Phase transitions for particles in $\mathbb{R}^3$

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Overview

1. Introduction to statistical mechanics:
   Partition functions and statistical ensembles

2. Phase transitions: conjectures

3. Mathematical results:
   a step in the right direction

4. Proof ideas

Mechanics – Thermodynamics – Statistical Mechanics

- Classical mechanics: ODEs for particle positions and velocities $x_1, \dots, x_N$, $v_1 = \dot{x}_1, \dots, v_N = \dot{x}_N$. E.g.:

$$\ddot{x}_i(t) = -\sum_{j \neq i} \nabla V\Big(x_i(t) - x_j(t)\Big), \quad i = 1, \dots, N.$$

  N interacting particles, pair potential $v(x-y)$.

- Thermodynamics: No modelization of individual particles. Instead, macroscopic quantities like pressure p, temperature T, energy, heat, entropy...
- Statistical mechanics: interpret macroscopic quantities of thermodynamics as averages of microscopic quantities from mechanics. E.g. absolute temperature (Kelvin, not Celsius!)

$$\text{Temperature } T \propto \frac{1}{N}\Big\langle \sum_{i=1}^{N} \frac{1}{2} \dot{x}_i^2 \Big\rangle \text{ average kinetic energy.}$$

  Particle number N of the order of 10^{23}: large.

Averages I: microcanonical ensemble

- Average over long periods of time:

$$\frac{1}{\Delta t}\int_0^{\Delta t}\Big(\sum_{i=1}^N \frac{1}{2}\dot{x}_i^2(s)\Big)\mathrm{d}s, \quad \Delta t \to \infty.$$

  Ergodic theory? Time average = space average ? ...

- Average over invariant probability distribution for positions and velocities: N particles in box $\Lambda = [0,L]^3$. Energy

$$\boxed{H(\boldsymbol{x},\boldsymbol{v}) := \sum_{i=1}^N \frac{1}{2}v_i^2 + \sum_{1\le i<j\le N} v(x_i - x_j), \quad (\boldsymbol{x},\boldsymbol{v}) \in \Lambda^N \times (\mathbb{R}^3)^N.}$$

  Uniform distribution on energy shell $E - \delta E \le H \le E$

$$\Big\langle \sum_{i=1}^N \frac{1}{2}v_i^2 \Big\rangle_{E,N,\Lambda;\delta E}$$

$$:= \frac{1}{\Omega(E,N,\Lambda;\delta E)} \times \frac{1}{N!}\int_{\Lambda\times\mathbb{R}^{3N}} \Big(\sum_{i=1}^N \frac{1}{2}v_i^2\Big)\mathbf{1}_{\{E-\delta E\le H(\boldsymbol{x},\boldsymbol{v})\le E\}}\mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{v}.$$

  $\Omega(E,N,\Lambda;\delta E)$ = Normalization constant = partition function.

Averages II: canonical and grand-canonical ensemble

Box $\Lambda = [0, L]^3 \subset \mathbb{R}^3$.

- Microcanonical: Energy E fixed, particles number N fixed. Partition function

$$\Omega(E, N, \Lambda; \delta E) := \frac{1}{N!} \Big| \Big\{ (\boldsymbol{x}, \boldsymbol{v}) \in \Lambda^N \times \mathbb{R}^{3N} \, \Big| \, E - \delta E \leq H(\boldsymbol{x}, \boldsymbol{v}) \leq E \Big\} \Big|.$$

Isolated system – no energy or particle exchanged with environment.

Other invariant measures (ensembles):

- Canonical: Energy E random, particle number N fixed. Partition function

$$Z(\beta, N, \Lambda) = \frac{1}{N!} \int_{\Lambda^N \times \mathbb{R}^{3N}} \exp\Big(-\beta H(\boldsymbol{x}, \boldsymbol{v}) \Big) \mathrm{d}x \, \mathrm{d}v.$$

$\beta > 0$ inverse temperature. Energy exchanged with heat bath...

- Grand-canonical: Energy E random, particle number N random. Part. fct.

$$\Xi(\beta, \mu, \Lambda) = 1 + \sum_{N=1}^{\infty} \frac{\exp(\beta \mu N)}{N!} \int_{\Lambda^N \times \mathbb{R}^{3N}} \exp\Big(-\beta H(\boldsymbol{x}, \boldsymbol{v}) \Big) \mathrm{d}x \, \mathrm{d}v.$$

$\mu \in \mathbb{R}$ chemical potential. Heat bath + particle reservoir.

