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Reexamination of the theoretical basis of Tolman's law

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**Computational
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Tolman's law

Surface tension of nanodispersed phases in equilibrium:[1]

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

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] …

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

- … accounts for an influence of the radius on the surface tension, but not for **curvature independent effects**,

- … is often linearized; if the **dependence of δ on the radius** becomes complicated, Tolman's law is of limited use as an empirical relation;

- … is derived from a thermodynamic approach based on the **Gibbs adsorption equation in the version** $d\gamma = -\Gamma\, d\mu$ (at constant T).
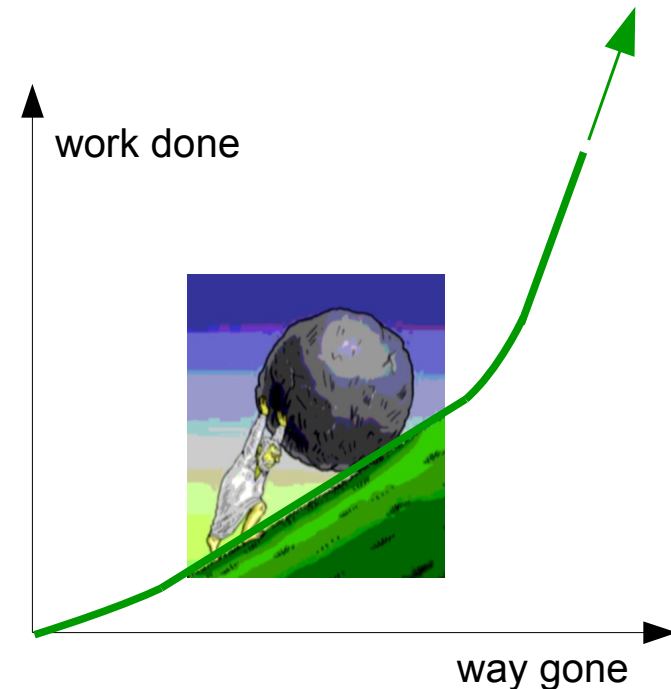
[1]R. C. Tolman, The effect of droplet size on surface tension, *J. Chem. Phys.* 17(3), 333, **1949**.

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."
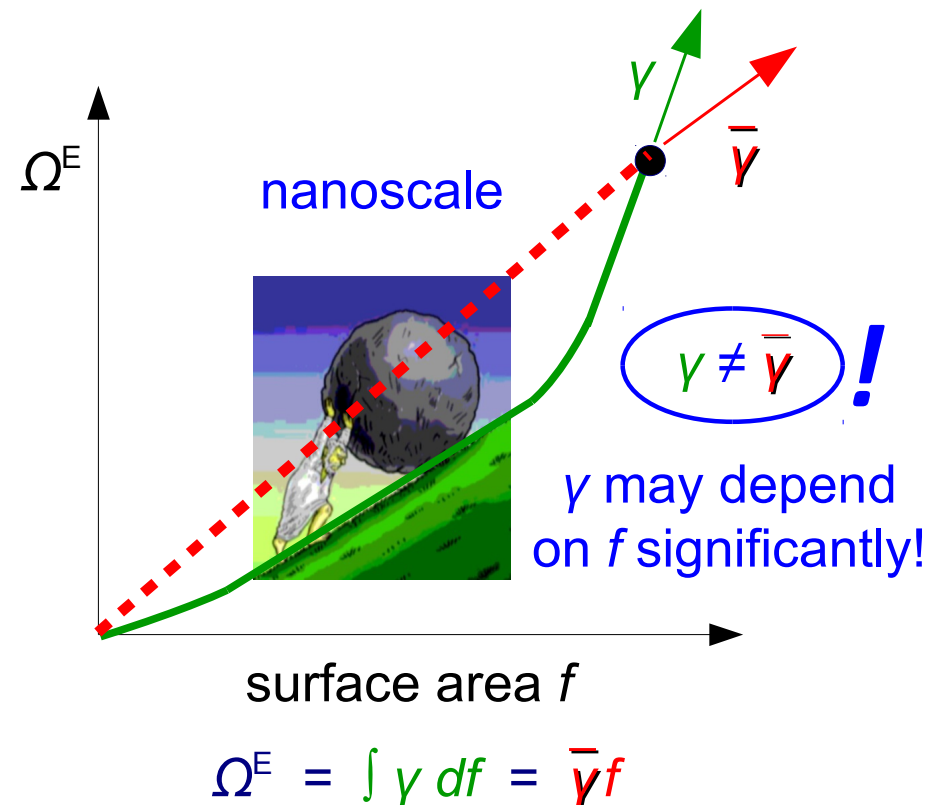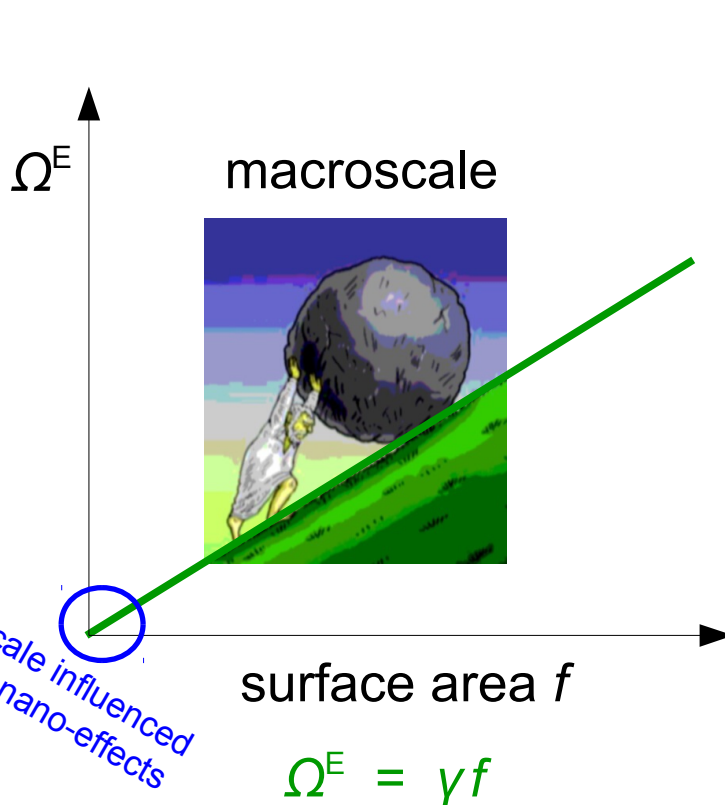
Camus, *The Myth of Sisyphus*

