Phase transitions in the unconstrained ensemble

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Left to right: Latella, Campa, Casetti, Perez-Madrid

References

- I. Latella et al. , *Phys. Rev. Lett.*, **114**, 230601 (2015)
- A. Campa et al., *J. Stat. Mech: Theory and Experiment*, **073205** (2016)
- I. Latella et al., *Phys. Rev. E*, **95**, 012140 (2017)
- A. Campa et al., *Entropy*, **20**, 907 (2018)
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Previous related work

- I. Latella and A. Perez-Madrid, *Phys. Rev. E*, **88**, 042135 (2013)

Plan

- Additivity and long-range interactions
- The replica energy
- The unconstrained ensemble
- $1/r^{\alpha}$ interactions in the mean-field approximation
- The modified Thirring model

Additivity

- Additivity is a basic property of systems with short-range interactions. It implies that energy E is a *linear homogenous* function of entropy S, volume V and number of particles N
- Systems with power-law decaying interactions are non additive if the power α is smaller or equal than the dimension d of the embedding space. Examples are self-gravitating systems, Coulomb and dipolar systems, two-dimensional fluids, etc.
- Non additive interactions lead to *ensemble inequivalence*, which implies negative specific heat, temperature jumps, broken ergodicity, etc.

The replica energy

$\mathscr{N}$ replicas of a system of N particles with energy E, entropy S and volume V.
$E_t = \mathscr{N} E$, $S_t = \mathscr{N} S$, $V_t = \mathscr{N} V$, $N_t = \mathscr{N} N$
Thermodynamic relation (Hill, 2001)

$$\mathrm{d}E_t = T\mathrm{d}S_t - P\mathrm{d}V_t + \mu\mathrm{d}N_t + \mathscr{E}\mathrm{d}\mathscr{N},$$

We call $\mathscr{E}$ the replica energy. It vanishes if each system is additive.
Proof: $\mathscr{N}_1 \to \mathscr{N}_2 = \xi\mathscr{N}_1$ while $S_1 \to S_2 = S_1/\xi$, $V_1 \to V_2 = V_1/\xi$, $N_1 \to N_2 = N_1/\xi$. Then $\mathrm{d}S_t = \mathrm{d}V_t = \mathrm{d}N_t = 0$, implying $\mathrm{d}E_t = \mathscr{E}\mathrm{d}\mathscr{N}$. But in an additive system the energy is a *linear homogeneous function* of entropy, volume and number of particles, i.e. $E_2 \equiv E(S_2, V_2, N_2) = E(S_1/\xi, V_1/\xi, N_1/\xi) = E(S_1, V_1, N_1)/\xi \equiv E_1/\xi$, and therefore $\mathrm{d}E_t = 0$, requiring $\mathscr{E} = 0$.
Hence, $\mathscr{E} \neq 0$ implies non additivity.

Thermodynamic relations: violation of Gibbs-Duhem

Integrating Hill's equation for fixed single system properties,

$$E\mathrm{d}\mathscr{N} = TS\mathrm{d}\mathscr{N} - PV\mathrm{d}\mathscr{N} + \mu N\mathrm{d}\mathscr{N} + \mathscr{E}\mathrm{d}\mathscr{N}$$

which yields

$$E_t = TS_t - PV_t + \mu N_t + \mathscr{E}\mathscr{N}$$

and, for the single system,

$$E = TS - PV + \mu N + \mathscr{E}.$$

Differentiating this relation and taking into account the first principle ($T\mathrm{d}S$ equation)

$$\mathrm{d}\mathscr{E} = -S\mathrm{d}T + V\mathrm{d}P - N\mathrm{d}\mu.$$

which shows that T, P and μ can become independent only if $\mathscr{E} \neq 0$ (violation of Gibbs-Duhem). Moreover,

$$\mathscr{E} = E - TS + PV - \mu N$$

which allows to compute $\mathscr{E}$ from S and the equation of state.

The unconstrained ensemble: probability distribution

Let $p_i(V,N)$ be the Gibbs-Boltzmann probability of a (discrete) state

$$p_i(V,N) = \frac{\exp\left[-\alpha N - \beta E_i(V,N) - \gamma V\right]}{\Upsilon}$$

where the normalization is given by

$$\Upsilon = \sum_{i,V,N} \exp\left[-\alpha N - \beta E_i(V,N) - \gamma V\right].$$

The change in the average energy $\bar{E} = \sum_{i,V,N} E_i(V,N) p_i(V,N)$ due to an infinitesimal change of the probability is

$$\mathrm{d}\bar{E} = \sum_{i,V,N} E_i(V,N)\mathrm{d}p_i(V,N)$$

.

