Phase coexistence, Interface tension and convexity of thermodynamic potentials

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II ICTP-SAIFR Condensed Matter Theory in the Metropolis

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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

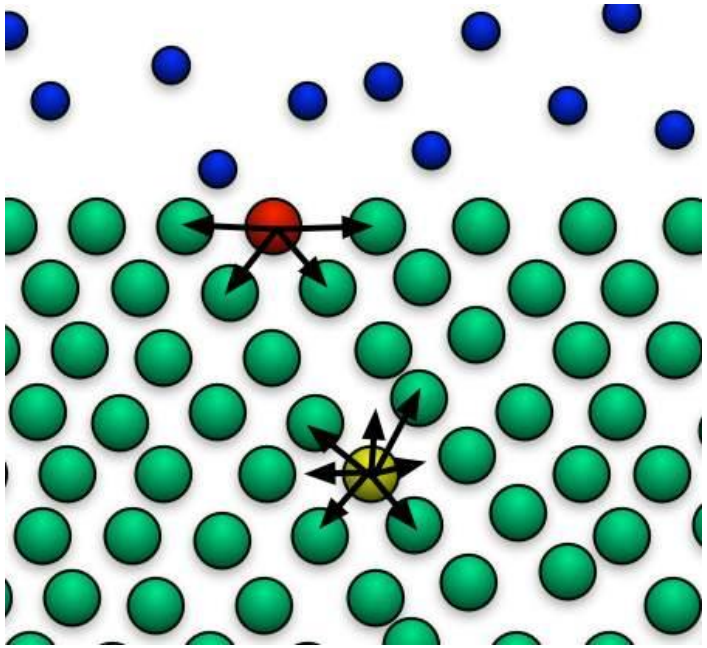
2nd law of thermodynamics

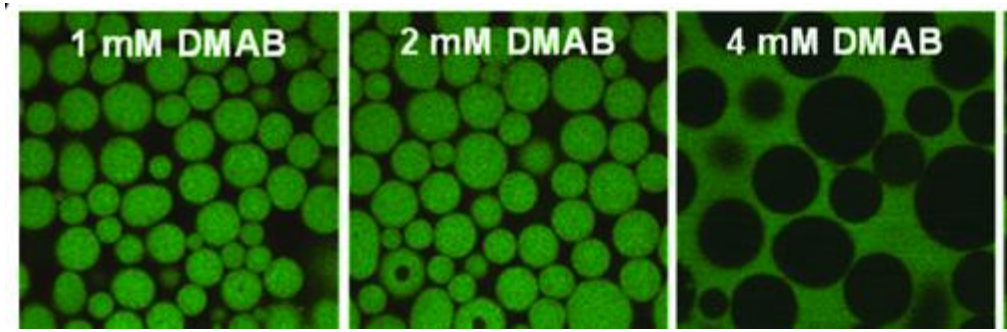
entropy is a concave function of its variables

$$\frac{\partial^2 S}{\partial E^2} < 0$$

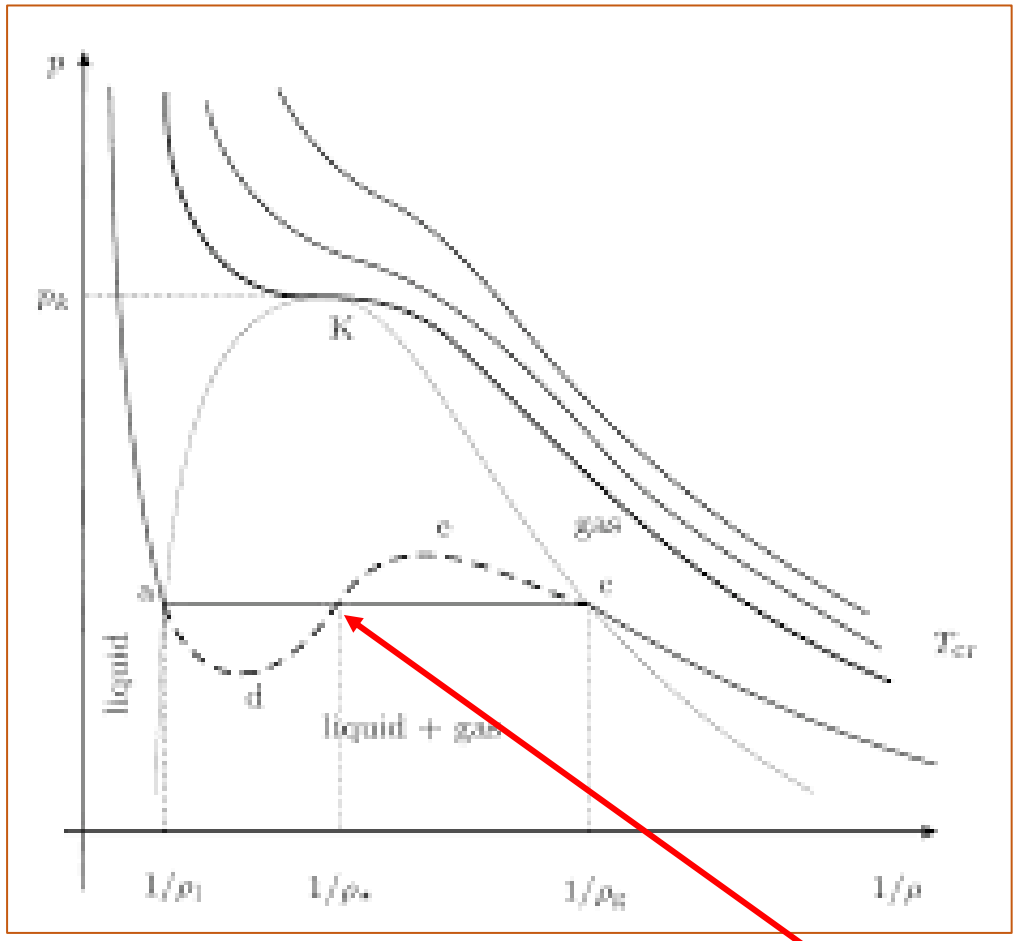
by analogy to mechanics, the situation $\frac{\partial^2 S}{\partial E^2} > 0$, though forbidden, is called unstable