Thermodynamic limit. Entropy and free energy

Particle number $N \approx 10^{23}$ very large $\Rightarrow$ approximate with limit $N \to \infty$.
Keep parameters β, μ and particle and energy densities fixed.

$$\boxed{\begin{gathered} N \to \infty, \quad |\Lambda| = L^3 \to \infty, \quad |E| \to \infty, \\ \beta,\ \mu,\ \rho = \frac{N}{|\Lambda|},\ u = \frac{E}{|\Lambda|}\ \text{fest.} \end{gathered}}$$

Asymptotics of partition functions define physically relevant quantities.
Boltzmann entropy $S = k \log W$.

$$s(u,\rho) = \lim \frac{1}{|\Lambda|} \log \Omega(E, N, \Lambda; \delta E) \quad \text{entropy}$$
$$f(\beta,\rho) = -\lim \frac{1}{\beta|\Lambda|} \log Z(\beta, N, \Lambda) \quad \text{free energy}$$
$$p(\beta,\mu) = \lim \frac{1}{\beta|\Lambda|} \log \Xi(\beta, \mu, \Lambda) \quad \text{pressure.}$$

Limits exist under suitable assmptions on $vV(x_i - x_j)$.
Change of ensembles with Legendre transforms:

$$f(\beta,\rho) = \inf_{u \in \mathbb{R}} \big(u - \beta^{-1} s(u,\rho)\big), \qquad p(\beta,\mu) = \sup_{\rho > 0} \big(\mu\rho - f(\beta,\rho)\big).$$

Convexity $\Rightarrow$ inverse relations as well.

Derivatives vs. expected values

Observation:

$$-\frac{1}{|\Lambda|}\frac{\partial}{\partial\beta}\log Z(\beta,N,\Lambda)=\frac{1}{|\Lambda|}\frac{\int H\exp(-\beta H)\mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{v}}{\int\exp(-\beta H)\mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{v}}.$$

$\Rightarrow$ if limits and differentiation can be exchanged:

$$\frac{\partial}{\partial\beta}(\beta f(\beta,\rho))=\lim\Big\langle\frac{H(\boldsymbol{x},\boldsymbol{v})}{|\Lambda|}\Big\rangle_{\beta,N,\Lambda}$$

β-derivative $\leftrightarrow$ average energy density. Similarly

$$\frac{\partial}{\partial\mu}p(\beta,\mu)=\lim\Big\langle\frac{N}{|\Lambda|}\Big\rangle_{\beta,\mu,\Lambda}$$

μ-derivative $\leftrightarrow$ average particle density .

Kinetic energy in the canonical ensemble: $H=\sum\frac{1}{2}v_i^2+U(x_1,\dots,x_N)\Rightarrow$ Integrals factorize, $v_1,\dots,v_N$ normally distributed,

$$\Big\langle\sum_{i=1}^{N}\frac{1}{2}v_i^2\Big\rangle_{\beta,N,\Lambda}=\frac{3}{2}N\beta^{-1}=\frac{3}{2}NT$$

$\beta^{-1}\propto$ average kinetic energy $\rightarrow$ temperature.

Formalism statistical mechanics (classical, equilibrium):
Description of finite systems by probability measures on phase space (positions + velocities).

Different measures (ensembles) possible.
E.g. uniform distribution on energy shell.

Normalization constants (partition functions) are physically relevant.
E.g. $S = k \log W$.

Micro-macro:
For a given pair potential $V(x_i - x_j)$, the entropy, free energy and pressure are uniquely defined by asymptotics of high-dimensional integrals.

$\Rightarrow$ microscopic definition of macroscopic thermodynamic potentials.

2 Phase transitions

Question: are the entropy, free energy and pressure analytic functions? Kinks? strictly convex (concave) or with affine pieces?

Interpretation: Non-analyticity = Phase transition.
From ice to liquid water to vapor.
Small increase of temperature near boiling point 100°C
$\rightarrow$ abrupt change of material properties.

Can only happen in the limit $N, |\Lambda| \to \infty$!

Math: open.

Existence of phase transitions proven for

- Particle on lattices / Ising model on $\mathbb{Z}^2$ Peierls '36
- Widom-Rowlinson model: multi-body interaction Ruelle '71
- Four-body interaction + pair potential, van der Waals theory Lebowitz, Mazel, Presutti '99

Low temperature and density: conjectures

Conjecture I: $\exists \rho_0 > 0$ und curve $\rho_{\mathrm{sat}}(\beta)$ with

$$\rho_{\mathrm{sat}}(\beta) \approx \exp(-\mathrm{const}\beta) \to 0 \text{ at } \beta \to \infty \; (T \to 0)$$

such that $\rho \mapsto f(\beta, \rho)$

- analytic and strictly convex in $\rho < \rho_{\mathrm{sat}}(\beta)$,
- affine in $\rho_{\mathrm{sat}}(\beta) \leq \rho \leq \rho_0$.

Phase transition at $\rho = \rho_{\mathrm{sat}}(\beta)$.
Free energy as a function of density ρ has affine piece.