The unconstrained ensemble: entropy

Using the conservation of the probability $\sum_{i,V,N} \mathrm{d}p_i(V,N) = 0$ one gets

$$\mathrm{d}\bar{E} = -\frac{1}{\beta}\mathrm{d}\left[\sum_{i,V,N} p_i(V,N)\ln p_i(V,N)\right] - \frac{\alpha}{\beta}\mathrm{d}\bar{N} - \frac{\gamma}{\beta}\mathrm{d}\bar{V}$$

where $\bar{N}$ and $\bar{V}$ are the average number and volume. This is to be compared with the thermodynamic relation

$$\mathrm{d}\bar{E} = T\mathrm{d}S + \mu\mathrm{d}\bar{N} - P\mathrm{d}\bar{V},$$

which allows the identification of the intensive variables $k_B T = 1/\beta$, $P = \gamma/\beta$ and $\mu = -\alpha/\beta$, and the entropy

$$S = -k_B \sum_{i,V,N} p_i(V,N)\ln p_i(V,N)$$

The unconstrained ensemble: replica energy

Substituting the expression of the probability in the entropy, one gets

$$\mathscr{E} = \bar{E} - TS + P\bar{V} - \mu\bar{N},$$

where

$$\mathscr{E}(T, P, \mu) = -k_B T \ln \Upsilon(T, P, \mu),$$

is the replica energy or "subdivision potential" (Hill, 1963). One also obtains by differentiation

$$\mathrm{d}\mathscr{E} = -S\mathrm{d}T + \bar{V}\mathrm{d}P - \bar{N}\mathrm{d}\mu.$$

which implies

$$\left(\frac{\partial \mathscr{E}}{\partial T}\right)_{P,\mu} = -S, \; , \; \left(\frac{\partial \mathscr{E}}{\partial P}\right)_{T,\mu} = \bar{V}, \; \left(\frac{\partial \mathscr{E}}{\partial \mu}\right)_{T,P} = -\bar{N}.$$

Relation with other ensembles-I

The unconstrained partition function can be written as

$$\Upsilon(T, P, \mu) = \sum_{V,N} Z(T, V, N)\ e^{\mu N/(k_B T)} e^{-PV/(k_B T)},$$

where

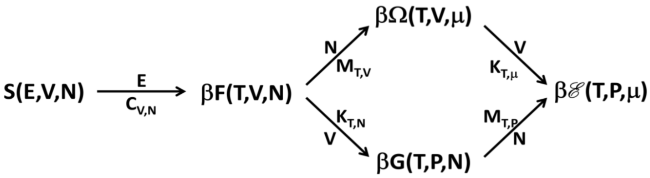
$$Z(T, V, N) = \sum_{i} e^{-E_i(V,N)/(k_B T)}$$

is the canonical partition function. Υ can also be connected with the grand-canonical ensemble

$$\Upsilon(T, P, \mu) = \int \mathrm{d}V \Xi(T, V, \mu) e^{-PV/(k_B T)},$$

where $\Xi(T, V, \mu)$ is the grand canonical partition function.

Relation with other ensembles-II



$\Upsilon = e^{-\beta \mathscr{E}}$

$$e^{-\beta \mathscr{E}(T,P,\mu)} = \int \mathrm{d}V e^{-\beta(\Omega(T,V,\mu)+PV)}$$

where $C_{V,N} = (\partial E/\partial T)_{V,N}$, $M_{T,V} = (\partial N/\partial \mu)_{T,V}$, etc.

Long-range $1/r^\alpha$ interaction

We consider an ensemble of systems, each with Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{N} \frac{|\mathbf{p}_j|^2}{2m} + W(\mathbf{q}_1, \ldots, \mathbf{q}_N)$$

with, e.g.,

$$W = \sum_{i,j}^{N} \frac{-G}{|\mathbf{q}_i - \mathbf{q}_j|_{reg}^{\alpha}}$$

The microcanonical volume is

$$\omega = \int \frac{\rho(E)}{h^{dN} N!} \mathrm{d}^{2dN}\Gamma$$

with

$$\rho(E) = \delta(E - \mathcal{H})$$

Ideal gas plus long-range

Separate the contribution of the "ideal gas" from the one of long-range

$$S - S^{(I)} = S^{(LR)} \text{ and } E = E^{(I)} + E^{(LR)} = E^{(I)} + W,$$

hence the replica energy is given by

$$\mathscr{E} = W - TS^{(LR)} + P^{(LR)}V - \mu^{(LR)}N \text{ since } TS^{(I)} = E^{(I)} + P^{(I)}V - \mu^{(I)}N$$