Phase coexistence





thermodynamic instability in mean-field approaches



1873

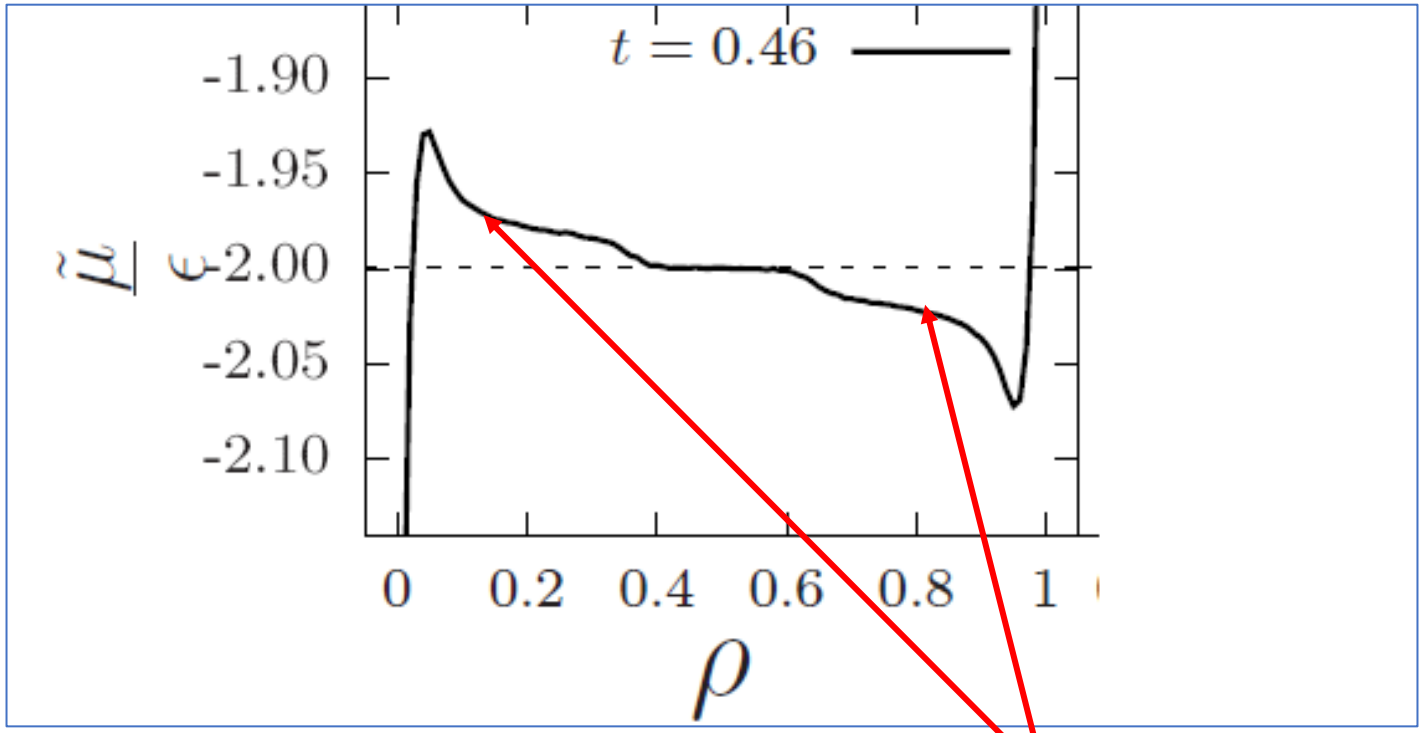
$$\frac{\partial^2 F}{\partial V^2} > 0, \qquad \text{2nd law}$$

thermodynamic instability

Ok!
Van der Waals loops – from mean field model calculations which **ignore** coexistence

Thermodynamic instabilities in numerical experiments

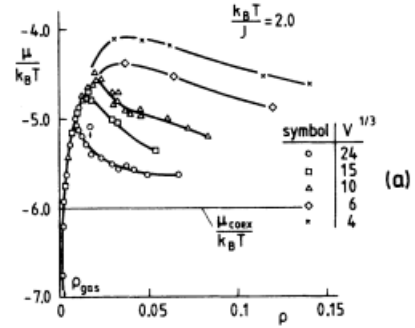
2d lattice gas



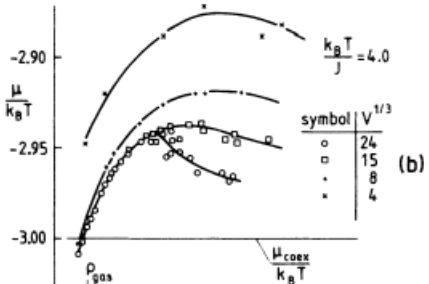
thermodynamic instabilities

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

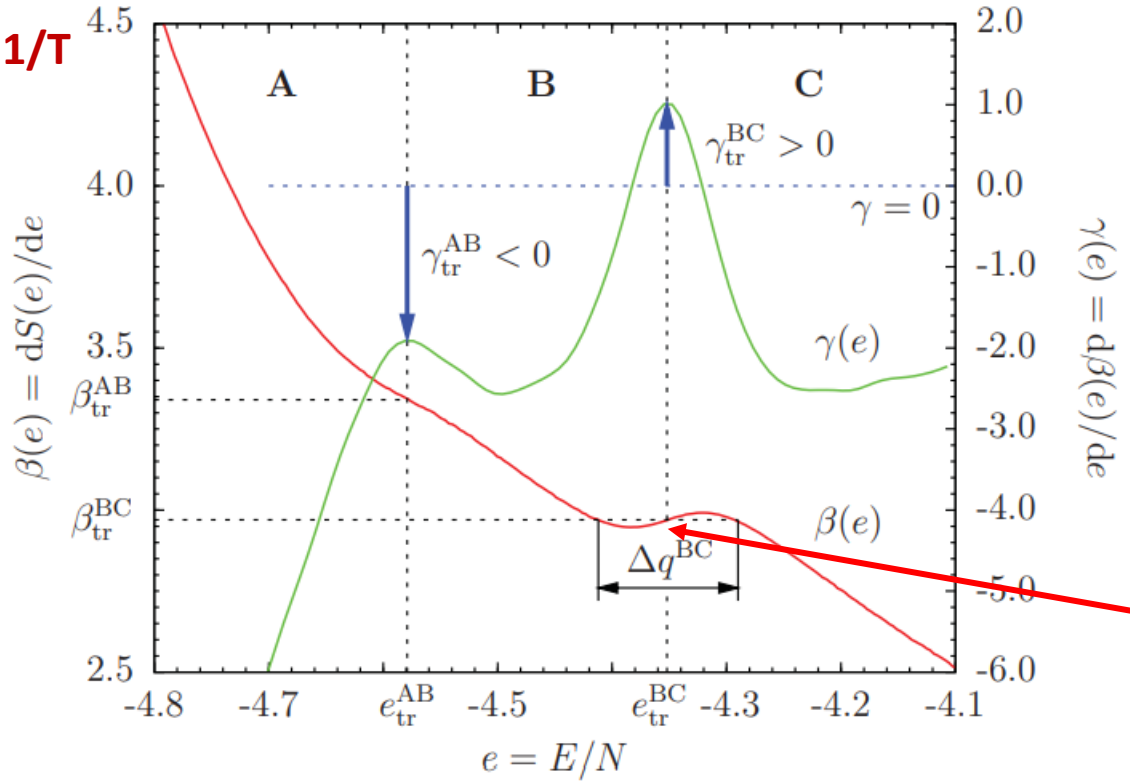


FIG. 1. (Color online) Inverse temperature $\beta(e)$ and its derivative $\gamma(e)$ as functions of the energy per particle, $e = E/N$, exemplified for an elastic polymer with 102 monomers.

