On Thermodynamics of Small Systems

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Hill's general assumptions for Stat Mech of Small Systems

- Fix 3 variables $\Leftrightarrow$ fix ensemble
- Consider $\mathcal{N} \rightarrow \infty$ realizations of the same small system
- Study average values & fluctuations over $\mathcal{N} \rightarrow \infty$ realizations

Hill's assumptions on phase transitions (PTs):

- Bulk free energy of phases is same at coexistence

  (taken from the macroscopic systems!)

- Surface interface between two phases costs energy

$\Rightarrow$ **phases of small system cannot coexist (Bimodality)**

For a macroscopic critique see L. G. Moretto

Q: How to check Hill's assumptions?

A: Using exactly solvable models for small system

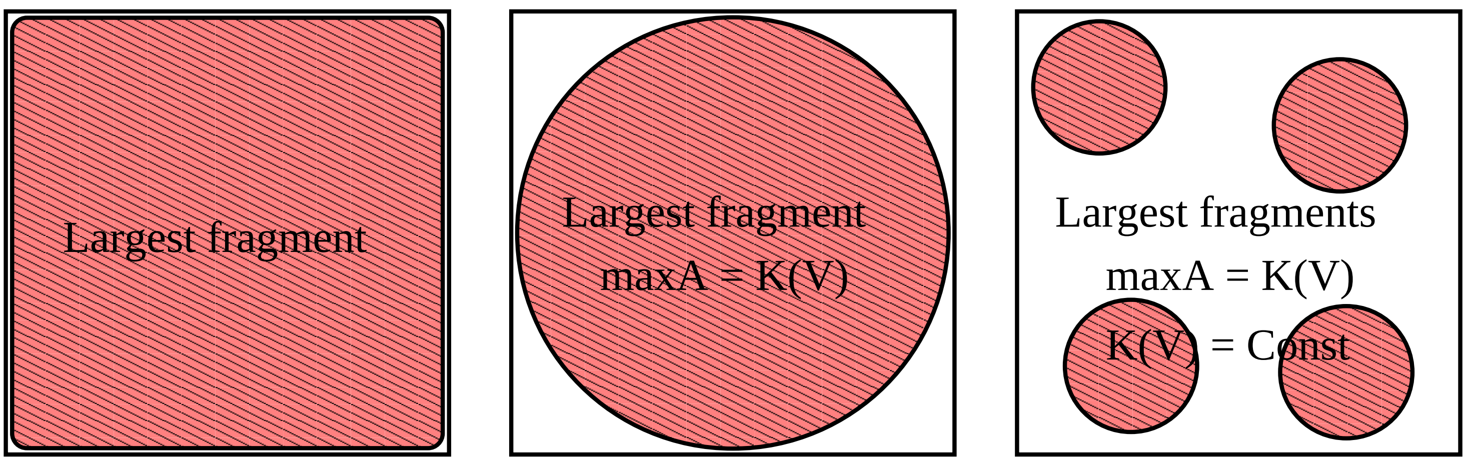
Advantage: Exact solution relates several phenomena

Problem: Where to get the non mean-field exact solution?

Constrained SMM = CSMM

CSMM is a simplified version of SMM **with:**

- no Coulomb interaction, no asymmetry;
- with hard core repulsion;
- CONSTRAINT: **largest fragment must be smaller than volume** V $\Rightarrow$ accounts for some effects of finite V



SMM **CSMM** **CSMM**

SMM grand canonical partition (GCP):

$$\mathcal{Z}(V,T,\mu) \equiv \sum_{A=0}^{\infty} \exp\left(\frac{\mu A}{T}\right) Z_A^{can}(V-bA,T)\ \Theta(V-bA)\ , \qquad (1.1)$$

constrained by $\sum_{k}^{K(V)} k\ n_k = A$ where $K(V) = \alpha V/b$ & $\alpha \leq 1$

b eigen volume of nucleon,
$V_{av} = V - bA$ available volume,
n_k occupation number of k-nucleon fragment

Technical problem: how to solve this partition exactly?