Conjecture II: $\exists \mu_0 > 0$ and curve $\mu_{\mathrm{sat}}(\beta)$ such that $\mu \mapsto p(\beta, \mu)$

- analytic in $\mu < \mu_{\mathrm{sat}}(\beta)$
- analytic in $\mu_{\mathrm{sat}}(\beta) \leq \mu \leq \mu_0$
- $\mu \mapsto \frac{\partial p}{\partial \mu}(\beta, \mu)$ has jump discontinuity at $\mu_{\mathrm{sat}}(\beta)$.

Phase transition at $\mu = \mu_{\mathrm{sat}}(\beta)$.
Pressure as function of μ has a kink.

3 Low temperature and low density: a partial result

Under suitable assumptions on pair potential $V(x-y)$:

$$e_\infty := \lim_{N\to\infty} \frac{1}{N} \inf_{x_1,\dots,x_N\in\mathbb{R}^3} \sum_{1\le i<j\le N} V(x_i - x_j) \in (-\infty, 0).$$

Theorem (J '12)

$\exists \nu^* > 0$ such that as $\beta\to\infty$ (μ fixed):

$$\begin{aligned} \forall \mu < e_\infty : &\qquad \frac{\partial p}{\partial \mu}(\beta,\mu) = O(\exp(-\beta\nu^*)) \to 0 \\ \forall \mu > e_\infty : &\qquad \liminf \frac{\partial p}{\partial \mu}(\beta,\mu) \ge \rho_0 > 0. \end{aligned}$$

Step towards kink of $\mu \mapsto p(\beta,\mu)$ at $\mu \approx e_\infty$.

Theorem (J '12)

Suppose there is a phase transition at $\rho_{\mathrm{sat}}(\beta)\to 0$. Then

$$\mu_{\mathrm{sat}}(\beta) = e_\infty + O(\beta^{-1}\log\beta) \quad (\beta\to\infty).$$

Tells us where to look for phase transitions.

4 Proof ingredient I: cluster expansions

Set $z = \exp(\beta\mu)$. Remember:

$$p(\beta,\mu) = \lim_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \log \left(1 + \sum_{N=1}^{\infty} \frac{z^N}{N!} \int_{\Lambda^N\times\mathbb{R}^{3N}} \exp(-\beta H)\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{v} \right).$$

Right-hand side is power series in z:

$$\boxed{p(\beta,\mu) = \lim_{|\Lambda|\to\infty} \sum_{n=1}^{\infty} b_{n,\Lambda}(\beta) z^n, \quad z = \exp(\beta\mu).}$$

Mayer expansion, cluster expansion. Known:

- For every fixed box, radius of convergence $R_\Lambda(\beta) > 0$.
- Bounds that are uniform in $\Lambda \to$

$$R(\beta) = \liminf_{|\Lambda|\to\infty} R_\Lambda(\beta) > 0.$$

- Pressure is analytic in $z = \exp(\beta\mu) < R(\beta)$.

Asymptotics of coefficients and radius of convergence J' 12

$$\liminf_{\beta\to\infty} \frac{1}{\beta} \log R(\beta) = e_\infty.$$

Proof ingredient II: droplet sizes

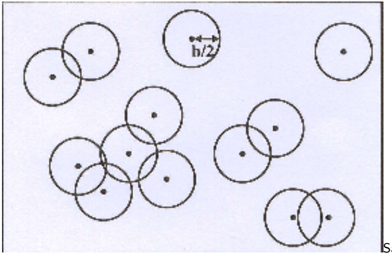
Assume: pair potential v has compact support. Variational representation

$$f(\beta,\rho) = \inf\Big\{ f\big(\beta,\rho,(\rho_k)_{k\in\mathbb{N}}\big) \mid \sum_{k=1}^{\infty} k\rho_k \leq \rho \Big\}.$$

$f(\beta,\rho,(\rho_k)) =$ restricted free energy

$$f\big(\beta,\rho,(\rho_k)\big) = -\lim \frac{1}{\beta|\Lambda|}\log\frac{1}{N!}\int \mathbf{1}\Big(\forall k:\ \frac{N_k(\boldsymbol{x})}{|\Lambda|}\approx\rho_k\Big) e^{-\beta H(\boldsymbol{x},\boldsymbol{v})}\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{v}$$

$N_k(x_1,\ldots,x_N) =$ number of droplets with k particles.



Sator, Phys. Rep. 376 (2003)

At low temperature and low density: have good bounds for restricted free energy, deduce bounds for free energy $f(\beta,\rho)$.

J., König, Metzger '11; J., König '12

Summary & Outlook

Summary:
Asymptotics of high-dimensional, parameter-dependent integrals
$\Rightarrow$ functions of parameters. Analytic?

Question still open, but partial mathematical results consistent with physics.

Connections:

- Probability theory: large deviations, Gibbs measures, point processes, percolation...
- Analysis: energy minimizers and energy landscape, crystallization, Wulff shapes.
- Combinatorics: cluster expansions related to counting connected graphs; random combinatorial structures.

Also:
Dynamics of phase transitions: nucleation barriers? Metastability? e.g. for Markov processes with prescribed invariant measure.