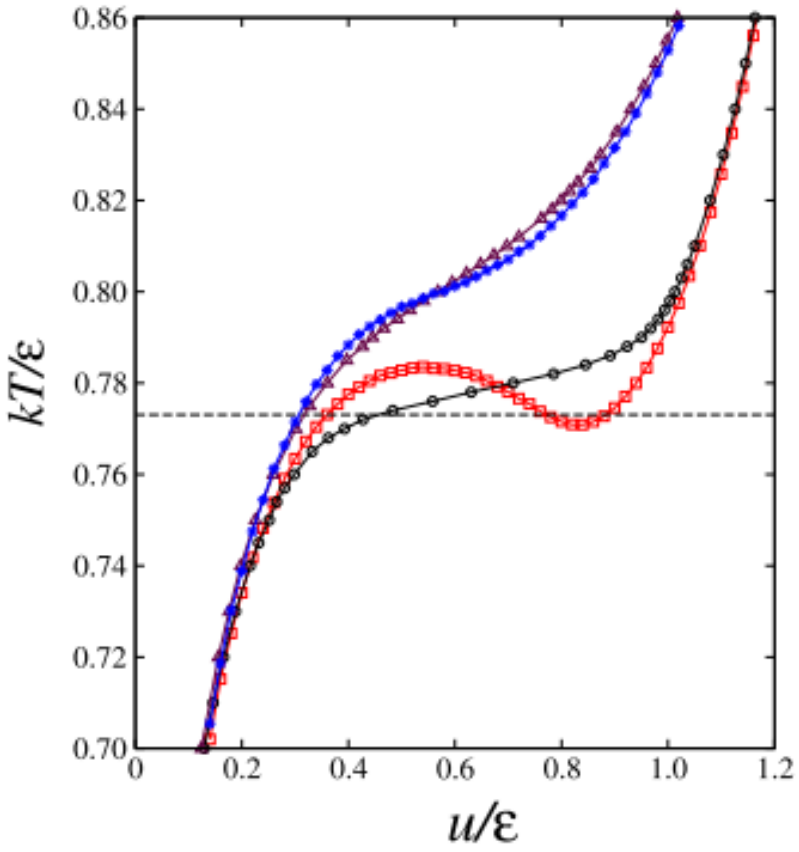
PRE 2011, Landau group

microcanonical ensemble simulations and TEMPERATURE loops

thermodynamic instability

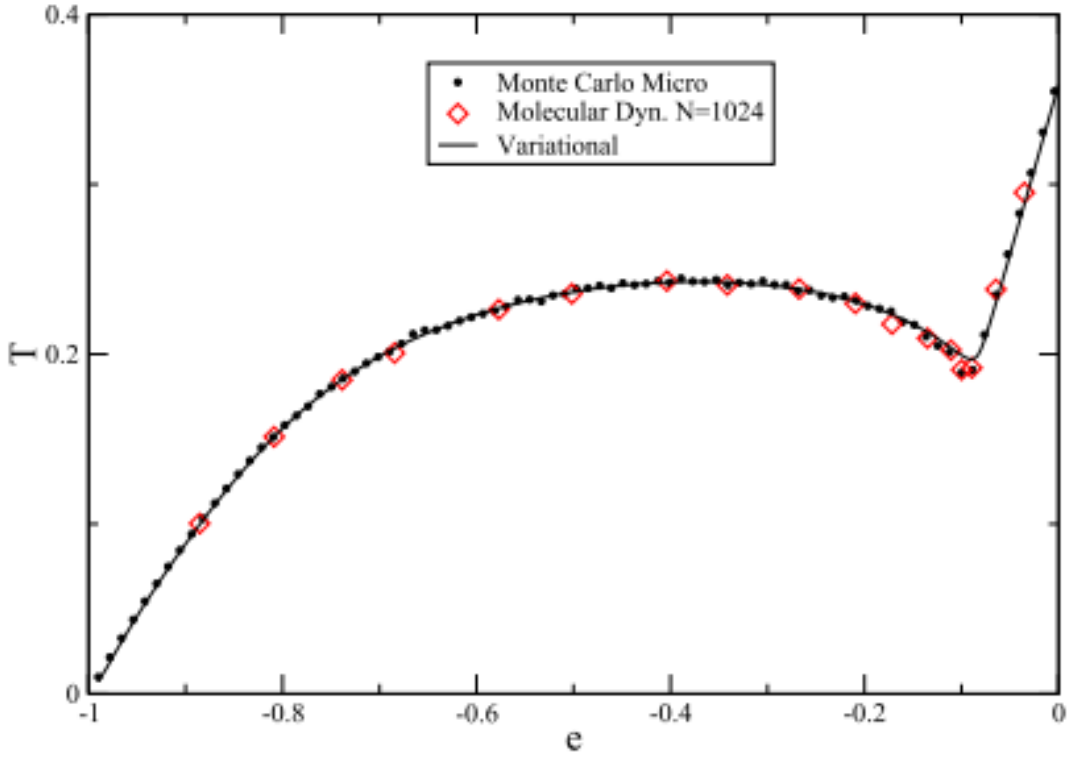
Numerical simulations and "instabilities"

