Large deviations and distribution of cracks for a chain of atoms at low temperature

Sabine Jansen
LMU Munich

with Wolfgang König, Bernd Schmidt, Florian Theil

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Initial question

For a chain of atoms that is known to crystallize at zero temperature (= periodic energy minimizers), what can you say about its low-temperature behavior?

In particular: what about elongated chains in which the average spacings is forced to be larger than the ground state spacing?

Distribution of (micro-)cracks?

Related: models for fracture in continuum mechanics Braides, Cicalese '07; Scardia, Zanini, Schlömerkemper '11...: Surface energy / Boundary layers in non-convex discrete systems.

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Math appeal (to me)

Link Ruelle's transfer operator for infinite-range interactions $\leftrightarrow$ structure of energy functionals for infinite configurations.

Leads to a **proof of large deviation principle** via **fixed point equation**.

Outline

1. Warm-up: nearest-neighbor chain / renewal process
2. Zero temperature: energy functionals for infinite configurations
3. Large deviation principle as $\beta \to \infty$
4. Transfer operators
5. Gaussian approximation
6. Decay of correlations

Nearest-neighbor chains

Lennard-Jones-like potential $v : \mathbb{R}_+ \to \mathbb{R} \cup \{\infty\}$, minimizer a.

$0 = x_1 < \cdots < x_N$ particles on a line.

$\beta > 0$ inverse temperature, $p > 0$ pressure.

Gibbs measure in constant pressure ensemble:

$$\frac{1}{\text{norm.}} \exp\left(-\beta \Big(\sum_{i=1}^{N-1} v(x_{i+1} - x_i) + p x_N \Big) \right)$$

Spacings $z_i = x_{i+1} - x_i$, $i = 1, \ldots, N-1$ are i.i.d. with average length

$$\ell(\beta, p) = \frac{\int_0^\infty r \exp(-\beta[v(r) + pr])\mathrm{d}r}{\int_0^\infty \exp(-\beta[v(r) + pr])\mathrm{d}r}.$$

Limits:

- First, $N \to \infty$ at fixed β, p.
- Second, $\beta \to \infty$ at fixed ℓ. Pressure $p = p(\beta, \ell)$.

Elongated chain $\ell > a$, $\beta \to \infty$:

$$\frac{\int_0^\infty r \exp(-\beta[v(r) + pr])\mathrm{d}r}{\int_0^\infty \exp(-\beta[v(r) + pr])\mathrm{d}r} = \ell$$

$p(\beta, \ell) \to 0$ exponentially fast.

With high probability, spacing $z_i \approx a$.

With exponentially small probability, $z_i > a + \delta$.

Conditional law : roughly exponential, small parameter $\beta p(\beta, \ell)$.

$$\boxed{\ell = a + \text{prob. of broken bond} \times \frac{1}{\beta p_\beta}.}$$

Chain alternates approximately crystalline domains with broken bonds.

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Beyond nearest neighbor:

- (Free) energy penalty for suboptimal spacing $z_i \gg a$?
- Location of broken bonds independent?
  Effective interactions between defects?
  Related to decay of correlations!

Zero temperature: energy functionals

$m \in \mathbb{N} \cup \{\infty\}$ truncation parameter, $p \geq 0$ pressure.

Gibbs energy

$$\mathcal{E}_N(z_1, \ldots, z_{N-1}) = \sum_{\substack{1 \leq i < j \leq N: \\ |j-i| \leq m}} v\big(z_i + \cdots + z_{j-1}\big) + p \sum_{i=1}^{N-1} z_i.$$

Ground state energy

$$E_N = \inf_{z_1, \ldots, z_{N-1} \geq 0} \mathcal{E}_N(z_1, \ldots, z_{N-1}).$$

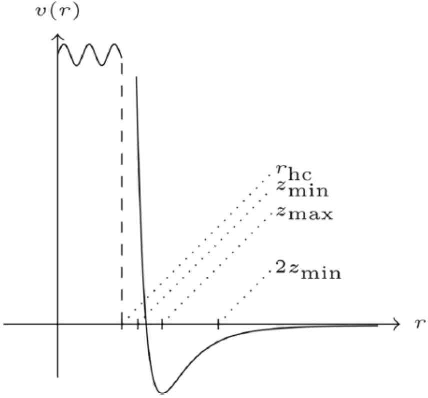
Energy per particle

$$e_0 = \lim_{N \to \infty} \frac{E_N}{N}$$

Surface correction

$$e_{\mathrm{surf}} = \lim_{N \to \infty} (E_N - N e_0) = \lim_{N, M \to \infty} \big(E_N + E_M - E_{N+M}\big)$$

$=$ energy penalty for a broken bond.


