Surface property corrections to the classical nucleation theory

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Yasuoka and Matsumoto (1998):

- Canonical MD simulation
- Limited time interval
- Conditions change over time
MD simulation of nucleation (II)

• Integration time step: typically between 2 and 5 fs

• Feasible simulation time: on the order of nanoseconds

• A saturated vapour with a volume of $10^{-20}$ m$^3$ contains:
  - 800 000 molecules (saturated methane at 114 K)
  - 7 000 000 molecules (saturated CO$_2$ at 253 K)

• Minimal nucleation rate accessible by direct simulation:

\[
\text{#nuclei} / (\text{volume } V \times \text{time } \Delta t) = \text{nucleation rate } J
\]

\[
10 \quad / \quad (10^{-20} \text{ m}^3 \quad x \quad 10^{-9} \text{ s}) = 10^{30} / \text{m}^3\text{s}
\]

experiment up to $10^{23} / \text{m}^3\text{s}$

direct MD simulation above $10^{30} / \text{m}^3\text{s}$
MD simulation of nucleation (III)

CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, CO\textsubscript{2}: Good agreement with classical nucleation theory.

CNT:

- Capillarity
  \( Y = Y_0 \),
- incompressible,
- spherical drops,
- collision rate
  \[ \rho (2\pi m T)^{-1/2} \].

![Graph showing nucleation rate vs. density supersaturation ratio]
Typical scenario:

- $k$ component vapour
- nearly pure liquid

The other $k-1$ components have a “carrier gas” effect:

- thermalization
- “work” of the drop

Opposite influences on $J$...

[Graph with data points and labels]

- CNT / Wedekind et al.
- $\triangle > 50$  $\square > 100$  $\blacksquare > 150$
McDonald’s daemon (I)

Grand canonical MD simulation (Cielinski):

- test insertion/deletion steps alternating with MD steps
- fixed values of $\mu$, $V$, and $T$
- test insertion of a molecule at a random position:
  $$P = \min \left( 1, \exp \left( \frac{\mu - \Delta U_{\text{pot}}}{T} \right) \frac{V}{\Lambda^3 (N + 1)} \right)$$
- test deletion of a random molecule:
  $$P = \min \left( 1, \exp \left( -\frac{\mu - \Delta U_{\text{pot}}}{T} \right) \frac{V}{\Lambda^3 N} \right)$$
- equal number of insertions and deletions ($\approx 10^{-4} N$ per step)

Stationary sampling of the supersaturated state ...
McDonald’s daemon (II)

The diagram shows the relationship between excess pressure in units of $\varepsilon\sigma^{-3}$ and density in units of $\sigma^3$ for different temperatures $T = 0.7\varepsilon$ and $T = 0.85\varepsilon$. The curves represent different chemical potential supersaturations $S_p$ and $S_\mu$.

- For $T = 0.7\varepsilon$, the excess pressure increases with supersaturation $S_p$ and $S_\mu$.
- For $T = 0.85\varepsilon$, the excess pressure shows a distinct behavior, possibly indicating a phase transition or a critical point.

The figure also illustrates the NVT (constant number of particles, volume, and temperature) and $\mu VT$ (constant chemical potential, volume, and temperature) ensembles, showing how the chemical potential differentials affect the system at these temperatures.
Requirement for a steady state:

Elimination of liquid drops ...

\[ P_{\infty}(n) = \int_0^n \frac{\exp(2F_n/T)}{\int_0^\infty \exp(2F_n/T)} \]

\[ n^*_{\text{CNT}} \]

LJTS

\[ S_{\mu} = 2.496 \]

\[ T = 0.7 \, \varepsilon \]

- Requirement for a steady state: Elimination of liquid drops ...

- Diagram showing the relationship between threshold size (molecules) and intervention rate (LJ units, natural logarithm).

- Equation for the probability distribution function at infinite time.

- Integral representation of the probability distribution.

- Identification of specific points on the graph, such as \( n^*_{\text{CNT}} \).

- LJTS and LJTS transposed markers.