TEMPERATURE loops and negative specific heat



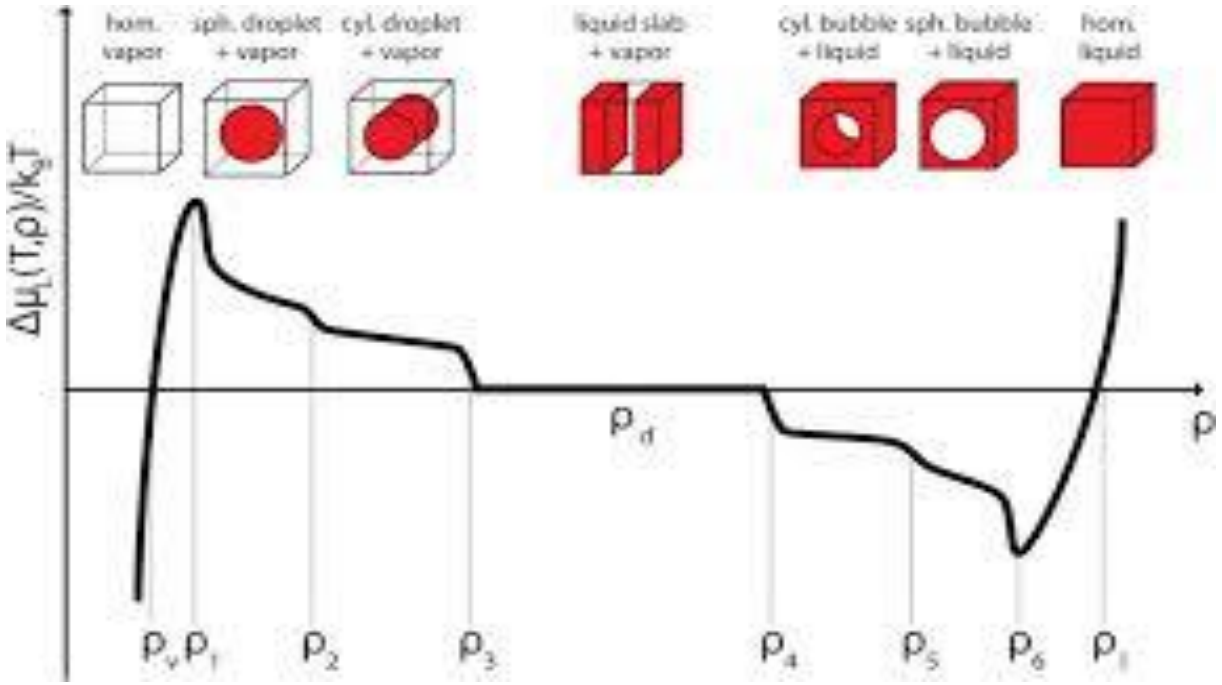
Potts model, 2020

Long-range ring model, 2018



II. Thermodynamic "instability" of the chemical potential does not exist

Simulations: loops in the chemical potential



Aint cresce com densidade

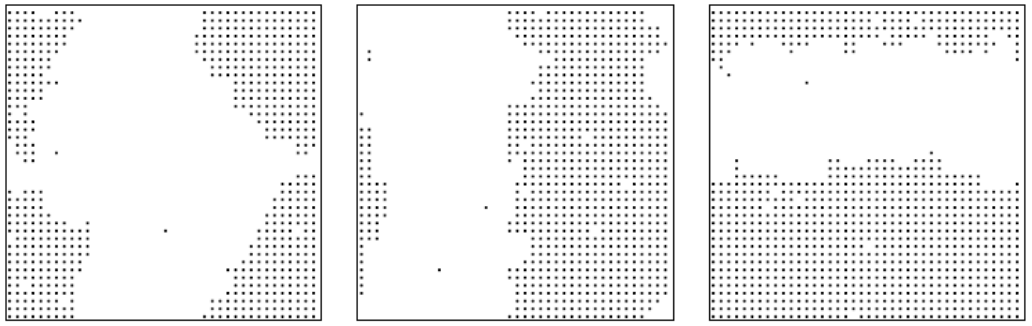
Aint diminui com densidade

Aint = constante

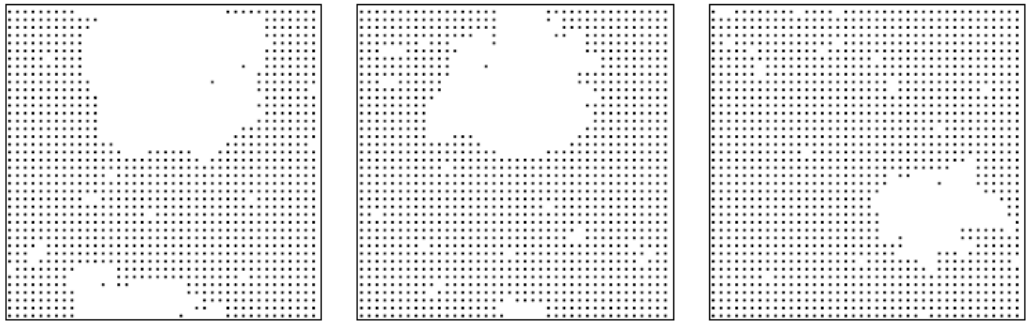
Binder's group (2012) LJ fluid

Simulations: loops in the chemical potential

(a) $\rho = 0,1$ (b) $\rho = 0,2$ (c) $\rho = 0,3$

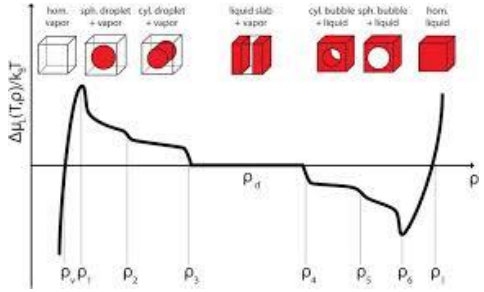


(d) $\rho = 0,4$ (e) $\rho = 0,5$ (f) $\rho = 0,6$

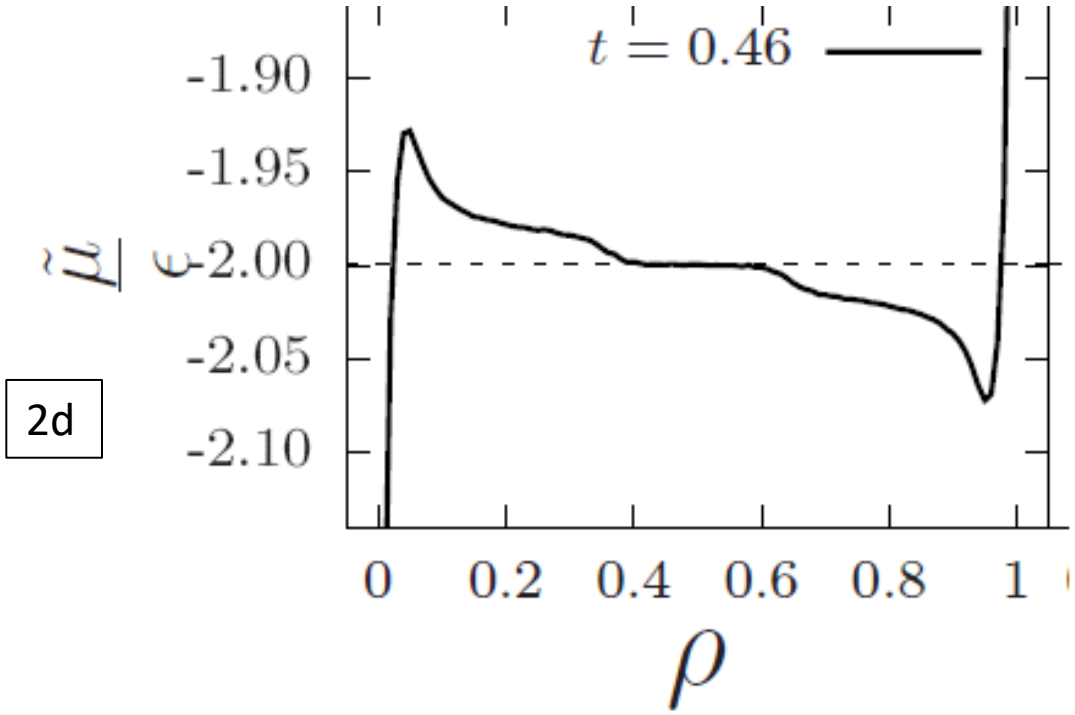


(g) $\rho = 0,7$ (h) $\rho = 0,8$ (i) $\rho = 0,9$

3d

