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Thermodynamics
Prof. Dr.-Ing. H. Hasse

Tolman's law and the adsorption equation for nanodispersed phases

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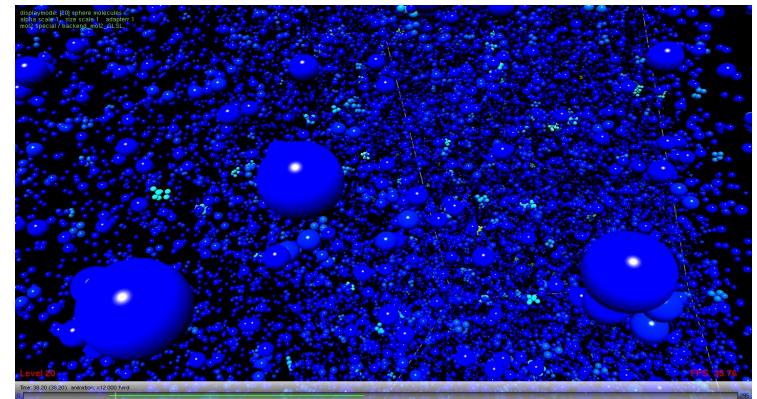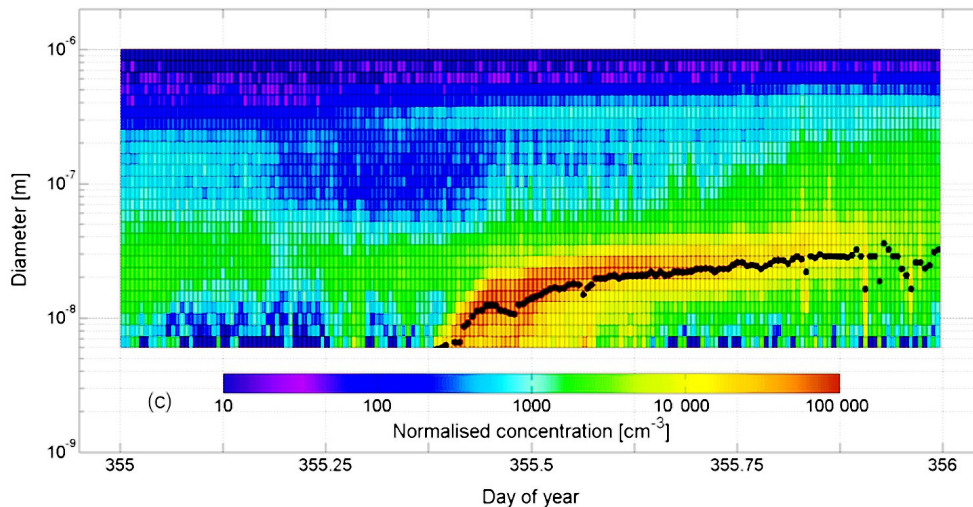
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**Computational
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Nucleation and atmospheric aerosols

aerosols in the atmosphere[1]
… in Budapest, December 21, 2014
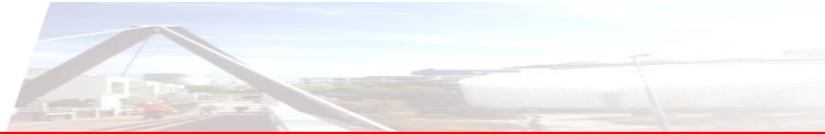
**nucleation in
supersaturated vapors**

[1]Salma *et al.*, *Atm. Chem. Phys.* 16, 7837, **2016**.

Most widespread approach:
Classical nucleation theory (CNT).

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

How does the surface tension γ of dispersed phases depend on their size?

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Tolman's law

Surface tension of nanodispersed phases in equilibrium:[1]

$$\frac{d \ln R_L}{d \ln \gamma} = 1 + \frac{1}{2}\left(\frac{\delta}{R_L} + \left[\frac{\delta}{R_L} \right]^2 + \frac{1}{3}\left[\frac{\delta}{R_L} \right]^3 \right) \longrightarrow \quad \frac{\gamma_0}{\gamma} = 1 + \frac{2\,\delta}{R_L} + O\left(\left[\frac{\delta}{R_L} \right]^2 \right)$$

Estimate by Tolman:[1] $\delta = +1$ Å.