Mean-field potential

$$W = \frac{1}{2}\int n(\mathbf{x})\Phi(\mathbf{x})\mathrm{d}^d\mathbf{x} \text{ with } \Phi(\mathbf{x}) = \int \mathrm{d}\mathbf{x}' \frac{-Gn(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^{\alpha}_{reg}}$$

where $n(\mathbf{x})$ is the number density. Entropy

$$S = -\int n(\mathbf{x}) \ln\left[\lambda_T^d n(\mathbf{x})\right] \mathrm{d}^d\mathbf{x} + \frac{2+d}{2}N$$

where $\lambda_T = h/\sqrt{2\pi m T}$ is the thermal wavelength

Replica energy: general formula

Chemical potential is constant to guarantee the absence of currents

$$\mu = \mu_0(\mathbf{x}) + \Phi(\mathbf{x})$$

which implies

$$\mu N = T \int \mathrm{d}^d\mathbf{x}\; n(\mathbf{x}) \ln \left[\lambda_T^d n(\mathbf{x})\right] + 2W.$$

$\mu_0(\mathbf{x})$ is determined in such a way that

$$n(\mathbf{x}) = \lambda_T^{-d} \exp\left\{-[\Phi(\mathbf{x}) - \mu]/T\right\}$$

All ideal gas contributions can be obtained explicitly from these expression and as a consequence $\mu^{(LR)}N = -TS^{(LR)} + 2W$, which gives

$$\mathscr{E} = -W + P^{(LR)}V.$$

Replica energy: explicit expression for $1/r^\alpha$

Virial theorem states in this case

$$dNT + \alpha W = dPV.$$

Hence,

$$P^{(LR)}V = \frac{\alpha W}{d}$$

. Thus, the replica energy becomes

$$\mathscr{E} = -(1 - \frac{\alpha}{d})W,$$

It vanishes for $\alpha = d$, when the system becomes short-range. (The expression cannot be used for $\alpha > d$.)

The modified Thirring model

Hamiltonian

$$\mathcal{H}(\mathbf{p},\mathbf{q}) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i>j}^{N} \phi(\mathbf{q}_i,\mathbf{q}_j)$$

with potential

$$\phi(\mathbf{q}_i,\mathbf{q}_j) = -2\nu\left[\theta_{V_0}(\mathbf{q}_i)\theta_{V_0}(\mathbf{q}_j) + b\theta_{V_1}(\mathbf{q}_i)\theta_{V_1}(\mathbf{q}_j)\right]$$

Total potential energy

$$\hat{W}(N_0,N_1) \equiv \sum_{i>j}^{N} \phi(\mathbf{q}_i,\mathbf{q}_j) = -\nu\left(N_0^2 + bN_1^2\right),$$

where N_0 is the number of particles in V_0 and $N_1 = N - N_0$ is the number of particles in V_1 for a given configuration. **Particles have a volume** σ.

The Thirring model in the unconstrained ensemble

Canonical partition function

$$Z(T,V,N) = \int \frac{\mathrm{d}^{3N}\mathbf{q}\ \mathrm{d}^{3N}\mathbf{p}}{h^{3N}N!} e^{-\beta\mathcal{H}(\mathbf{p},\mathbf{q})} = \int \frac{\mathrm{d}^{3N}\mathbf{q}}{N!}\ \frac{e^{-\beta\hat{W}(N_0,N_1)}}{\lambda_T^{3N}},$$

Unconstrained partition function

$$\Upsilon(T,P,\mu) = \int \mathrm{d}V \sum_N \int \frac{\mathrm{d}^{3N}\mathbf{q}}{N!} \lambda_T^{-3N} e^{-\beta\hat{W}(N_0,N_1)} e^{\beta\mu N} e^{-\beta PV}$$

Thirring's method

$$\int \frac{\mathrm{d}^{3N}\mathbf{q}}{N!} \to \sum_{N_0,N_1} \delta_{N,N_0+N_1} \frac{(V_0 - N_0\sigma)^{N_0}}{N_0!} \frac{(V_1 - N_1\sigma)^{N_1}}{N_1!}$$