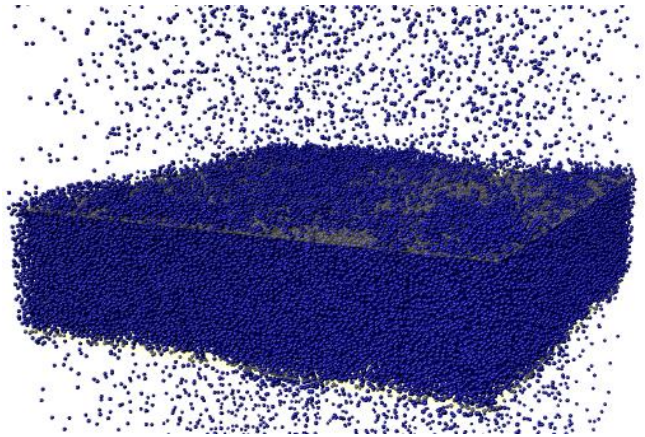


2d



THERMODYNAMICS OF COEXISTENCE

$$F_{cx}(T, V, N, A_{int}) = F_{bulk}(T, V, N) + F_{int}$$



$$F_{int} = \gamma A_{int}$$

surface tension

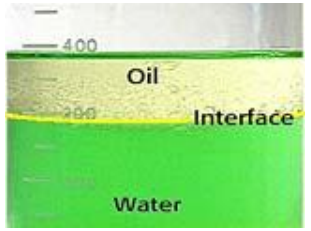
area of interface

Free energy and chemical potential

homogeneous system

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

system at coexistence



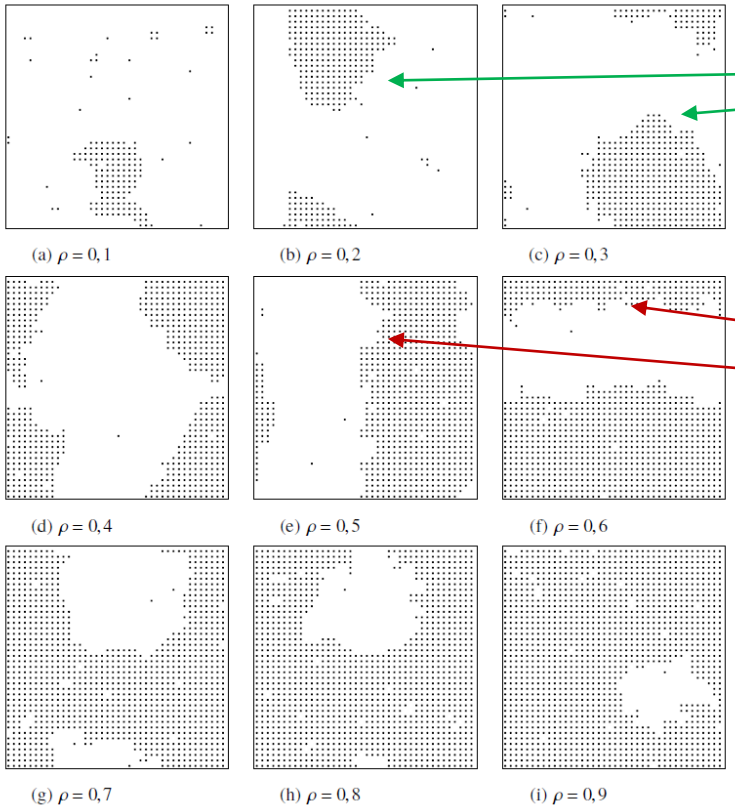
$$F_{cx}(T,V,N) = F_{bulk} + \gamma(T) A_{int}\ (T,V,N)$$

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

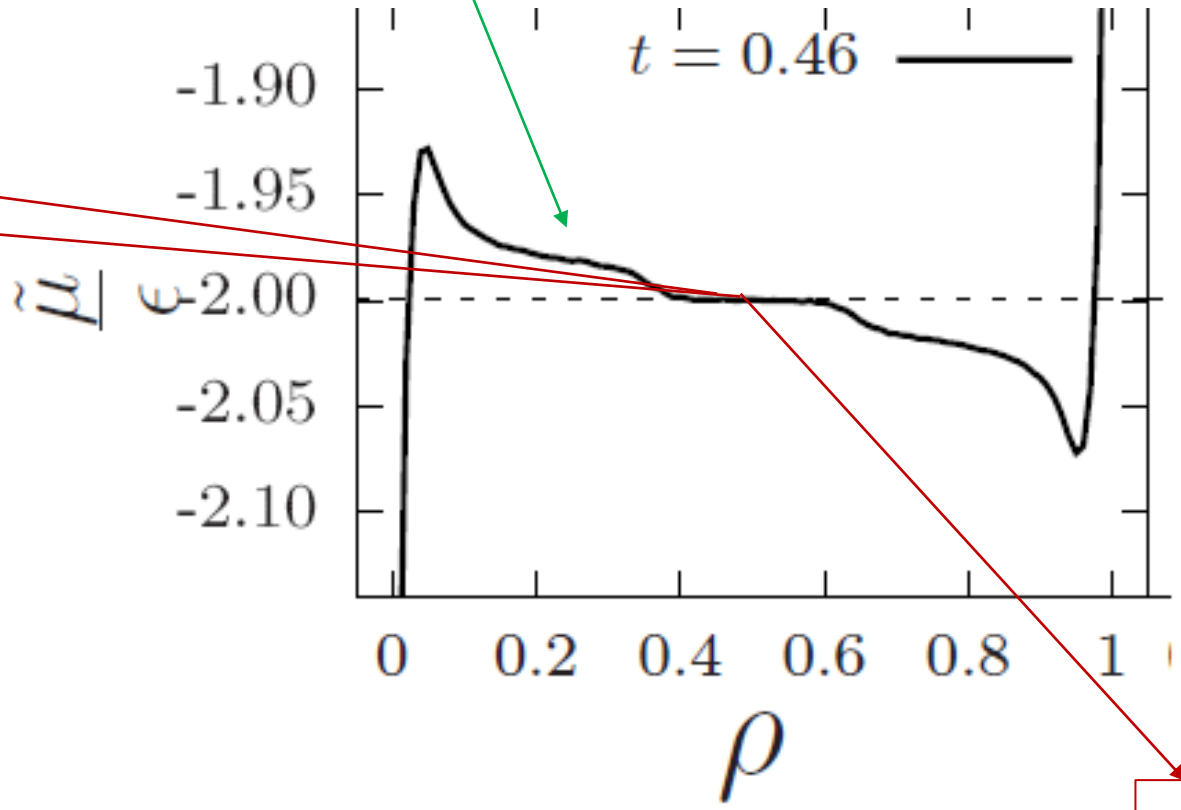
or

$$\tilde{\mu}_{cx}(T,V,N) = \left(\frac{\partial F_{bulk}}{\partial N}\right)_{T,V} + \gamma(T)\left(\frac{\partial A_{int}}{\partial N}\right)_{T,V}$$