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

Therein, the **Tolman length δ** ist given by[1]

$$\delta = R_e - R_L.$$

equimolar radius R_e
Laplace radius R_L

[1]R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.* 17(3), 333, **1949**.

Tolman's law: A critical reexamination

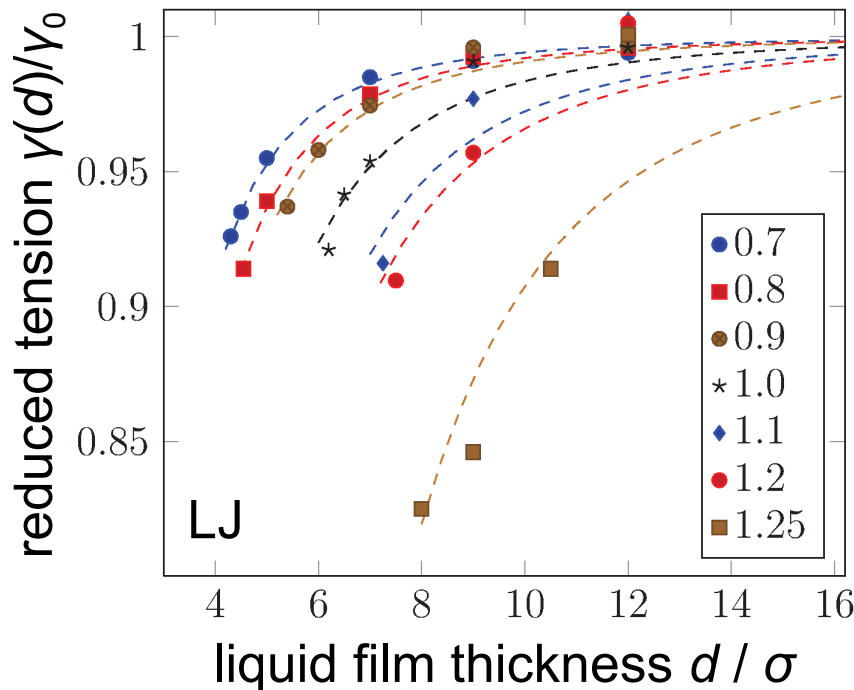The relation obtained by Tolman[1] for the surface tension of droplets …

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

$$\longrightarrow$$

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

- … 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 γ on curvature is monotonous (otherwise, the behavior of δ 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.

[1] R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.* 17(3), 333, **1949**.
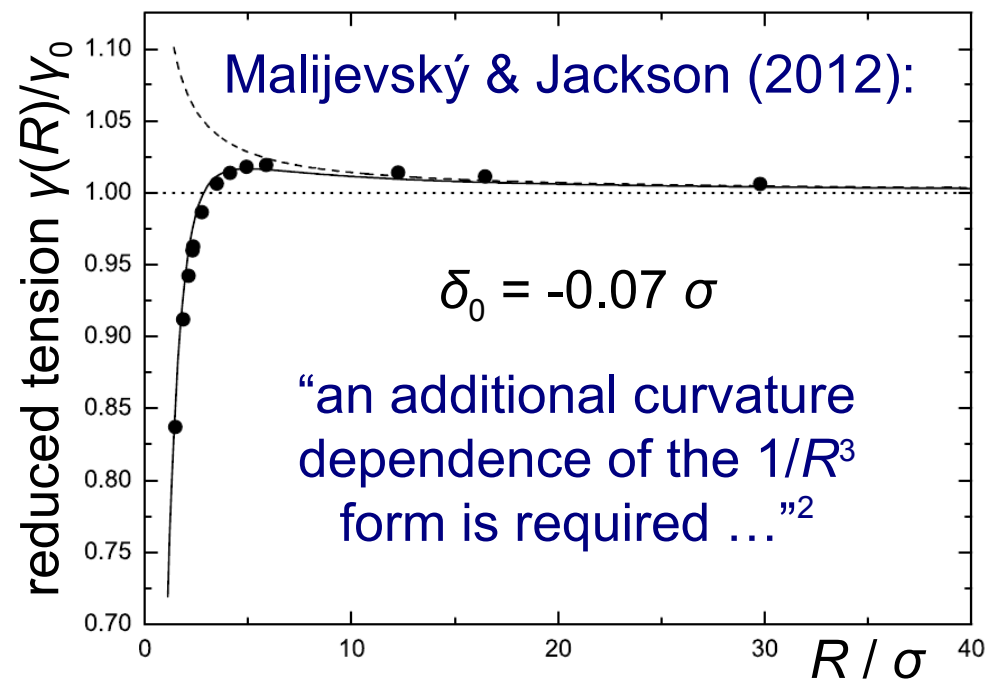
Curvature-independent non-linear effects[1, 2]

