Phase coexistence, Interface tension and convexity of thermodynamic potentials

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plan of the talk

• thermodynamic instabilities – a common feature in the last decade publications; ensemble inequivalence?

• pseudo thermodynamic instability for coexisting phases – correct interpretation of the field variables
  • interface thermodynamics
  • the case of the lattice gas
  • equivalence of ensembles for small systems?
1. Thermodynamic instabilities
2nd law of thermodynamics

entropy is a concave function of its variables

\[ \frac{\partial^2 S}{\partial E^2} < 0 \]

by analogy to mechanics, the situation \( \frac{\partial^2 S}{\partial E^2} > 0 \),

though forbidden, is called unstable
Phase coexistence
thermodynamic instability in mean-field approaches

\[ \frac{\partial^2 F}{\partial V^2} > 0, \quad \text{2nd law} \]

1873

Ok!
Van der Waals loops – from mean field model calculations which ignore coexistence
Thermodynamic instabilities in numerical experiments

2d lattice gas

thermodynamic instabilities

canonical ensemble simulations and chemical potential loops

2nd law demands \( \frac{\partial^2 F}{\partial N^2} > 0 \)

1984
Numerical simulations and “instabilities”

1/T

FIG. 1. (Color online) Inverse temperature $\beta(e)$ and its derivative $\gamma(e)$ as functions of the energy per particle, $e = E/N$, exemplified for an elastic polymer with 102 monomers. 

PRE 2011, Landau group
Numerical simulations and “instabilities”

Long-range ring model, 2018

TEMPERATURE loops and negative specific heat

Potts model, 2020
II. Thermodynamic “instability” of the chemical potential does not exist
Simulations: loops in the chemical potential

Binder’s group (2012) LJ fluid
Simulations: loops in the chemical potential
THERMODYNAMICS OF COEXISTENCE

\[ F_{cx}(T, V, N, A_{int}) = F_{bulk}(T, V, N) + F_{int} \]

\[ F_{int} = \gamma A_{int} \]

- surface tension
- area of interface
Free energy and chemical potential

\[ \mu(T,V,N) = \left( \frac{\partial F}{\partial N} \right)_{T,V} \]

homogeneous system

\[ \mu_{cx}(T,V,N) = \left( \frac{\partial F_{cx}}{\partial N} \right)_{T,V,A_{int}} \]

system at coexistence

\[ F_{cx}(T,V,N) = F_{bulk} + \gamma(T)A_{int}(T,V,N) \]

or

\[ \tilde{\mu}_{cx}(T,V,N) = \left( \frac{\partial F_{bulk}}{\partial N} \right)_{T,V} + \gamma(T) \left( \frac{\partial A_{int}}{\partial N} \right)_{T,V} \]
loops and surface tension
Our results for interface tension

\[ F_{int} = \gamma \cdot A_{int} \]

Exact result (Onsager 1944) x simulation data
Our results for interface tension

\[ \frac{\gamma}{\epsilon} \]

\( t = 0.46 \)

\( t = 0.50 \)

Resultado exato de Onsager
(Pseudo) Chemical potential in the *canonical* ensemble

\[ \frac{\partial F(T, V, N)}{\partial N} \approx F(T, V, N + 1) - F(T, V, N) = -k_B T \ln \left[ \frac{Z(T, V, N + 1)}{Z(T, V, N)} \right] \]

\[ = -k_B T \ln \left[ \frac{1}{(N + 1)} \left( \sum_{\tilde{r}_{N+1}} \exp(-\beta \Delta E) \right) \right] \]

\[ \mu(T, V, N) + \gamma \left( \frac{\partial A_{int}}{\partial N} \right)_{T,V} = \left( \frac{\partial F}{\partial N} \right)_{T,V} \]
(pseudo) Chemical potential in the grandcanonical ensemble

\[
P(N; T, V, \tilde{\mu}) = \frac{e^{\beta \mu N} Z_{cx}(T, V, N)}{\mathcal{Z}(T, V, \mu)}
\]

\[
\left. \frac{\partial P(N)}{\partial N} \right|_{\bar{N}} = 0 \quad \leftrightarrow \quad \tilde{\mu} = \tilde{\mu}(\bar{N})
\]
Canonical - grand ensemble equivalence?
Canonical - microcanonical equivalence?
conclusions

- True phase coexistence chemical potential has no loops
- Interface tension is easily calculated in the canonical ensemble
- A word of caution: the role of the interface contribution must be investigated in the case of temperature loops