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

Differential and absolute quantities

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

macroscale

Ω^E

surface area f

scale influenced by nano-effects

$\Omega^E = \gamma f$

nanoscale

Ω^E

γ $\bar{\gamma}$

$\gamma \neq \bar{\gamma}$ **!**

γ may depend on f significantly!

surface area f

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

(The excess grand potential Ω^E is not necessarily a first-order homogeneous function of the area f.)

Dividing surface: Laplace radius

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

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

$$\boxed{p^I - p^{II} \; = \; 2\gamma / R_L}$$

Laplace radius R_L chosen as dividing surface[1–3]

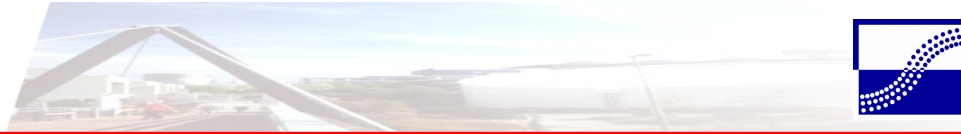Coefficient C vanishes only for the choice $R = R_L$.[3, 4]

[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., $\boldsymbol{\mu} \, \boldsymbol{dN} = \sum_{1 \leq i \leq \nu} \mu_i \, dN_i$. However, the focus here is on single-component systems, where μ, N, etc., are scalars.
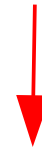
Adsorption equation for macrosystems

A comparison of the total differential for the Helmholtz free energy

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

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

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

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

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

Notation: $\boldsymbol{\mu}$, $\boldsymbol{N}$, etc., are vectors, e.g., $\boldsymbol{N} = (N_1, \ldots, N_\nu)$, for ν components. Accordingly, e.g., $\boldsymbol{\mu}\,d\boldsymbol{N} = \sum_{1 \le i \le \nu} \mu_i\,dN_i$. 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

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

Adsorption equation for nanosystems

A comparison of the total differential

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

$$\boxed{\gamma \neq \bar{\gamma}}\;!$$

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

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

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

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

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

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

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

Tolman's law: Theoretical derivation

Adsorption equation for macrosystems   **Gibbs-Duhem equation**

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

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

single component, isothermal   single component, isothermal

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

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

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

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

$\Gamma\,(\rho^{I} - \rho^{II})^{-1}$ expressed in terms of $\delta = R_e - R_L$

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

$p^{I} - p^{II}$ expressed as $2\gamma / R_L$

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

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

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

Tolman's law: Reexamination

Adsorption equation for nanosystems   **Gibbs-Duhem equation**

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

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

single component,
isothermal

single component,
isothermal

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

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

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

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

$= d\mu$

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

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

Tolman's law: Reexamination

$$= d\mu$$

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

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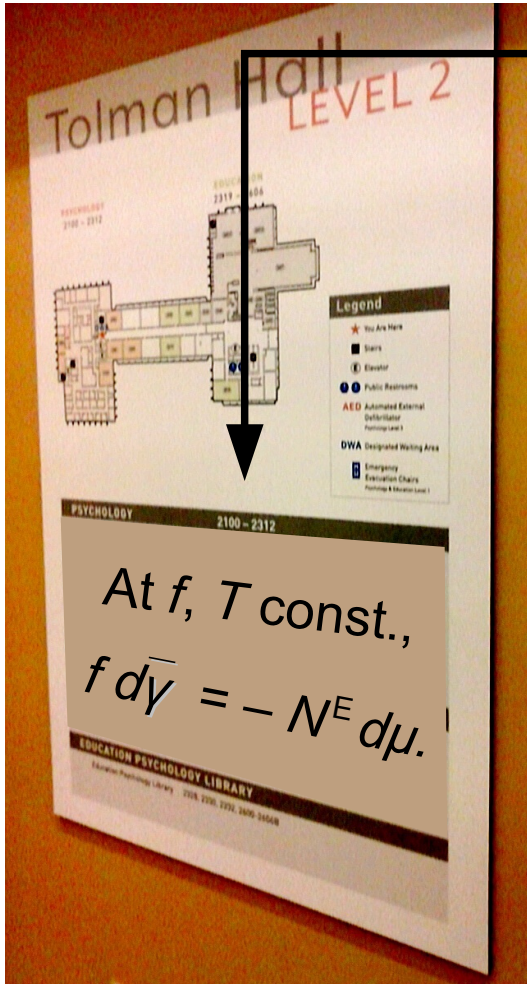
Surface tension, i.e., a differential excess quantity:

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

Surface free energy, an absolute excess quantity:

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

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

Tolman's law: Reexamination

$$= d\mu$$

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

(Gibbs adsorption equation + Gibbs-Duhem equation)

At f, T const.,

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

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:

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

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

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

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

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.**

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