Surface tension of thin films[1]

Relation with $\gamma(R)$ for droplets[1, 2]

LJ

Legend: 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.25

reduced tension $\gamma(d)/\gamma_0$

liquid film thickness d / σ

Malijevský & Jackson (2012):

$\delta_0 = -0.07\ \sigma$

"an additional curvature dependence of the $1/R^3$ form is required …"[2]

reduced tension $\gamma(R)/\gamma_0$

R / σ

Correlation: $\dfrac{\gamma(d,\ T)}{\gamma_0(T)} = 1 - \dfrac{b(T)}{d^3}$

[1]Werth *et al.*, *Physica A* 392, 2359, **2013**.

[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*
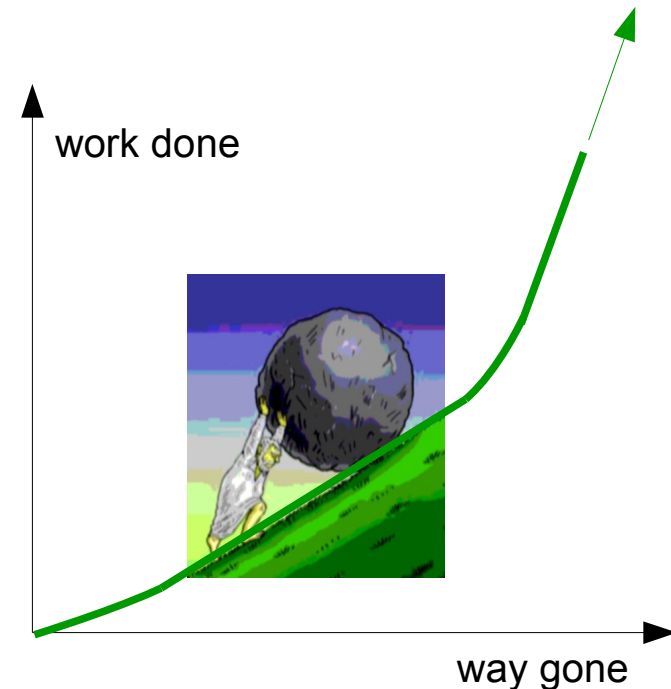
(Note that the work is not necessarily a first-order homogeneous function in terms of the way gone.)

Differential and absolute quantities

Example: Excess grand potential Ω^E of an interface with the area f

macroscale

nanoscale

γ may depend on f significantly!

