to be taken into account. Thermodynamic and mechanical considerations suggest that $\gamma \rightarrow 0$ holds for $R \rightarrow 0$. This behavior is usually discussed in terms of Tolman’s law.

Remarks on Tolman’s law and its use in practice:

(1) It is not enough to consider linear effects in $1/R$ only.

(2) Finite-size effects occur even without curvature.

(3) Its theoretical basis is questionable.