loops and surface tension

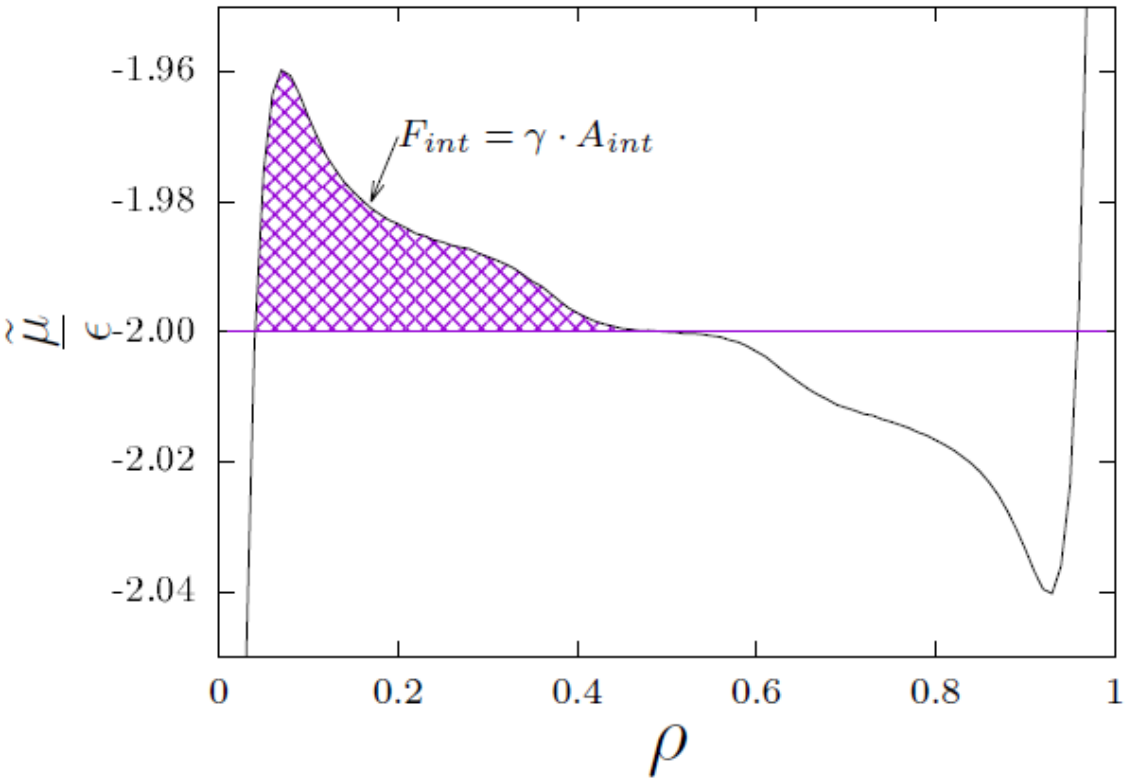


$$\gamma \left(\frac{\partial A_{int}}{\partial N} \right)_{T,V}$$

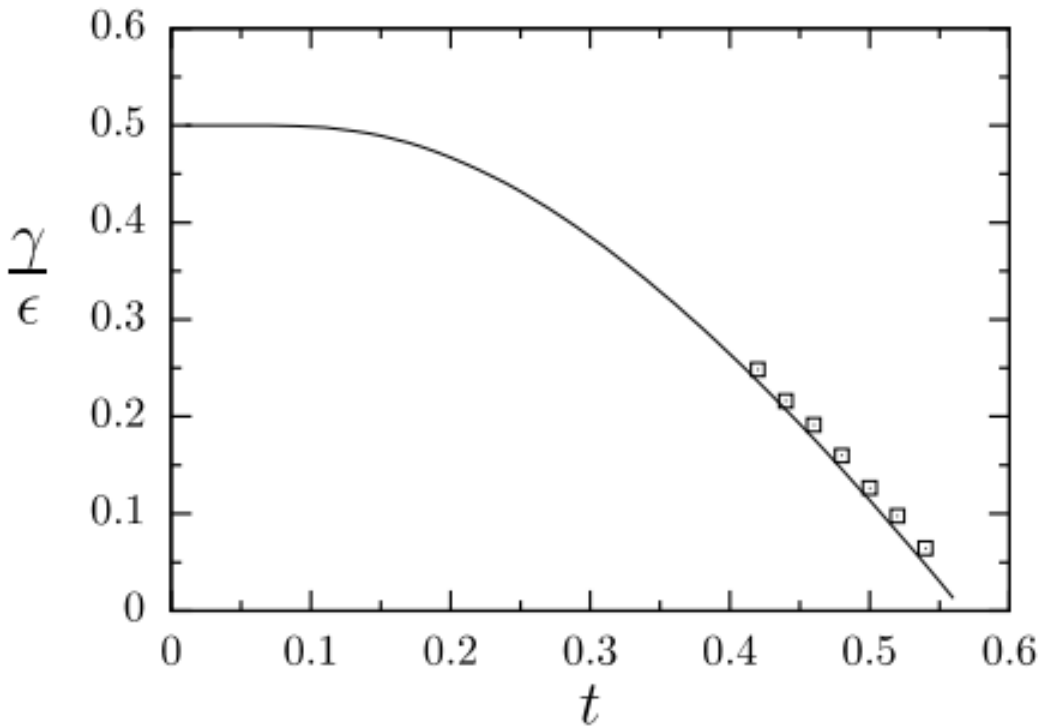


$$\mu(T, V, N)$$

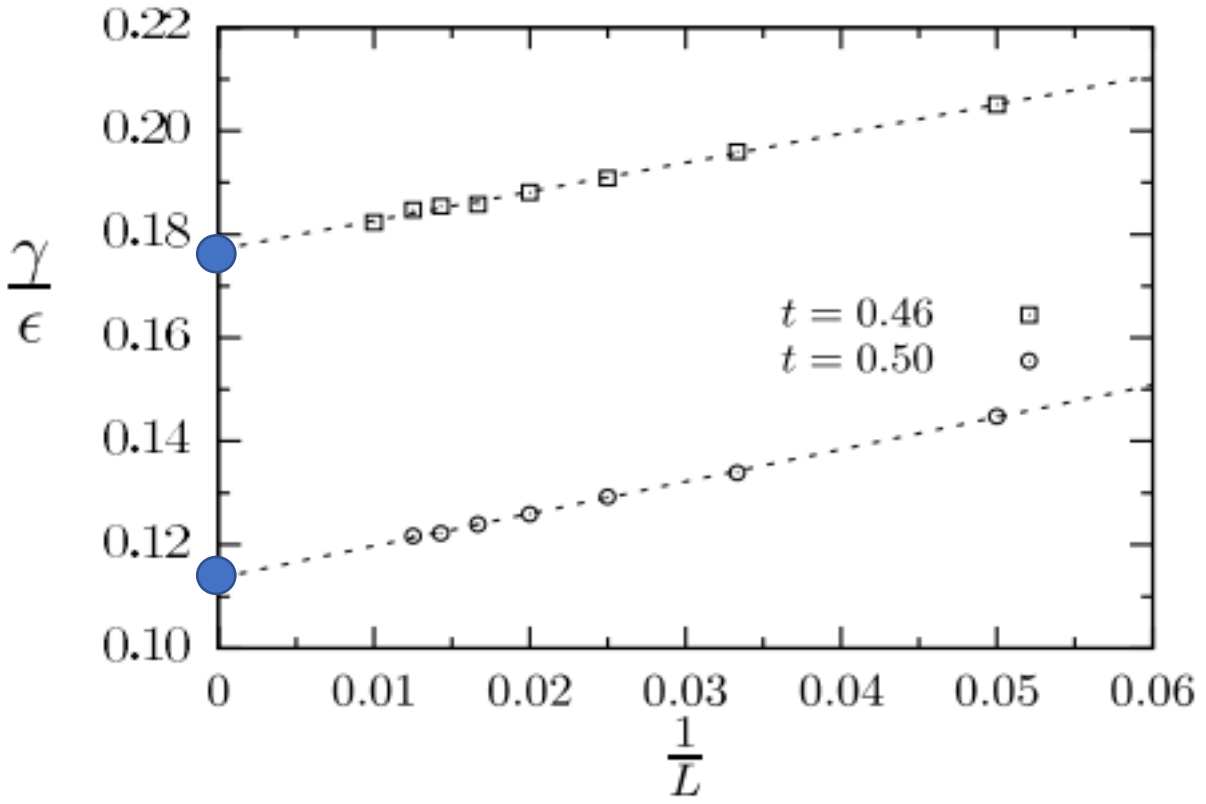
Our results for interface tension



Exact result (Onsager 1944) x simulation data



Our results for interface tension

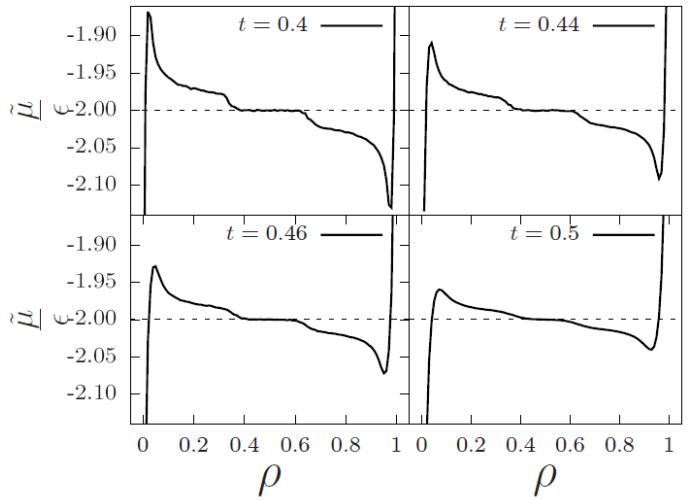


Resultado exato de Onsager

(Pseudo) Chemical potential in the **canonical** ensemble