The Laplace-Fourier Transform

- **Main Problem:** the standard approach, the Laplace transform method, **does not work** because of the additional V dependence in $K(V)$

- CSMM GCP can be found by the **Laplace-Fourier technique**

K.A.B. arXiv:nucl-th/0406033

The following identity for any function G

$$G(V) = \int_{-\infty}^{+\infty} d\xi \ \delta(V - \xi) \ G(\xi) = \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{\sqrt{2\pi}} \ e^{i\eta(V-\xi)} \ G(\xi) \,, \quad (1.2)$$

allows us to reduce an **arbitrary** V-dependence in GCP to **exponential!**

$$\mathcal{Z}(\lambda, T.\mu) \ \equiv \ \int_0^{\infty} dV \ e^{-\lambda V} \ Z(V, T, \mu) = \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} \frac{d\eta}{\sqrt{2\pi}} \ \frac{e^{-i\eta\xi}}{\lambda - i\eta \ - \ \mathcal{F}(\xi, \lambda - i\eta)} \quad (1.3)$$

is **a Laplace-Fourier transform** and $\mathcal{F}(\xi, \tilde{\lambda})$ is defined as

$$\mathcal{F}(\xi, \tilde{\lambda}) = \sum_{k=1}^{K(\xi)} \phi_k(T) \ e^{\frac{(\mu - \tilde{\lambda} bT)k}{T}} = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \left[z_1 \ e^{\frac{\mu - \tilde{\lambda} bT}{T}} + \sum_{k=2}^{K(\xi)} k^{-\tau} e^{\frac{(\mu + W - \tilde{\lambda} bT)k - \sigma k^{2/3}}{T}} \right].$$

Here $\phi_k(T)$ is the one-particle distribution function of a k-nucleon fragment, $z_1 = 4$ is the number of nucleon d.o.f., $W(T)$ is binding energy per nucleon, σ is the surface tension coefficient.

After **the inverse Laplace transform** the GCP becomes

$$\mathcal{Z}(V, T, \mu) \ = \sum_{\{\lambda_n\}} e^{\lambda_n V} \left[1 - \frac{\partial \mathcal{F}(V, \lambda_n)}{\partial \lambda_n} \right]^{-1}, \quad (1.4)$$

the simple poles in (1.3) are defined by $\lambda_n \ = \ \mathcal{F}(V, \lambda_n)$

Singularities of Isobaric Partition

GCP is reduced to sum over all singularities λ_n $(n = 0, 1, 2, ..)$ of **Isobaric Partition** $\Leftrightarrow$ **collective states of the same GCP**

K.A.B. arXiv:nucl-th/0406033

- Simple poles: $\lambda_n = R_n + iI_n$

$$\lambda_n = \mathcal{F}(V, \lambda_n) \ \Rightarrow \begin{cases} R_n = \sum\limits_{k=1}^{K(V)} \tilde{\phi}_k(T)\ e^{\frac{Re(\nu_n)\,k}{T}} \cos(I_n bk)\,, \\ I_n = -\sum\limits_{k=1}^{K(V)} \tilde{\phi}_k(T)\ e^{\frac{Re(\nu_n)\,k}{T}} \sin(I_n bk)\,. \end{cases} \qquad (1.5)$$

- Effective chemical potential $\nu_n \equiv \nu(\lambda_n) = \mu + W(T) - \lambda_n bT$
- Reduced distribution $\tilde{\phi}_k(T)$ **has no bulk free energy**
- **Real root meaning** $(R_0; I_0 = 0)$:

(i) Root R_0 exists for any $(T,\ \mu)$

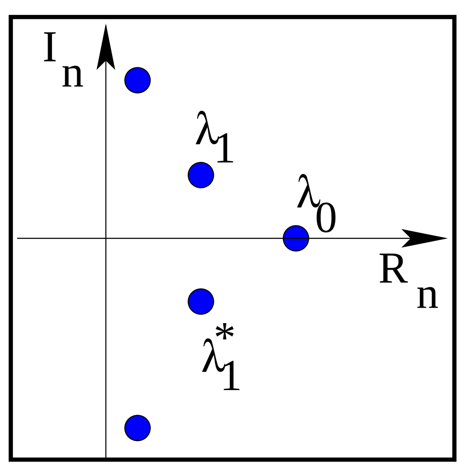
(ii) TR_0 is constrained grand canonical gas pressure:

$$TR_0 = T\left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \left[z_1\ e^{\frac{\mu - R_0 bT}{T}} + \sum_{k=2}^{K(V)} k^{-\tau} e^{\frac{(\mu + W - R_0 bT)k - \sigma k^{2/3}}{T}}\right]. \qquad (1.6)$$

- For $I_n \neq 0$ $\Rightarrow$ $R_0 > R_{n>0}$,

(**inequality** $\cos(I_n k) \leq 1$ cannot be **equality** for all k simultaneously!)

$\Rightarrow$ **The gas pressure is the farthest right singularity**



Meaning of the Complex Roots $\lambda_{n>0}$

- **Eqs. for** R_n & I_n $\Rightarrow$ Roots $n > 0$ come in complex conjugate pairs: if λ_n is a root, then λ_n^* is a root too.

