Thermodynamics 2009

Steady state molecular dynamics
simulation of vapour to liquid nucleation

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MD simulation of a single droplet

- Vapour and liquid are equilibrated separately
- A small ($N_t < 10000$) droplet is inserted into the vapour
- If the droplet cannot evaporate completely, an equilibrium is established within a few nanoseconds

truncated-shifted LJ fluid ($r_c = 2.5$)
Equilibrium vapour pressure

Equilibrium condition for a droplet containing $N_\ell$ atoms:

$$p = p(T, N_\ell)$$

$\Delta G$ at constant $p$ and $T$:
1 unstable equilibrium

$\Delta F$ at constant $V$ and $T$:
1 unstable equilibrium
1 stable equilibrium
Single droplet in equilibrium

Argon (truncated-shifted LJ model)

“standard” classical theory

classical theory with “pressure effect”

\[ N^* = \left( \frac{2\sigma a}{3\Delta \mu} \right)^3 \]

\[ N^* = \left( \frac{2\sigma a}{3[\Delta \mu - \nu^*(p - p_s)]} \right)^3 \]
Droplet surface tension

For small droplets, the TOLMAN length
\[ \delta = R_e - R_\sigma \]
is significantly elevated.

TOLMAN equation:
\[
\frac{\sigma}{\sigma_\infty} \approx \frac{R_e + \delta_\infty}{R_e - \delta_\infty}
\]
Grand canonical MD

Algorithm: MC insertion/deletion steps alternating with MD steps

- test insertion of a molecule at a random position

\[
P_{\text{ins}} = \min \left[ 1, \exp \left( \frac{\mu - \Delta U_{\text{pot}}}{kT} \right) \frac{V}{\Lambda^3 (N + 1)} \right]
\]

- test deletion of a random molecule

\[
P_{\text{del}} = \min \left[ 1, \exp \left( \frac{-\mu - \Delta U_{\text{pot}}}{kT} \right) \frac{V}{\Lambda^3 N} \right]
\]

Thermodynamic conditions of supersaturated state are maintained
Interactive presentation: MCDONALD‘s dæmon
**Intervention rate** $J_\theta$ and nucleation rate $J$

Not all of the removed droplets would eventually reach macroscopic size.

$$J = J_\theta q(\theta)$$

Probability for a droplet of growing from size $\theta$ to infinity:

$$q(\theta) = \frac{\int_{1}^{\theta} \exp(2\beta F)dN_\ell}{\int_{1}^{\infty} \exp(2\beta F)dN_\ell},$$

and in particular: $q(N^*) \approx 1/2$

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**Graph**

- **Axis**:
  - X: Threshold size $\theta$ in atoms
  - Y: $\ln(J_\theta/\text{cm}^3\text{S}^{-1})$

- **Data Points**:
  - CNT shifted to $\ln J = 56.5$
  - Standard classical theory (CNT)

- **Additional Information**:
  - Argon $T = 97$ K
  - $S_\mu = 2.496$
GCMD simulation of nucleation: Results

Graph showing the relationship between supersaturation in terms of the chemical potential and the logarithm of the nucleation rate as a function of temperature. The graph compares the standard CNT, CNT with pressure effect and prefactor $C = 200$, and McDonald's daemon.
Conclusion

• MD simulation of equilibria allows sampling over an arbitrary time interval, eventually leading to the desired level of accuracy

• Single droplets are stable in the canonical ensemble and yield the critical droplet size

• A supersaturated vapour near the spinodal line can be stabilized by grand canonical MD simulation with MCDONALD‘s daemon

• MCDONALD‘s daemon allows to simulate the instationary nucleation process in the steady state

• The classical theory leads to excellent results for argon