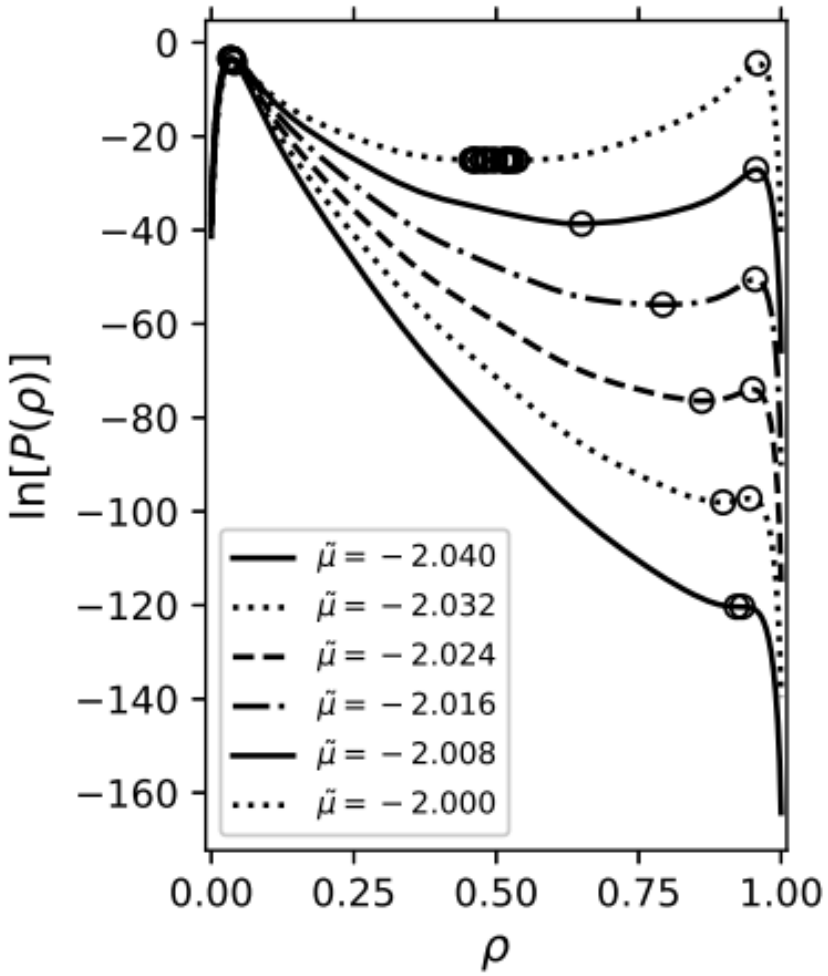
$$\frac{\partial F(T,V,N)}{\partial N} \approx F(T,V,N+1) - F(T,V,N) = -k_B T \ln\left[\frac{Z(T,V,N+1)}{Z(T,V,N)}\right]$$

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



$$\mu(T,V,N) + \gamma\left(\frac{\partial A_{int}}{\partial N}\right)_{T,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

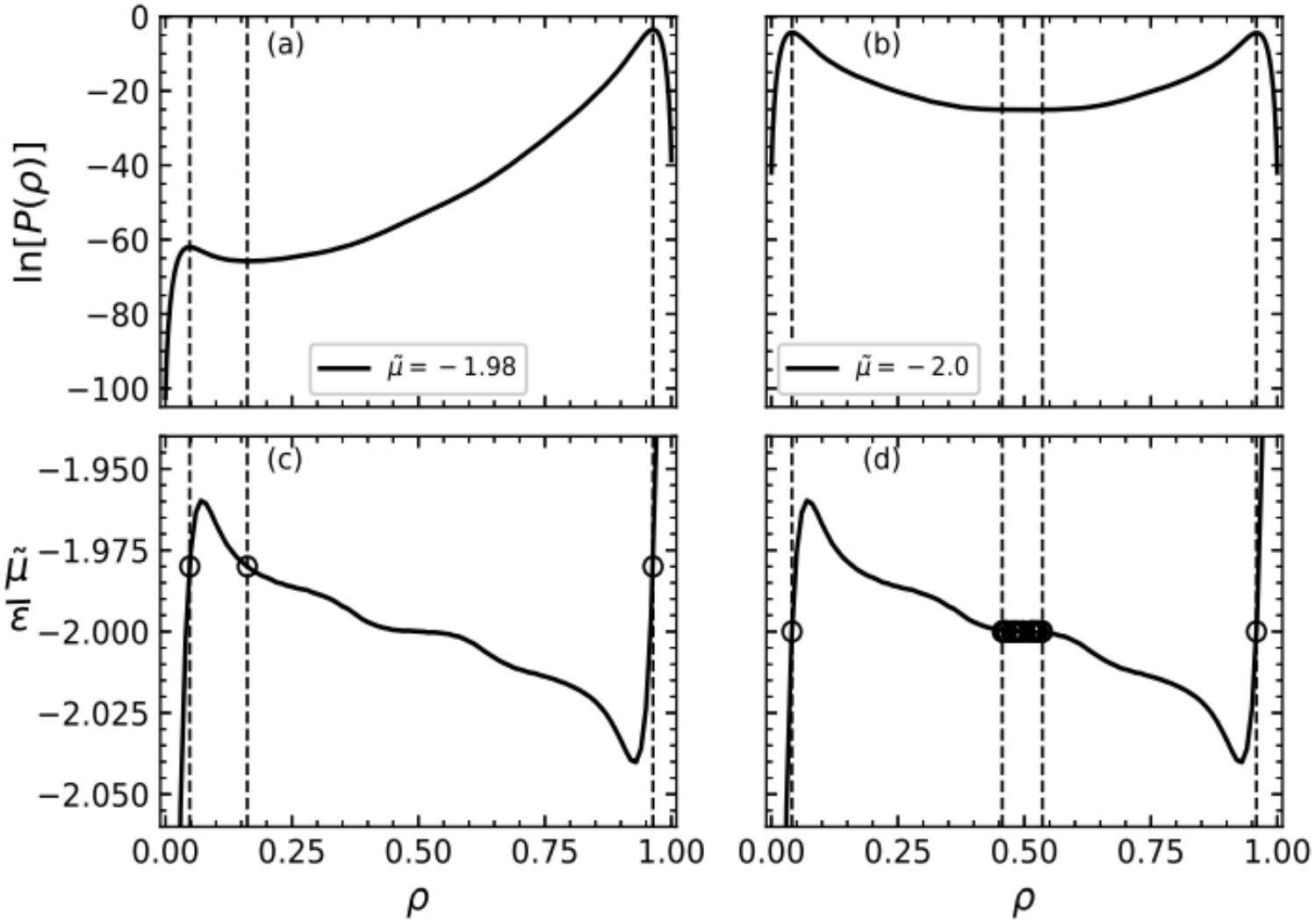
(pseudo)Chemical potential in the grandcanonical ensemble