- CNT transposed marker.
McDonald’s dæmon (IV)

Nucleation rate in units of $\sigma^{-4}(\varepsilon/m)^{1/2}$

- Classical nucleation theory
- McDonald’s dæmon
- MC-FFS (van Meel et al.)

Pressure supersaturation $p/p_s(T)$

Chemical potential supersaturation

LJTS $T = 0.45 \varepsilon$

LJTS $T = 0.65 \varepsilon$

LJTS $T = 0.7 \varepsilon$

LJTS $T = 0.75 \varepsilon$

LJTS $T = 0.8 \varepsilon$

LJTS $T = 0.85 \varepsilon$
The critical liquid drop size (l)

Curved vapour-liquid equilibria:

- Liquid drop, metastable vapour
- Gas bubble, metastable liquid
Cluster criteria for the liquid phase:

Stillinger: molecules with a distance of $1.5\sigma$ or less are liquid.

Ten Wolde and Frenkel (TWF): molecules with at least four neighbors within a distance of $1.5\sigma$ are liquid.

Arithmetic mean, $n$ neighbors ($a_n$): a molecule is liquid if the density in the sphere containing its $n$ nearest neighbors exceeds $(\rho' + \rho'')/2$.

Geometric mean, $n$ neighbors ($g_n$): analogous, the required density is $(\rho' \rho'')^{1/2}$.

Nuclei can also be determined as bi-connected (instead of connected) components, such that no nucleus can be separated by removing a single molecule (TWF' and $g'_2$ criteria).
The critical liquid drop size (III)

Carbon dioxide

\[ T = 237 \text{ K} \]
\[ \rho = 1.89 \text{ mol/l} \]

- \( g_2 \) (geom. mean)
- \( a_2 \) (arithm. mean)
- \( a_8 \) (arithm. mean)

Ten Wolde-Frenkel
Stillinger

\[ n^{2/3} \] scaling
The critical liquid drop size (IV)

Simulation results confirm the classical predictions for $n^*$.
Tolman theory and cylindrical interfaces (I)

**Simulation approach**

LJTS fluid, generic wall model, Dispersive energy $\varepsilon_{fw} = \zeta \varepsilon$

**Equilibrium state**

Cylindrical meniscus, based on arithm. mean density

![Simulation diagram](image)

![Equilibrium state diagram](image)
Gibbs adsorption eqn.
\[ d\gamma = -\Gamma d\mu \]

Tolman (cylindrical)
\[ \frac{\gamma}{R} \frac{dR}{d\gamma} = 1 + \left( \frac{\delta}{R} + \frac{\delta^2}{2R^2} \right)^{-1} \]
\[ \frac{\gamma_0}{\gamma} \approx 1 + \frac{\delta_0}{R} + \frac{2\ell^2}{R^2} \]

Young-Tolman
\[ \cos \theta = \frac{\Delta \gamma_s}{\gamma} \approx \left( \frac{\gamma_0}{\Delta \gamma_s} + \frac{2\delta_0}{h} \right)^{-1} \]
Tolman theory and cylindrical interfaces (III)

Qualitative observations:

- Only for a narrow range of $\zeta$ values there is a contact angle.
- For a temperature-independent magnitude of $\zeta$, the contact angle becomes rectangular as $\Delta \gamma_s = 0$.
- First-order wetting transition.
- General tendency: $\Delta \gamma_s \sim \Delta \rho \Delta \zeta$.
- The curvature influence on $\theta$ is negligible at high temperatures.
Tolman theory and cylindrical interfaces (IV)

Cylindrical Tolman and Block length from MD simulation:

**Symmetrical LJSTS liquid-liquid**

\[
\frac{T}{\varepsilon} = 1 \quad \text{grand canonical route}
\]

**LJTS vapour-liquid** \((r_c = 2^{7/6} \sigma)\)

\[
\frac{\text{relative deviation}}{\gamma} = \frac{\Delta y}{y}
\]

- Block length \(\ell \) “close to” \(1 \sigma\)
- \(\delta = -0.02 \sigma, \ell = 0.3 \sigma\)

(Source: Block et al., 2010)
Analysis of spherical interfaces (I)

The variational route (TA method)

Canonical partition function:

\[
\Delta F = -T \ln \left( \exp \left( -\frac{\Delta U}{T} \right) \right) \\
= f(\langle \Delta U \rangle, \langle \Delta U^2 \rangle, \langle \Delta U^3 \rangle) + O(\langle \Delta U^4 \rangle)
\]

For small deformations:

\[
\gamma = \frac{\Delta F}{\Delta A} \quad \text{with} \quad A = 4\pi Q^2 + O(\delta Q)
\]

Nonlinear terms are essential.