scale influenced by nano-effects

$d\Omega^E = \gamma\, df$

$\Omega^E = \gamma f$

$d\Omega^E = \gamma\, df$

surface area f

Differential and absolute quantities

Example: Excess grand potential Ω^E of an interface with the area f

macroscale

$$d\Omega^E = \gamma\, df$$

$$\Omega^E = \gamma f$$

nanoscale

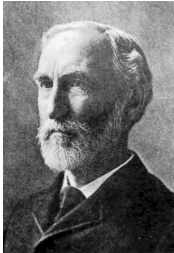$\gamma \neq \bar{\gamma}$!
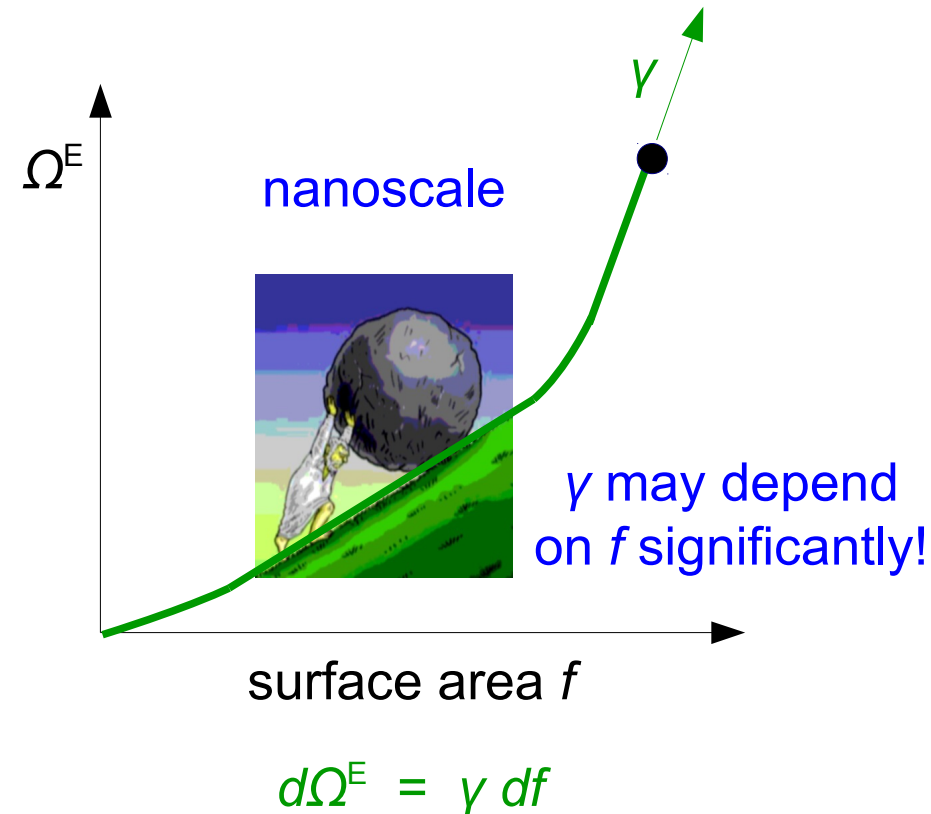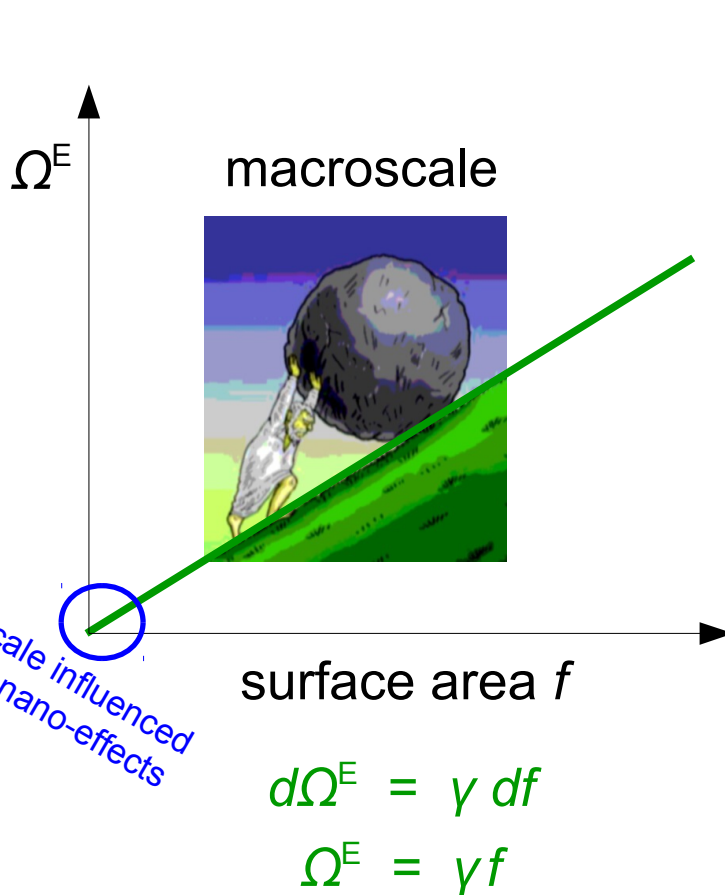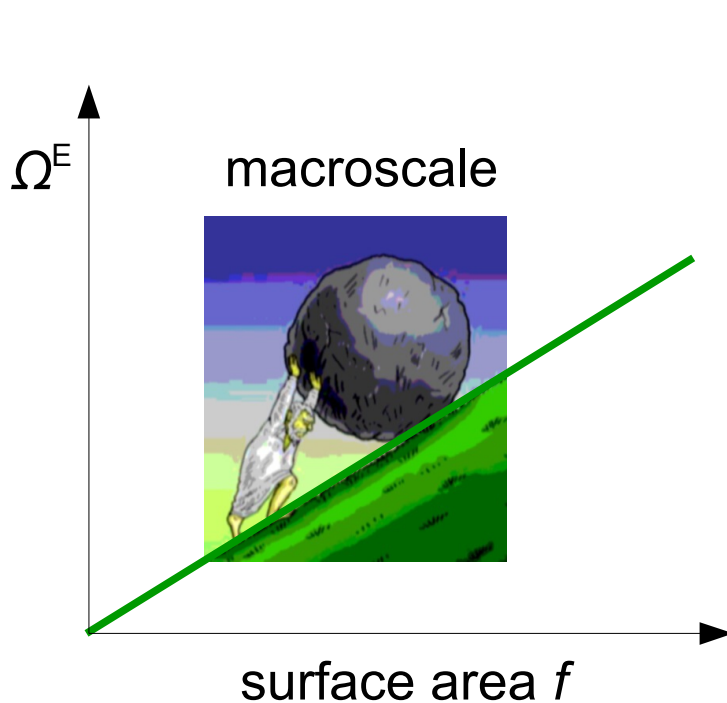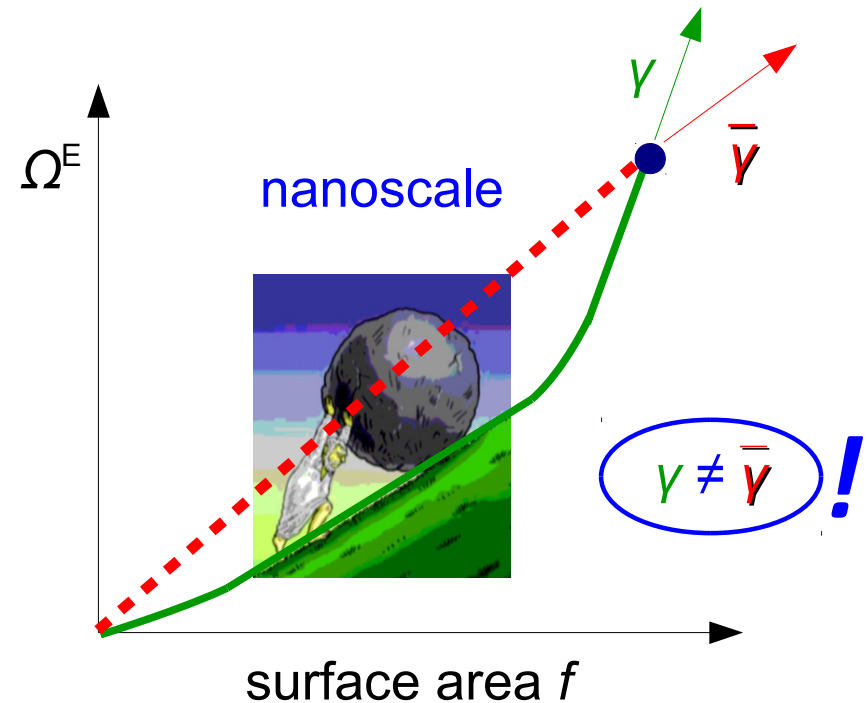
$$d\Omega^E = \gamma\, df$$