$\Rightarrow$ **Partition is always real**

- **From GCP** $\mathcal{Z}(V,T,\mu) = \sum_{\{\lambda_n\}} e^{\lambda_n V} \left[1 - \frac{\partial \mathcal{F}(V,\lambda_n)}{\partial \lambda_n}\right]^{-1}$,

$\Rightarrow$ $-Re(\lambda_n)VT = -R_n VT$ **is free energy of** λ_n **state.**

$\Rightarrow$ **Gaseous state is always stable since** $-R_0 VT < -R_{n>0} VT$

$\Rightarrow$ $n > 0$ **states are metastable for finite** V

- **From correspondence:**

Statistical Operator $\Longleftrightarrow$ Convolution Operator

$$e^{-\frac{\hat{H}}{T}} \Longleftrightarrow e^{-\frac{i\hat{H}t}{\hbar}}$$

$\Rightarrow$ $\frac{1}{T}$ **is complex time** t

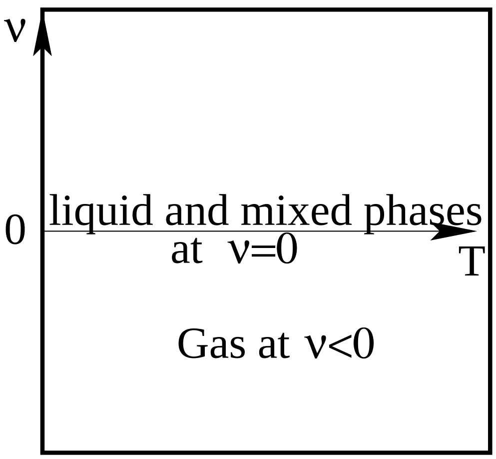
$\Rightarrow$ $\cos\left(\frac{I_n bTk}{T}\right) = \cos\left(\frac{itk}{\tau_n}\right) = \frac{1}{2}\left[e^{-k\frac{t}{\tau_n}} + e^{k\frac{t}{\tau_n}}\right]$

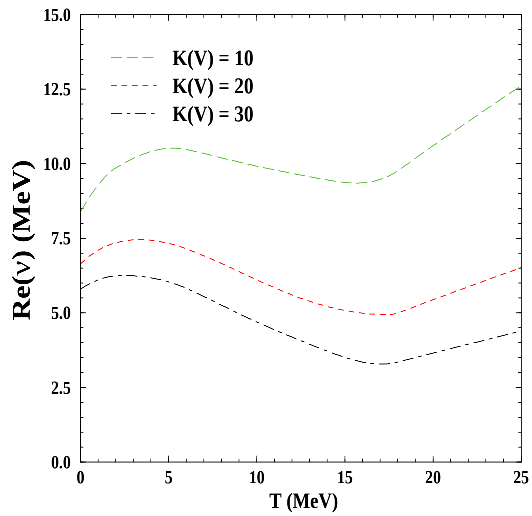
$\Rightarrow$ $\sin\left(\frac{I_n bTk}{T}\right) = \sin\left(\frac{itk}{\tau_n}\right) = \frac{1}{2i}\left[e^{-k\frac{t}{\tau_n}} - e^{k\frac{t}{\tau_n}}\right]$

$\Rightarrow$ $\tau_n = \pm\frac{1}{|I_n|bT}$ **is formation/decay time**

$\Rightarrow$ **Gaseous phase is stable because** $\tau_0 = \pm\infty$

Finite Volume Analogs of Phases





mixed phase: 3 and more roots $\lambda_{n>0}$

gas state: single root λ_0

Phase boundaries for

$V \to \infty$ $\qquad\qquad$ $V < \infty$

For finite volume and

- any T and $Re(\nu) < Re(\nu_1(T))$: **gas**
- any T and $\infty > Re(\nu) \geq Re(\nu_1(T))$: **mixed phase**

  for $Re(\nu) > T \;\Rightarrow\; \tau_n \approx \pm\frac{K(V)}{\pi n T} \Rightarrow$ for large $K(V)$
  τ_n of metastable states **increases**
  Interesting: for $T \to 0 \;\Rightarrow\; \tau_n \to \pm\infty$

- for any T and $Re(\nu) \to \infty$: **liquid phase**=densest state

Important: for $V < \infty \;\Rightarrow\; Re(\nu_0) < Re(\nu_1) < Re(\nu_2)...$

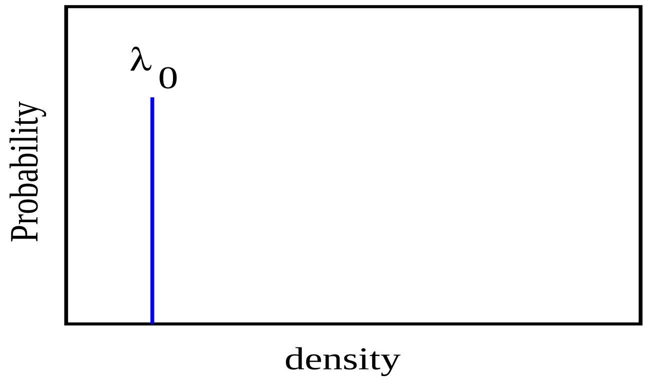
$\Rightarrow$ For the same value of μ the λ_n **states are not in a true chemical equilibrium**

