IX International conference

Stochastic and Analytic methods in Mathematical Physics

Yerevan, Armenia, September 3-8, 2012

Cluster expansion in the canonical ensemble (joint work with E. Pulvirenti, Università di Roma 3).

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1. The model

Configuration $\mathbf{q} \equiv \{q_1, \dots, q_N\}$ of N particles in a box $\Lambda \subset \mathbb{R}^d$ interacting with a pair potential $V : \mathbb{R}^d \to \mathbb{R}$:

$$\text{(stable)} \qquad \sum_{1 \le i < j \le N} V(q_i - q_j) \ge -BN, \qquad \forall N, q_1, ..., q_N$$

$$\text{(tempered)} \qquad C(\beta) := \int_{\mathbb{R}^d} |e^{-\beta V(q)} - 1| dq < \infty, \qquad \forall \beta > 0$$

Hamiltonian:

$$H_\Lambda(\mathbf{q}) := \sum_{1 \le i < j \le N} V(q_i, q_j)$$

Canonical partition function:

$$Z_{\beta,\Lambda,N} := \frac{1}{N!} \int_{\Lambda^N} dq_1 \dots dq_N \, e^{-\beta H_\Lambda(\mathbf{q})}$$

Grand canonical partition function:

$$\Xi_{\beta,\Lambda}(z) := \sum_{N \ge 0} z^N Z_{\beta,\Lambda,N} \qquad z: \text{ activity}$$

2. Thermodynamics

Free energy (for density ρ):

$$f_\beta(\rho) := \lim_{|\Lambda|, N\to\infty,\, N=\lfloor\rho|\Lambda|\rfloor} f_{\beta,\Lambda}(N), \text{ where } f_{\beta,\Lambda}(N) := -\frac{1}{\beta|\Lambda|}\log Z^{per}_{\beta,\Lambda,N}.$$

Compute eqn of state, corrections to ideal gas: Mayer,... 40's.

Working with the grand canonical ensemble:

$$(1) \qquad \beta p_\beta(z) := \lim_{|\Lambda|\to\infty} \frac{1}{|\Lambda|}\log \Xi_{\beta,\Lambda}(z) = \sum_{n\geq 1} b_n z^n$$

$$(2) \qquad \rho(z) := \lim_{|\Lambda|\to\infty} \frac{1}{|\Lambda|} z\frac{\partial}{\partial z}\log \Xi_{\beta,\Lambda}(z) = \sum_{n\geq 1} n b_n z^n$$

Invert (2) and replace $z(\rho)$ in (1):

$$\beta p_\beta(\rho) = \rho\left(1 - \sum_{m\geq 1}\frac{m}{m+1}\beta_m\rho^m\right) \qquad \textit{virial} \text{ expansion}$$

At $\Lambda\to\infty$, p_β and f_β are related via the Legendre transform:

$$f_\beta(\rho) = \sup_z\{\rho\log z - p_\beta(z)\} = \rho\log z(\rho) - p_\beta(z(\rho))$$

3. Why grand canonical?

Using Mayer's idea:

$$e^{-\beta H_\Lambda^{per}(\mathbf{q})} = \prod_{1\le i<j\le N} (1 + e^{-\beta V^{per}(q_i - q_j)} - 1) = \sum_{E\subset\mathcal{E}(N)} \prod_{\{i,j\}\in E} f_{i,j},$$

where

$$\mathcal{E}(N) := \{\{i,j\} : i,j \in \{1,...,N\},\, i \neq j\} \quad \text{and} \quad f_{i,j} := e^{-\beta V^{per}(q_i - q_j)} - 1$$

Defining $w_\Lambda(g) := \int_{\Lambda^{|g|}} \prod_{\{i,j\}\in E(g)} f_{i,j} \prod_{i=1}^{|g|} dq_i$, we obtain the b_n's:

$$\sum_{N\ge 0} \frac{z^N}{N!} \sum_{g\in\mathcal{G}_N} w_\Lambda(g) = \exp\{\sum_{n\ge 1} \frac{z^n}{n!} \sum_{g\in\mathcal{C}_n} w_\Lambda(g)\}$$

with several generalizations.