Model's replica energy

$$\Upsilon(T,P,\mu) = \int \mathrm{d}V \sum_{N_0,N_1} e^{-\beta\hat{\mathscr{E}}(T,P,\mu,V,N_0,N_1)},$$

where

$$\begin{aligned}\hat{\mathscr{E}}(V,N_0,N_1) &= \hat{W}(N_0,N_1) + PV - T\sum_k N_k \\ &\quad + T\sum_k N_k \left[\ln\left(\frac{N_k\lambda_T^3}{V_k - N_k\sigma}\right) - 1 - \frac{\mu}{T}\right]\end{aligned}$$

in the Stirling approximation. In the saddle point limit

$$\mathscr{E} = \inf_{\{V,N_0,N_1\}} \hat{\mathscr{E}}(V,N_0,N_1)$$

Consistency equations and replica energy

$$
\begin{aligned}
P &= \frac{T\bar{N}_1}{\bar{V} - V_0 - N_1\sigma} \\
\mu &= -2\nu\bar{N}_0 + T\ln\left(\frac{\bar{N}_0\lambda_T^3}{V_0 - N_0\sigma}\right) + \frac{T\bar{N}_0\sigma}{V_0 - \bar{N}_0\sigma} \\
\mu &= -2b\nu\bar{N}_1 + T\ln\left(\frac{\bar{N}_1\lambda_T^3}{\bar{V} - V_0 - \bar{N}_1\sigma}\right) + \frac{T\bar{N}_1\sigma}{\bar{V} - V_0 - \bar{N}_1\sigma}
\end{aligned}
$$

that we have to solve in terms $\bar{V}$, $\bar{N}_0$, $\bar{N}_1$ as functions of T, P and μ. **For $\sigma = 0$ we obtain**

$$
\mu\bar{N} = T\sum_k \bar{N}_k \ln\left(\frac{\bar{N}_k}{V_k}\lambda_T^3\right) + 2W
$$

which gives

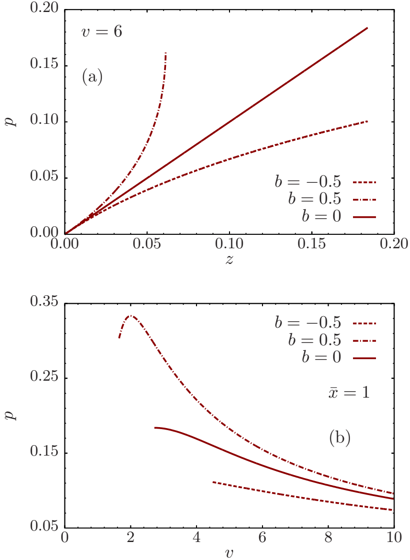
$$
\mathscr{E} = -W + P^{(\mathrm{LR})}\bar{V},
$$

$P^{(\mathrm{LR})} = P - \bar{N}T/\bar{V}$ is the long-range contribution to the pressure.

Main results for $\sigma = 0$

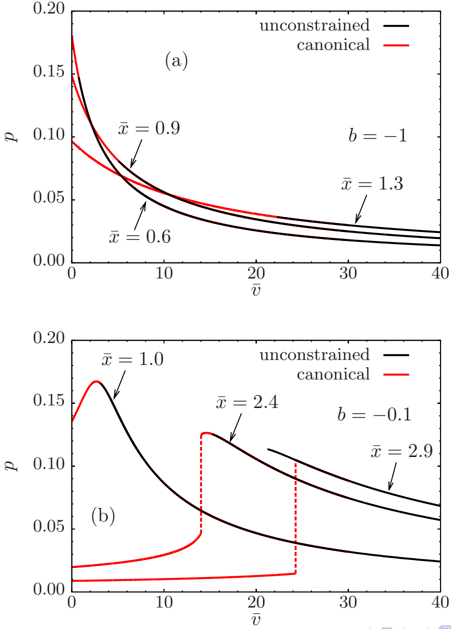
- Equilibrium configurations exist in the unconstrained ensemble only for $b < 0$ (repulsive interactions).
- For $b = 0$ (Thirring's model) no equilibrium states exist in the unconstrained ensemble.
- The unconstrained ensemble and the grand-canonical ensemble are equivalent for $b < 0$.
- In the grand-canonical ensemble equilibrium states exist also for $b \geq 0$, and some of these states have negative isothermal compressibility.
- No phase transition is present in the grand-canonical ensemble.
- The grand-canonical ensemble is inequivalent to the canonical ensemble. In this latter ensemble phase transitions of first order and a critical point are present (in analogy with Thirring's model).
- Negative compressibility states appear in the canonical ensemble also for $b < 0$

p-v and p-z planes: Grand canonical



$$z = \exp((\mu - \mu_0))/T), \ \mu_0 = T\ln(T\lambda_T^3/\nu V_0), \ p = \nu V_0 P/T^2$$

P-V and P-Z planes Unconstrained vs. canonical



Dimensionless replica energy

We define

$$v = \frac{V - V_0}{V_0}, \qquad x_0 = \frac{\nu N_0}{T}, \qquad x_1 = \frac{\nu N_1}{T} \qquad x = x_0 + x_1$$