$v(r)$
r_{hc}
z_{min}
z_{max}
$2z_{\mathrm{min}}$
r

Theorem

Under suitable assumptions on v, for $p \geq 0$ not too large:

$$e_0 = \sum_{k=m}^{\infty} v(ka) + pa, \quad a = \operatorname{argmin}\Big(\sum_{k=1}^{m} v(kr) + pr \Big)$$

Surface correction

$$e_{\mathrm{surf}} = -pa - \sum_{k=1}^{m} kv(ka) + 2 \min \mathcal{E}_{surf}$$

Energy functional for boundary layers $\sum_{j=1}^{\infty} (z_j - a)^2 < \infty$:

$$\mathcal{E}_{\mathrm{surf}}\big((z_j)_{j\in\mathbb{N}}\big) = \sum_{i=1}^{\infty} \Big(pz_i + \sum_{k=1}^{m} v(z_i + \cdots + z_{i+k-1}) - e_0 \Big).$$

related to Braides, Cicalese '07. Bulk energy for $p = 0$

$$\mathcal{E}_{\mathrm{bulk}}\big((z_j)_{j\in\mathbb{Z}}\big) = \sum_{\substack{i<j: \\ |j-i|\leq m}} \Big(v(z_i + \cdots + z_{j-1}) - v\big((j-i)a\big) \Big)$$

Will reappear as rate functions in LDP as $\beta \to \infty$.

Interaction of particle no. i with everyone to its right:

$$h(z_i, z_{i+1}, \dots) = \sum_{k=1}^{m} v(z_i + \cdots + z_{i+k-1}) + pz_i.$$

Surface energy functional satisfies

$$\boxed{\mathcal{E}_{\mathrm{surf}}(z_1, z_2, \dots) = \big(h(z_1, z_2, \dots) - e_0\big) + \mathcal{E}_{\mathrm{surf}}(z_2, z_3, \dots).}$$

For next-nearest neighbor interactions $m = 2$:

$$\inf \mathcal{E}_{\mathrm{surf}} = \inf\{u(z_1) : z_1 > 0\},$$

function u solves Bellman equation

$$\boxed{u(z_1) = \inf_{z_2 > 0} \Big(h(z_1, z_2) - e_0 + u(z_2)\Big)}$$

Turns out to be related to **eigenfunction equation for transfer operators**.

Low temperature: large deviations

Gibbs measure for N particles / $N-1$ spacings

$$\frac{1}{\text{norm.}} \exp\Big(-\beta \mathcal{E}_N(z_1,\dots,z_{N-1})\Big)$$

Measure on $\mathbb{R}_+^{N-1}$, $N\to\infty$: measure ν_β on $\mathbb{R}_+^{\mathbb{N}}$ = semi-infinite chain.

Measure on $\mathbb{R}_+^{\{-N/2,\dots,N/2-1\}}$, $N\to\infty$: measure μ_β on $\mathbb{R}_+^{\mathbb{Z}}$ = infinite chain.

Extended functionals $\overline{\mathcal{E}}_{\mathrm{bulk}}$, $\overline{\mathcal{E}}_{\mathrm{surf}}$:

$$\overline{\mathcal{E}}_{\mathrm{surf}}\big((z_j)_{j\in\mathbb{N}}\big) = \begin{cases} \mathcal{E}_{\mathrm{surf}}\big((z_j)_{j\in\mathbb{N}}\big), & \sum_j (z_j-a)^2<\infty, \\ \infty, & \text{else.} \end{cases}$$

Limit: $\beta\to\infty$ at fixed $p>0$.

Or: impose $z_j\le R$ before $N\to\infty$, then $p=0$ allowed as well.

Spaces $\mathbb{R}_+^{\mathbb{N}}$, $\mathbb{R}_+^{\mathbb{Z}}$ equipped with product topology.

Theorem

Under suitable assumptions on $v(r)$, $p > 0$ sufficiently small: As $\beta \to \infty$, the measures (μ_β) and (ν_β) satisfy the large deviation principle with speed β and good rate function $\overline{\mathcal{E}}_{\mathrm{bulk}}$ and $\overline{\mathcal{E}}_{\mathrm{surf}} - \inf \mathcal{E}_{\mathrm{surf}}$ respectively.