(Another combinatorial identity gives the β_n's.)

4. Cluster expansion method

Let the space of polymers be $(\Gamma \equiv \{\gamma_1, \ldots\}, \mathbb{G}, \omega \equiv \{\omega(\gamma_1), \ldots\})$ and

$$Z_{\Gamma,\omega} := \sum_{\{\gamma_1,\ldots,\gamma_n\}_\sim} \prod_{i=1}^{n} \omega(\gamma_i) = \exp\left\{ \sum_{I \in \mathcal{I}} c_I \omega^I \right\},$$

where I is a multi-index on Γ and

$$c_I = \frac{1}{I!} \sum_{G \subset \mathcal{G}_I} (-1)^{|E(G)|},$$

or equivalently

$$c_I = \frac{1}{I!} \frac{\partial^{\sum_\gamma I(\gamma)} \log Z_{\Gamma,\omega}}{\partial^{I(\gamma_1)}\omega(\gamma_1) \cdots \partial^{I(\gamma_n)}\omega(\gamma_n)} \Big|_{\omega(\gamma)=0}.$$

Thm: If $\sum_{\gamma \nsim \gamma'} |\omega(\gamma)| e^{a(\gamma)+c(\gamma)} \leq a(\gamma')$, then

$$\sum_{I:\, I(\gamma') \geq 1} |c_I \omega^I| e^{\sum_{\gamma \in \mathrm{supp}\, I} I(\gamma) c(\gamma)} \leq |\omega(\gamma')| e^{a(\gamma')+c(\gamma')}$$

5. Cluster expansion in the canonical ensemble

Let $\Gamma := \{V : V \subset \{1, \ldots, N\}\}$, $\tilde{\zeta}_\Lambda(g) := \int_{\Lambda^{|g|}} \prod_{i \in V(g)} \frac{dq_i}{|\Lambda|} \prod_{\{i,j\} \in E(g)} f_{i,j}$ and $\zeta_\Lambda(V) := \sum_{g \in \mathcal{C}_V} \tilde{\zeta}_\Lambda(g)$. We have:

$$Z_{\beta,\Lambda,N} = \frac{|\Lambda|^N}{N!} \sum_{\substack{\{g_1,\ldots,g_k\}_\sim \\ g_l \text{ connected}}} \prod_{l=1}^{k} \tilde{\zeta}_\Lambda(g_l) = \frac{|\Lambda|^N}{N!} \sum_{\substack{\{V_1,\ldots,V_k\}_\sim \\ |V_l| \geq 2, \forall l}} \prod_{l=1}^{k} \zeta_\Lambda(V_l),$$

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Then:

Thm: $\exists c_0 \equiv c_0(\beta,B) > 0$ independent of N,Λ s.t. if $\rho\, C(\beta) < c_0$:

$$\frac{1}{|\Lambda|}\log Z^{per}_{\beta,\Lambda,N} = \frac{1}{|\Lambda|}\log\frac{|\Lambda|^N}{N!} + \frac{N}{|\Lambda|}\sum_{n\ge 1} F_{\beta,N,\Lambda}(n), \qquad |F_{\beta,N,\Lambda}(n)| \le C e^{-cn}$$

with $N = \lfloor \rho|\Lambda| \rfloor$ and in the thermodynamic limit

$$\lim_{N,|\Lambda|\to\infty,\, N=\lfloor\rho|\Lambda|\rfloor} F_{\beta,N,\Lambda}(n) = \frac{1}{n+1}\beta_n \rho^{n+1},$$

$$\beta_n := \frac{1}{n!} \sum_{\substack{g\in\mathcal{B}_{n+1} \\ V(g)\ni\{1\}}} \int_{(\mathbb{R}^d)^n} \prod_{\{i,j\}\in E(g)} f_{i,j}\, dq_2 \dots dq_{n+1}, \qquad q_1 \equiv 0$$

6. Convergence

A flavor of the first order correction ρ^2:

$$\frac{1}{|\Lambda|}\sum_{V:\,|V|=2}\zeta(V)\sim\frac{1}{|\Lambda|}\binom{N}{2}\frac{1}{|\Lambda|}C_\Lambda(\beta),\quad C_\Lambda(\beta):=\int_\Lambda|e^{-\beta V(q)}-1|dq$$

(recall that: $\zeta_\Lambda(V):=\sum_{g\in\mathcal{C}_V}\int_{\Lambda^{|V|}}\prod_{i\in V}\frac{dq_i}{|\Lambda|}\prod_{\{i,j\}\in E(g)}f_{i,j}$).