$\Rightarrow$ **Mixed phase does not consist of 2 pure phases**

$\Rightarrow$ **The free energies of λ_0, λ_1, λ_2... states differ by a volume-like term. Not by a surface-like term!**

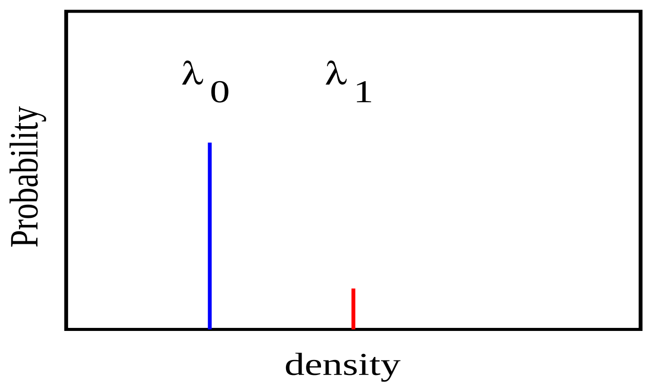
Counterexample for Bimodality

Fixing T and increasing μ ($\Leftrightarrow$ increasing average density ρ_{av})

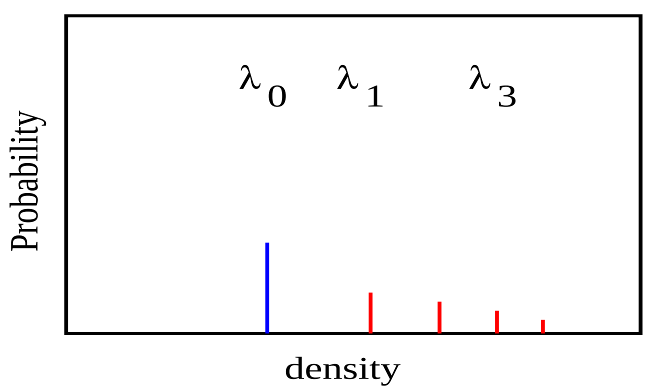


$$\rho_{av} = \sum_{\lambda_n} \rho_n w(\lambda_n)$$

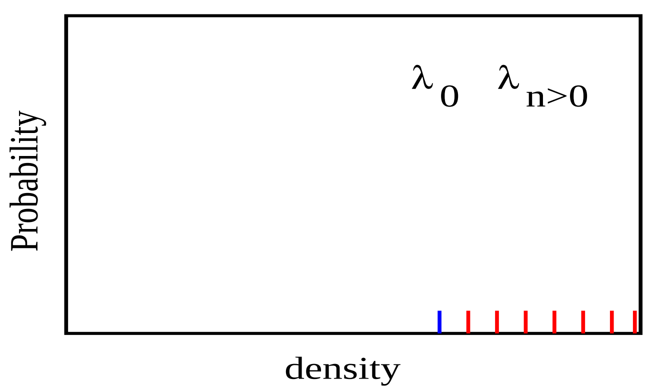
low av. densities: gas state $\Leftrightarrow$ single root λ_0



higher av. density: entering mixed phase $\Leftrightarrow$ 3 roots λ_n



even higher av. densities $\Leftrightarrow$ mixed phase with many roots $\lambda_{n>0}$



nearly highest av. density $\Leftrightarrow$ nearly liquid state: ∞ many roots λ_n

Conclusions

- Gaseous state is stable; all other $\lambda_{n>0}$ states are metastable.
- λ_n states of same partition are **not in true chemical equilibrium** at finite V.
- Metastable states do not lead to spinodal instabilities.
- Hill's assumptions on treating phase transitions in finite systems are incorrect.
- **Bimodality is an artifact of incorrect assumptions.**
- The formalism can distinguish the cases with and without phase transition.
- **No phase transition: formation/decay time $\tau_{n>0}$ is finite even for $V \to \infty$, i.e. the metastable states never become stable.**
- Phase transition: formation/decay time $\tau_{n>0} \to \infty$ for $V \to \infty$.
- The model allows one to study phases of small nuclear systems without going to thermodynamic limit.

Questions to be clarified

- What is the meaning of the usual spinodal instabilities?
- How the λ_n metastable states behave during the expansion?
- Can transport approach get the $\lambda_{n>1}$ states in equilibrium? If not, then what is missing?