Tolman length much smaller than based on other methods.

Main advantages of the variational route:

- Free energy differences are considered in a direct way.
- No mechanical equilibrium assumption is applied.
Analysis of spherical interfaces (II)

The virial route

Bakker-Buff equation:

\[ \gamma = R^{-2} \int_{\text{in}}^{\text{out}} dz z^2 [\rho_N(z) - \rho_T(z)] \]

\[ (2\gamma)^3 = -\Delta \rho^2 \int_{\text{in}}^{\text{out}} d\rho_N(z) z^3 \]

Irving-Kirkwood pressure tensor:

\[ \rho_N(z) = \sum_{\{i,j\} \in S(z)} \frac{f_{ij} \mathbf{s} \cdot \mathbf{r}_{ij}}{4\pi z^3 r_{ij}} + kT\rho(z) \]

The \( \rho_N \) profile has a minimum.

In the vicinity of the surface of tension radius, \( \rho_N \) decays.

Main advantages of the virial route:

- Equilibrium sampling – no unstable states are considered.
- The Tolman length is obtained directly as \( \delta = Q - R \).
Analysis of spherical interfaces (III)
Analysis of spherical interfaces (IV)

The grand canonical route

Excess Landau free energy:

$$\Sigma = \Omega(\rho) - \mu_{coex}(Q) \cdot [V' \rho'(Q) + V'' \rho''(Q)]$$

(from sampling of at $\mu, V, T$ const.)

Relation to the surface tension:

$$\Sigma = \int_0^{A(R)} \gamma dA = \hat{\gamma} 4\pi Q^2$$

The Tolman length is negative.

Contribution of the Block length causes the decay of $\gamma$.

Main advantages of the grand canonical route:

- A range of bubble/drop sizes is sampled at the same time.
- Leads to surface free energy (instead of surface tension).
The excess equimolar radius (I)

The standard Tolman approach is based on:

- The equimolar radius $Q$, related to the density profile.
- The surface of tension radius $R = \frac{2\gamma}{\Delta p}$, related to $\gamma$.
- The dependence of $\gamma$ on $1/R$, which is coupled to $\gamma$ itself.

As long as $\gamma(R)$ is disputed, so are $R$ and $\delta = Q - R$ as well ...

Idea: use $\varphi(\mu, T) = \frac{\Delta p}{2}$ instead of $1/R$, and "replace" $R$ by $P = \frac{\gamma_0}{\varphi}$.
The excess equimolar radius (II)

Van Giessen-Blokhuys eqn.

\[ -\delta_0 = \frac{1}{\gamma_0} \left( \lim_{Q \to \infty} \frac{d}{d(1/Q)} \varphi Q \right) \]

Equivalent expression for the zero-curvature Tolman length from the ratio between \( P \) and \( Q \):

\[ -\delta_0 = \lim_{1/Q \to 0} \frac{d}{d(1/Q)} \frac{Q}{P} \]

Theory in terms of \( P \) and \( Q \)

Simulation studies using the IK pressure tensor come to contradictory conclusions.