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Similar for convergence: $\sum_{V:\ V\ni 1}|\zeta_\Lambda(V)|e^{\alpha|V|}=\sum_{n\geq 2}\sum_{V:|V|=n}|\zeta_\Lambda(V)|e^{\alpha n}\leq$

$$\leq \sum_{n\geq 2}\binom{N-1}{n-1}e^{\alpha n}\int_{\Lambda^n}\prod_{i=1}^{n}\frac{dq_i}{|\Lambda|}e^{2\beta B n}\sum_{T\in\mathcal{T}_n}\prod_{\{i,j\}\in E(T)}|f_{i,j}|$$

$$\leq e^{(2\beta B+\alpha)}\sum_{n\geq 2}\frac{n^{n-2}}{(n-1)!}\left(\frac{N}{|\Lambda|}\right)^{n-1}\left(e^{(2\beta B+\alpha)}C_\Lambda(\beta)\right)^{n-1}$$

7. How to get the 2-connected coefficients

We have (let $A(I) := \cup_{V \in \mathrm{supp}\, I} V$):

$$\frac{1}{|\Lambda|}\sum_I c_I \zeta_\Lambda^I = \frac{N}{|\Lambda|}\sum_{n\geq 1}\frac{1}{n+1}\binom{N-1}{n}\sum_{I:A(I)=\{1,\dots,n+1\}} c_I\zeta_\Lambda^I$$

$$= \frac{N}{|\Lambda|}\sum_{n\geq 1}\frac{1}{n+1}\frac{(N-1)\dots(N-n)}{|\Lambda|^n}\frac{|\Lambda|^n}{n!}\sum_{I:A(I)=\{1,\dots,n+1\}} c_I\zeta_\Lambda^I$$

Two observations:

- Look at the order of volume: $n - \sum_{V \in \mathrm{supp}\, I}(|V|-1)I(V)$
  Hence, since $n+1 \leq \sum_{V \in \mathrm{supp}\, I}(|V|-1)+1$ we have:

$$I(V) = 1, \forall V \in \mathrm{supp}\, I, \text{ and}$$

$$n+1 = \sum_{V \in \mathrm{supp}\, I}(|V|-1)+1.$$

- Exact cancellations for the remaining terms: let $g = b_1 \cup b_2$, where $b_1 \equiv \{1, 2\}$ and $b_2 \equiv \{2, 3\}$ are the 2-conn. components. Note:

$$\sum_{I \sim g} c_I \zeta_\Lambda^I = \tilde{\zeta}_\Lambda(b_1) + \tilde{\zeta}_\Lambda(b_2) + c_1 \tilde{\zeta}_\Lambda(b_1 \cup b_2) + c_2 \tilde{\zeta}_\Lambda(b_1) \tilde{\zeta}_\Lambda(b_2) + \dots$$

Is it $c_1 + c_2 = 0$?

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One can use the combinatorial formula, or check that all mixed terms can only be found in:

$$\log \widehat{Z}(g) := \log(1 + \tilde{\zeta}_\Lambda(b_1) + \tilde{\zeta}_\Lambda(b_2) + \tilde{\zeta}_\Lambda(b_1 \cup b_2))$$

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(putting $= 0$ all other variables). But:

$$\ldots = \log \prod_{i=1,2} (1 + \tilde{\zeta}_\Lambda(b_i))$$

8. Questions

- Direct combinatorial proof?
- Can we get a better radius of convergence?
- Possible candidates for polymers (graphs, 2-connected graphs, trees, set of vertices,...)