$$\Omega^E = \int \gamma\, df = \bar{\gamma} f$$

Dividing surface: Arbitrary position

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

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

„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".[1]

[1]J. W. Gibbs, *Transact. CT Acad. Arts Sci.* 3, 343 – 524, **1878**.

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

$$X^{\text{System}} = X^I + X^{II} + X^E.$$

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

Dividing surface: Laplace radius

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

$$dA = \boldsymbol{\mu}\, d\boldsymbol{N} - p^{I}\, dV^{I} - p^{II}\, dV^{II} - S\, dT + \gamma\, df + \cancel{C\, dR_{L}} \quad \text{(where } C = 0 \text{ for } R = R_{L})$$

$$\boxed{p^{I} - p^{II} = 2\gamma / R_{L}}$$

Laplace radius R_{L} chosen as dividing surface[1–3]

Coefficient C vanishes only for the choice $R = R_{L}$.[3, 4]

[1]J. W. Gibbs, *Transact. CT Acad. Arts Sci.* 3, 343 – 524, **1878**.
[2]R. C. Tolman, *J. Chem. Phys.* 17(3), 333 – 337, **1949**.
[3]T. L. Hill, *J. Chem. Phys.* 19(9), 1203, **1951**.
[4]F. P. Buff, *J. Chem. Phys.* 23(3), 419 – 427, **1955**.

Notation: $\boldsymbol{\mu}$, $\boldsymbol{N}$, etc., are vectors, e.g., $\boldsymbol{N} = (N_{1}, \ldots, N_{\nu})$, for ν components. Accordingly, e.g., $\boldsymbol{\mu}\, d\boldsymbol{N} = \sum_{1 \leq i \leq \nu} \mu_{i}\, dN_{i}$. However, the focus here is on single-component systems, where μ, N, etc., are scalars.
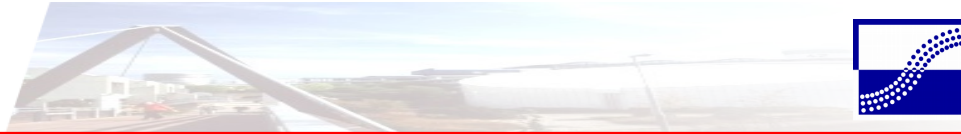
Adsorption equation for macrosystems

A comparison of the total differential for the Helmholtz free energy

$$dA \ = \ \boldsymbol{\mu} \, \boldsymbol{dN} - p^I \, dV^I - p^{II} \, dV^{II} - S \, dT + \gamma \, df + \cancel{C \, dR_L} \quad \text{(where } C = 0 \text{ for } R = R_L\text{)}$$

with the absolute quantity $A \ = \ \boldsymbol{\mu N} - p^I V^I - p^{II} V^{II} + \gamma f$ yields:

$$dA \ = \ \boldsymbol{\mu} \, \boldsymbol{dN} - p^I \, dV^I - p^{II} \, dV^{II} - S \, dT + \gamma \, df$$

$$dA \ = \ \boldsymbol{\mu} \, \boldsymbol{dN} + \boldsymbol{N} \, \boldsymbol{d\mu} - p^I \, dV^I - V^I \, dp^I - p^{II} \, dV^{II} - V^{II} \, dp^{II} + \gamma \, df + f \, d\gamma$$

$$0 \ = \ -\boldsymbol{N} \, \boldsymbol{d\mu} + V^I \, dp^I + V^{II} \, dp^{II} - S \, dT - f \, d\gamma$$

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

Adsorption equation for macrosystems

A comparison of the total differential for the Helmholtz free energy

$$dA \;=\; \boldsymbol{\mu}\,\boldsymbol{dN} - p^I\,dV^I - p^{II}\,dV^{II} - S\,dT + \gamma\,df + \cancel{C\,dR_L}$$

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

with the absolute quantity $A \;=\; \boldsymbol{\mu N} - p^I V^I - p^{II} V^{II} + \gamma f$ yields:

$$(\Omega^E = \gamma f)$$

$$f\,d\gamma \;=\; -\boldsymbol{N}\,\boldsymbol{d\mu} + V^I\,dp^I + V^{II}\,dp^{II} - S\,dT$$

$$0 \;=\; -\boldsymbol{N^I}\,\boldsymbol{d\mu} + V^I\,dp^I - S^I\,dT$$

$$0 \;=\; -\boldsymbol{N^{II}}\,\boldsymbol{d\mu} + V^{II}\,dp^{II} - S^{II}\,dT$$

$$f\,d\gamma \;=\; -N^E\,\boldsymbol{d\mu} - S^E\,dT$$

(with $\boldsymbol{N}^E$ given by $\boldsymbol{N} - \boldsymbol{N}^I - \boldsymbol{N}^{II}$, etc.)