Rescaled exclusion parameter a, reduced pressure p and chemical potential ξ

$$a = \frac{T\sigma}{\nu V_0}, \qquad p = \frac{\nu V_0}{T^2} P, \qquad \xi = \frac{\mu_T - \mu}{T},$$

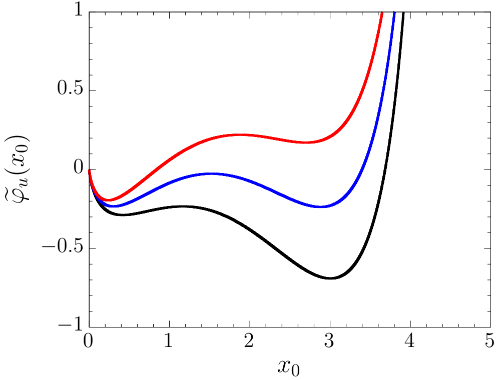
where

$$\mu_T = T \ln\left(\frac{T\lambda_T^3}{\nu V_0}\right),$$

Dimensionless replica energy $\hat{\varphi}_u = \nu\hat{\mathscr{E}}/T^2$

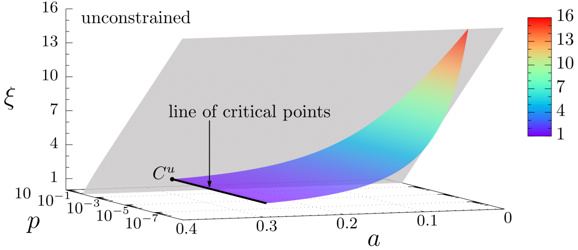
$$\hat{\varphi}_u(v, x_0, x_1) = x_0\left[\ln\left(\frac{x_0}{1 - ax_0}\right) - 1\right] + x_1\left[\ln\left(\frac{x_1}{v - ax_1}\right) - 1\right] + p(v+1) + (x_0 + x_1)\xi - x_0^2 - bx_1^2.$$

First order phase transition



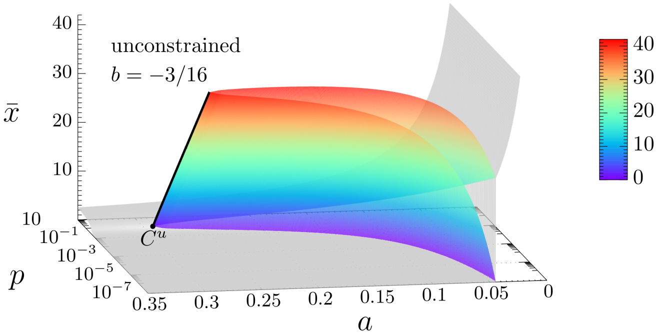
Rescaled replica energy as a function of x_0 for $\xi = 1.5$ (black), $\xi = 1.65$ (blue) and $\xi = 1.8$ (red), taking $a = 0.23$.

Phase diagram I



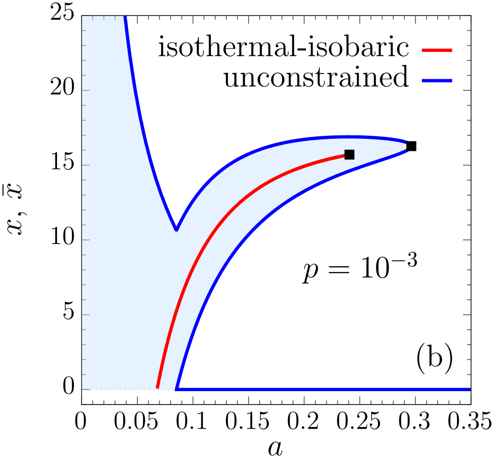
Phase diagram (p, a, ξ) in the unconstrained ensemble for any coupling $b < 0$

Phase diagram II



Phase diagram $(p, a, \bar{x})$ with $b = -3/16$.

Inequivalence



Cross section of the phase diagram for $b = -3/16$.

Conclusions

- Replica energy is the appropriate thermodynamic potential for long-range interacting non additive systems.
- The unconstrained ensemble allows for equilibrium states if interactions are long-range.
- Replica energy can be explicitly computed for some remarkable cases: $1/r^{\alpha}$ interactions in the mean-field approximation, generalized Thirring model, etc.
- The unconstrained ensemble can be inequivalent with other ensembles as explicitly demonstrated for the generalized Thirring's model (grand-canonical, canonical, etc.)
- Phase transitions can take place also in the unconstrained ensemble and demonstrate ensemble inequivalence.