Van Giessen, Blokhuis

\[ \delta = (-0.10 \pm 0.02) \sigma \]

LJTS with IK tensor

\[ T = 0.9 \varepsilon \]

\[ T = 0.85 \varepsilon \]

\[ T = 0.65 \varepsilon \]

Vrabec et al.
**The excess equimolar radius (III)**

### Tolman theory in $Q$, $R$, and $1/R$

**Tolman length:**

$$\delta = Q - R = Q - \frac{\nu}{\varphi}$$

**Full Tolman equation:**

$$\frac{\gamma}{R} \frac{dR}{dy} = 1 + \left( \frac{2\delta}{R} + \frac{2\delta^2}{R^2} + \frac{2\delta^3}{3R^3} \right)^{-1}$$

**First-order expansion:**

$$\frac{\nu}{\gamma} = 1 + \frac{2\nu_0}{R} + O\left( \frac{1}{R^2} \right)$$

### Tolman theory in $P$, $Q$, and $\varphi$

**Excess equimolar radius:**

$$\eta = Q - P = Q - \frac{\nu_0}{\varphi}$$

**Full Tolman equation:**

$$\frac{\varphi}{\gamma} \frac{d\gamma}{d\varphi} = 2 \left( 1 - \left[ \frac{\eta\varphi + \nu_0}{\gamma} \right]^3 \right)$$

**First-order expansion:**

$$\gamma = \nu_0 + 2\eta_0 \varphi + O\left( \varphi^2 \right)$$

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**How do these notations relate to each other?**

$$\eta_0 = \lim_{\varphi \to 0} \left( Q - \frac{\nu_0}{\varphi} \right) = -\lim_{R \to \infty} \left( Q - \frac{\gamma}{\varphi} \right) = -\delta_0$$
The excess equimolar radius (IV)

LJTS
- $\Delta \rho$ from IK tensor (Vrabec et al.)
- $\Delta \rho$ from density in-/outside

$T = 0.65 \varepsilon$
$T = 0.85 \varepsilon$
$T = 0.95 \varepsilon$
Correction of the classical nucleation theory (I)

Free energy of formation from simulation vs. CNT prediction:

LJTS fluid at $T = 0.7 \varepsilon$:
- NVT with $\rho = 0.004044/\sigma^3$ and $\mu VT$ with $S_\mu = 2.866$
- $t_{NVT} = 400 (m/\varepsilon)^{1/2} s$
- $t_{NVT} = 1050 (m/\varepsilon)^{1/2} s$
- $\mu VT (n < 50)$

But (almost) everybody agrees that $\gamma(R) \to 0$ for $R \to 0$ …

Deviation for $\gamma$  

Agreement for $n^*, J$, and $\Delta F_n = \int_0^n \gamma dA$

Could it be that the surface area is larger than CNT assumes?
Correction of the classical nucleation theory (II)

Equilibrium condition for critical droplets yields:

\[ 2 \, dV = R \, dA \]

interpretation

\[ dA = \frac{2dV}{R} \approx \frac{8\pi Q^2}{Q - \delta} \, dQ \]

This postulate implies:

- \( \delta \) positive
- \( \gamma \) smaller than \( \gamma_0 \)
- \( A \) greater than \( 4\pi Q^2 \)
- \( \Delta F_m, n^*, \) and \( J \) similar

(and vice versa)

Correlation based on \( \gamma, n^*, J \) — increase by \( \delta \), i.e. \((P + \delta) : P\)

increase by \( D_{\text{vap}}(\rho) \)

\[ T = 0.9 \, \epsilon \]

\[ T = 0.75 \, \epsilon \]

Correction of the classical nucleation theory (III)

LJTS

- Previous results
- Napari et al., 2009

Critical size converges to zero

$T = 0.8\, \varepsilon$

$T = 0.65\, \varepsilon$

Critical liquid drop size in molecules vs. chemical potential supersaturation ratio.
Correction of the classical nucleation theory (IV)

\[ P = \frac{\gamma}{\phi} \text{ in units of } \sigma \]

\[ \phi = \frac{\Delta \rho}{2} \text{ in units of } \sigma \varepsilon^3 \]

\[ \phi = \frac{\Delta \rho}{2} \text{ in units of } \varepsilon / \sigma^3 \]

\[ T = 0.7 \varepsilon \]

LJTS scenario

\[ \lim Q = 0 \]

Tolman scenario

\[ \sigma \]

\[ \varepsilon \]

\[ \Delta \rho \]

\[ \phi \]

\[ \gamma \]

\[ Q \]

\[ R \]
Conclusion

I know that I know nothing.

We must move beyond contradictory results and huge error bars.

This is surely possible.