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

$$d\gamma \;=\; -\boldsymbol{\Gamma}\,\boldsymbol{d\mu}.$$

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Adsorption equation for nanosystems

A comparison of the total differential $\gamma \neq \bar{\gamma}$!

$$dA = \boldsymbol{\mu}\,\boldsymbol{dN} - p^I\,dV^I - p^{II}\,dV^{II} - S\,dT + \gamma\,df + C\,dR_L$$

with the absolute quantity $A = \boldsymbol{\mu N} - p^I V^I - p^{II} V^{II} + \bar{\gamma} f$ yields:

$$f\,d\bar{\gamma} + (\bar{\gamma} - \gamma)\,df = -\boldsymbol{N}\,\boldsymbol{d\mu} + V^I\,dp^I + V^{II}\,dp^{II} - S\,dT$$

$$0 = -\boldsymbol{N^I}\,\boldsymbol{d\mu} + V^I\,dp^I - S^I\,dT$$

$$0 = -\boldsymbol{N^{II}}\,\boldsymbol{d\mu} + V^{II}\,dp^{II} - S^{II}\,dT$$

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

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

$$d\bar{\gamma} + (\bar{\gamma} - \gamma)\,d\ln f = -\boldsymbol{\Gamma}\,\boldsymbol{d\mu}.$$

Tolman's law: Theoretical derivation

Adsorption equation for macrosystems

$$d\gamma \ = \ - \boldsymbol{\Gamma \, d\mu} - \zeta \, dT$$

Laplace radius chosen as dividing surface[1, 2]

single component,
isothermal

$$p^{I} - p^{II} \ = \ 2\gamma / R_{L}$$

$$d\gamma \ = \ - \Gamma \, d\mu$$

The coefficient C vanishes only for $R = R_{L}$.[1]

adsorption $\Gamma \ = \ N^{E} / f$

[1]T. L. Hill, On Gibbs' theory of surface tension, *J. Chem. Phys.* 19(9), 1203, **1951**.

[2]R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.* 17(3), 333, **1949**.

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Tolman's law: Theoretical derivation

Adsorption equation for macrosystems

$$d\gamma = -\boldsymbol{\Gamma}\, \boldsymbol{d\mu} - \zeta\, dT$$

Laplace radius chosen as dividing surface[1]

$$p^{I} - p^{II} = 2\gamma / R_{L}$$

single component,
isothermal

$$d\gamma = -\Gamma\, d\mu$$

The adsorption is $\Gamma \neq 0$, whenever:

adsorption $\Gamma = N^{E} / f$

Dividing surface $R_{L} \neq$ equimolar surface R_{e}

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

$$\delta = R_{e} - R_{L}.$$

[1]R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.* 17(3), 333, **1949**.

Tolman's law: Theoretical derivation

Adsorption equation for macrosystems

$$d\gamma = -\boldsymbol{\Gamma\, d\mu} - \zeta\, dT$$

single component,
isothermal

$$d\gamma = -\Gamma\, d\mu$$

Tolman's law: $\gamma_0 / \gamma = 1 + 2\delta / R_L + \dots$

$\Gamma\, (\rho^I - \rho^{II})^{-1}$ expressed in terms of δ
$p^I - p^{II}$ expressed as $2\gamma / R_L$

$$d\gamma = -\Gamma\, (\rho^I - \rho^{II})^{-1}\, d(p^I - p^{II})$$

Gibbs-Duhem equation

$$\boldsymbol{N\, d\mu} = V\, dp - S\, dT$$

single component,
isothermal

$$\rho\, d\mu = dp$$

$$\mu = \mu^I = \mu^{II}$$

$$\rho^I\, d\mu = dp^I$$
$$\rho^{II}\, d\mu = dp^{II}$$

$$(\rho^I - \rho^{II})\, d\mu = d(p^I - p^{II})$$

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Tolman's law: Reexamination

Adsorption equation for nanosystems

$$f\,d\gamma + (\overline{\gamma} - \gamma)\,df = -N^E\,d\mu - S^E\,dT$$

single component,
isothermal

$$f\,d\gamma + (\overline{\gamma} - \gamma)\,df = -N^E\,d\mu$$

$$f\,d\overline{\gamma} + (\overline{\gamma} - \gamma)\,df = -N^E\,(\rho' - \rho'')^{-1}\,d(p' - p'')$$