$A \subset \mathbb{R}_+^{\mathbb{Z}}$, $O \subset \mathbb{R}_+^{\mathbb{Z}}$ closed / open (product topology):

$$\limsup_{\beta\to\infty} \frac{1}{\beta} \log \mu_\beta(A) \leq - \inf_A \overline{\mathcal{E}}_{\mathrm{bulk}}$$

$$\liminf_{\beta\to\infty} \frac{1}{\beta} \log \mu_\beta(O) \geq - \inf_O \overline{\mathcal{E}}_{\mathrm{bulk}}$$

Probability of seeing spacing $z_1 \approx r > a$

$$\mu_\beta\big(\{(z_j) : \ z_1 \approx r\}\big) \approx \exp\Big(-\beta \inf_{\{(z_j):\ z_1 = r\}} \mathcal{E}_{\mathrm{bulk}}((z_j))\Big)$$

Transfer operator for next-nearest neighbor interactions: $m = 2$

$h(z_1, z_2) = pz_1 + v(z_1) + v(z_1, z_2)$.

Gibbs measure for finite N:

$$\boxed{\frac{1}{\text{norm.}} \mathrm{e}^{-\beta h(z_1,z_2)} \mathrm{e}^{-\beta h(z_2,z_3)} \cdots \mathrm{e}^{-\beta h(z_{N-1},z_N)} \times \mathrm{e}^{-\beta (pz_1 + v(z_1))}.}$$

Integral operator

$$(K_\beta f)(z_1) = \int \mathrm{e}^{-\beta h(z_1,z_2)} f(z_2) \mathrm{d}z_2.$$

Principal eigenvalue $\lambda_\beta > 0$, right principal eigenfunction $\varphi_\beta > 0$

$$K_\beta \varphi_\beta = \lambda_\beta \varphi_\beta, \quad \int \varphi_\beta(z) \mathrm{d}z = 1.$$

Measure ν_β for semi-infinite chain is Markov chain with initial law $\varphi_\beta(z_1)\mathrm{d}z_1$ and transition kernel

$$P_\beta(z_1, \mathrm{d}z_2) = \frac{1}{\lambda_\beta \varphi_\beta(z_1)} K_\beta(z_1, z_2) \varphi_\beta(z_2) \mathrm{d}z_2.$$

Measure μ_β for infinite chain: stationary Markov chain.

Ruelle's transfer operator for $m = \infty$

Operator acts on functions $f : \mathbb{R}_+^{\mathbb{N}} \to \mathbb{R}$,

$$(\mathcal{L}_\beta f)(z_2, z_3, \dots) = \int \mathrm{e}^{-\beta h(z_1, z_2, \dots)} f(z_1, z_2, \dots) \mathrm{d}z_1.$$

Dual operator acts on measures

$$\big(\mathcal{L}_\beta^* \nu\big)\big(\mathrm{d}z_1 \mathrm{d}z_2 \cdots\big) = \mathrm{e}^{-\beta h(z_1, z_2 \cdots)} \mathrm{d}z_1 \otimes \nu\big(\mathrm{d}z_2 \mathrm{d}z_3 \cdots\big).$$

Think $\mathcal{L}_\beta = K_\beta^*$, $\mathcal{L}_\beta^* = K_\beta$.

Proposition

There exist $\lambda_0(\beta) > 0$ and a probability measure ν_β on $\mathbb{R}_+^{\mathbb{N}}$ such that

$$\mathcal{L}_\beta^* \nu_\beta = \lambda_0(\beta) \nu_\beta.$$

The pair $(\lambda_0(\beta), \nu_\beta)$ is uniquely defined and ν_β is the surface Gibbs measure.

Proof: Uniqueness of infinite-volume Gibbs measures + arguments from Ruelle '68.
See also Ruelle '78 book Thermodynamic formalism and Gallavotti, Miracle-Solé '70.

From transfer operator to LDP

Preliminary lemma: $\lambda_0(\beta) = \exp(-\beta[e_0 + o(1)])$.