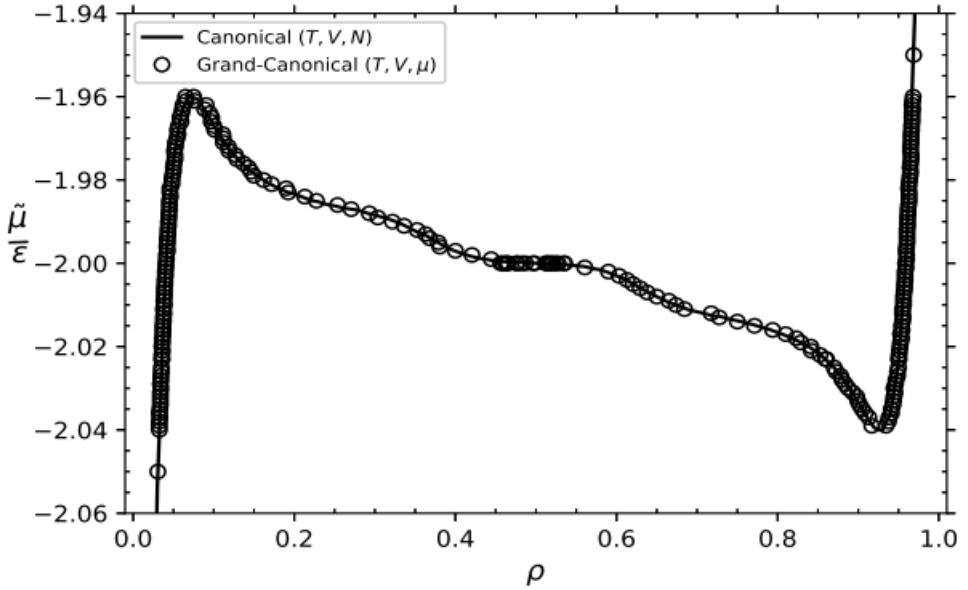


$$P(N;T,V,\tilde{\mu}) = \frac{e^{\beta\tilde{\mu}N} Z_{cx}(T,V,N)}{\Xi(T,V,\mu)}$$

$$\left.\frac{\partial P(N)}{\partial N}\right|_{\bar{N}} = 0 \quad \leftrightarrow \quad \tilde{\mu} = \tilde{\mu}\,(\bar{N})$$

Canonical - grand ensemble equivalence ?





Canonical - microcanonical equivalence ?

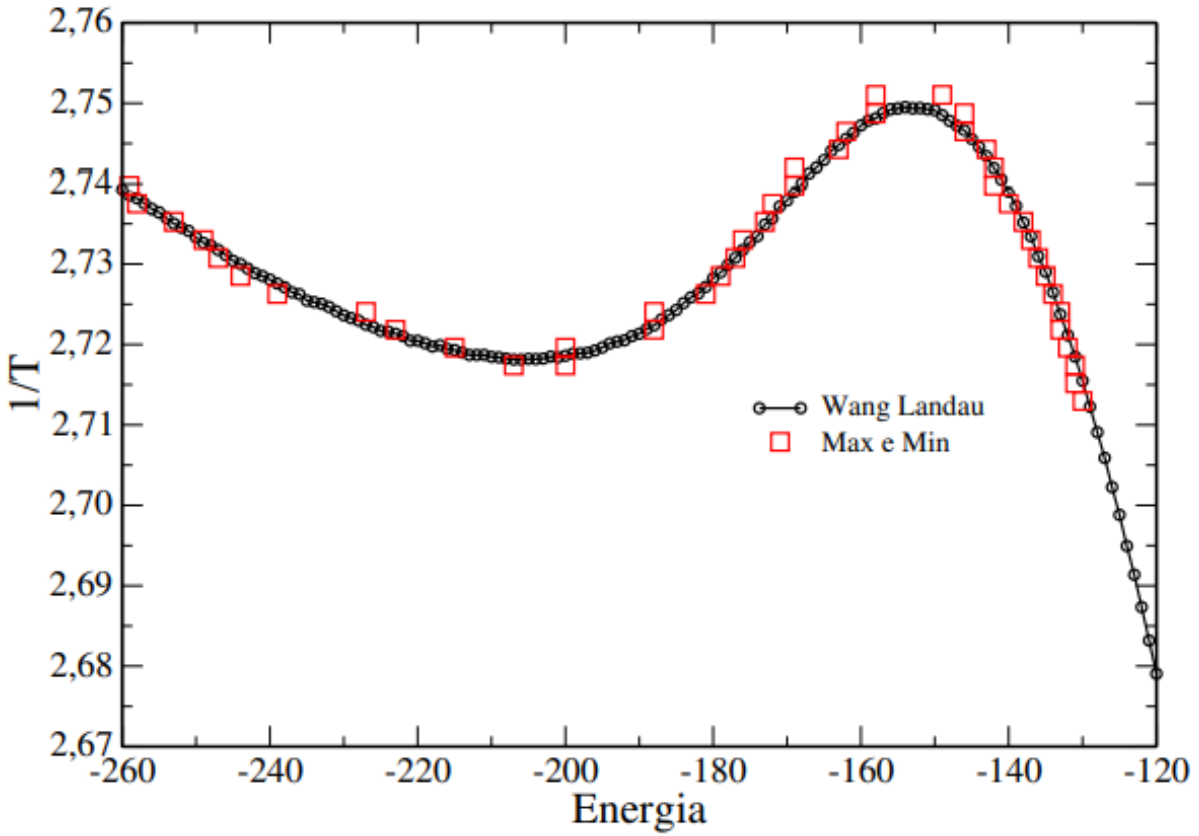


Figura 4.32 Comparação dos resultados obtidos para o inverso da temperatura em função da energia, através do método Wang Landau e a partir dos máximos e mínimos nas distribuições de energia (ensemble canônico). Rede de tamanho $L = 200$ e 1% (ensemble microcanônico) de concentração (400 partículas).

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