Gibbs-Duhem equation

$$N\,d\mu = V\,dp - S\,dT$$

single component,
isothermal

$$\rho\,d\mu = dp$$

$$\mu = \mu' = \mu''$$

$$\rho'\,d\mu = dp'$$
$$\rho''\,d\mu = dp''$$

$$(\rho' - \rho'')\,d\mu = d(p' - p'')$$

$$= d\mu$$

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Tolman's law: Reexamination

$= d\mu$

$$f\, d\overline{\gamma} + (\overline{\gamma} - \gamma)\, df \;=\; -N^E\, (\rho' - \rho'')^{-1}\, d(p' - p'')$$

(Gibbs adsorption equation + Gibbs-Duhem equation)
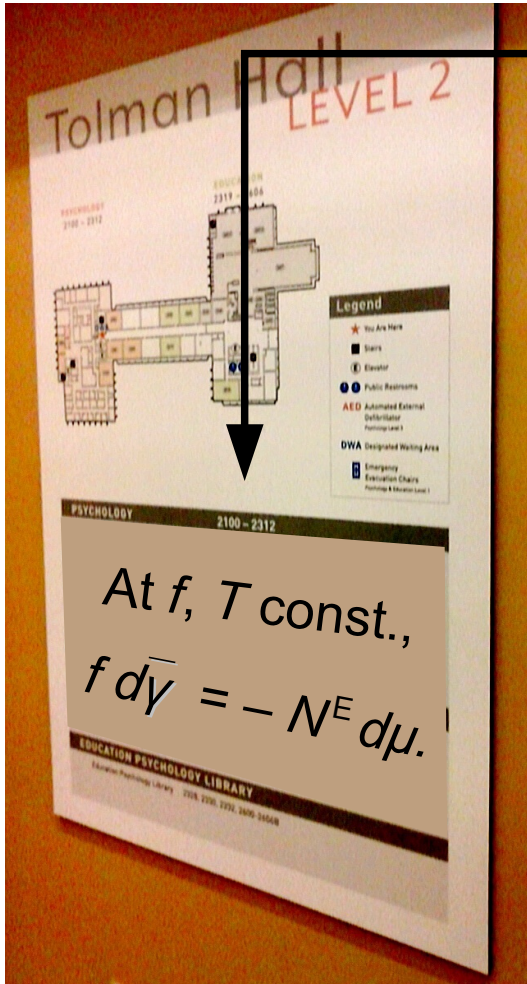
Surface tension, i.e., a differential excess quantity:

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

Surface free energy, an absolute excess quantity:

$$A^E \;=\; \Omega^E + \mu N^E \;=\; \overline{\gamma} f + \mu N^E$$

Dependence $\gamma(R_L)$, $\overline{\gamma}(R_L)$, and $\mu(R_L)$ at constant T?

Tolman's law: Reexamination

$= d\mu$

$$f\, d\bar{\gamma} + (\bar{\gamma} - \gamma)\, df = -N^E (\rho^I - \rho^{II})^{-1}\, d(p^I - p^{II})$$

(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 $A^E(N^E, T, f)$, partial derivative:

$$(\partial A^E / \partial f)_{N^E, T} = \bar{\gamma} + f\, (\partial \bar{\gamma} / \partial f)_{N^E, T} + N^E\, (\partial \mu / \partial f)_{N^E, T}$$

For $\gamma(f)$, $\bar{\gamma}(f)$, and $\mu(f)$, at constant T, as f varies:

$$f\, d\bar{\gamma} + (\bar{\gamma} - \gamma)\, df = -N^E d\mu \quad (\ldots \text{ by definition!})$$

$$-N^E d\mu = -N^E d\mu$$

At f, T const.,

$$f\, d\bar{\gamma} = -N^E d\mu.$$

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 $\gamma \to 0$ holds for $R \to 0$. 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.

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