1. Exponential tightness $\Rightarrow$ LDP along subsequences $(\beta_j)_{j\in\mathbb{N}}$ de Acosta '97.

2. Varadhan's lemma & fixed point equation

$$\nu_\beta(\mathrm{d}z_1\,\mathrm{d}z_2\cdots) = \frac{1}{\lambda_0(\beta)} \mathrm{e}^{-\beta h(z_1,z_2,\dots)} \mathrm{d}z_1 \otimes \nu_\beta(\mathrm{d}z_2\,\mathrm{d}z_3\cdots)$$

$\Rightarrow$ rate function I along subsequence (β_j) satisfies

$$I(z_1,z_2,\dots) = -e_0 + h(z_1,z_2,\dots) + I(z_2,z_3,\dots).$$

3. Unique solution is $I = \overline{\mathcal{E}}_{\mathrm{surf}}$!
$\Rightarrow$ Rate function does not depend on choice of subsequence (β_j).

Full LDP with rate function $\overline{\mathcal{E}}_{\mathrm{surf}}$ follows.

Low temperature: Gaussian approximation

$\mathcal{E}_{\mathrm{bulk}}$ has unique minimizer $z_j \equiv a$.

Hessian $\mathcal{H}_{ij} = \partial_{z_i}\partial_{z_j}\mathcal{E}_{\mathsf{bulk}}(\boldsymbol{a})$ positive definite.

μ^{Gauss} = Gaussian measure on $\mathbb{R}^{\mathbb{Z}}$ with covariance $\langle z_i z_j\rangle_{\mathrm{Gauss}} = (\mathcal{H}^{-1})_{ij}$.

Theorem

For $m < \infty$ (only finitely many neighbors interact):
Convergence of probability density functions of n-dimensional marginals

$$\lim_{\beta\to\infty} \int_{\mathbb{R}^n} \left|\beta^{-n/2}\rho_n^{(\beta)}(\boldsymbol{a} + \beta^{-1/2}\boldsymbol{s}) - \rho_n^{\mathrm{Gauss}}(\boldsymbol{s})\right| \mathrm{d}\boldsymbol{s} = 0.$$

Proof: Perturbation theory for β-dependent transfer operators.
Similar to semiclassical analysis. Needs good version of transfer operator for $m \geq 3$—usual symmetrized version does not work. Transfer operator no longer self-adjoint for $m \geq 3$.

Decay of correlations: first bounds

Non-uniform bounds valid under weak conditions on pair potential.

Exponent $s > 2$: $v(r) \sim -\mathrm{const}/r^s$, $v''(r) \sim -\mathrm{const}/r^{s-2}$ as $r \to \infty$.

Notation: $f_0 = f(z_0)$, $g_n = g(z_n)$.

Theorem

$m = \infty$: There exist $c, C > 0$ such that for all $\beta, p > 0$, as $n \to \infty$

$$\left|\mu_\beta(f_0 g_n) - \mu_\beta(f)\mu_\beta(g)\right| \leq (1 + O(1)) \frac{C\beta \exp(c\beta)}{n^{(s-2)(1-\varepsilon)}} \, ||f||_\infty \, ||g||_\infty$$

m finite: exponential decay

$$(1 - \mathrm{e}^{-c\beta})^n \, ||f||_\infty \, ||g||_\infty$$

Proof: Adapt Pollicott's method of conditional expectations.

Pollicott *Rates of mixing for potentials of summable variation*. Trans. Am. Math. Soc., 2000.

Decay of correlations: restricted Gibbs measure

Energy uniformly convex on $[z_{\min}, z_{\max}]^{N-1}$.

Restrict spacings to $z_j \in [z_{\min}, z_{\max}]$ before $N \to \infty$.

$\Rightarrow$ restricted bulk measure $\tilde{\mu}_\beta$.

Proposition

$m = \infty$: There exists $c, C > 0$ such that for all $\beta, p > 0$, all smooth $f, g : \mathbb{R}_+ \to \mathbb{R}$,

$$\left|\tilde{\mu}_\beta(f_i g_j) - \tilde{\mu}_\beta(f_i)\tilde{\mu}_\beta(g_j)\right| \leq \frac{c}{\beta |i-j|^s} \tilde{\mu}_\beta(|f'|^2)\tilde{\mu}_\beta(|g'|^2).$$

m finite: uniform exponential decay $\exp(-\gamma|i-j|)$, γ independent of β.

Decay of correlations similar to Gaussian measure with covariance matrix $(\beta\, \mathrm{D}^2 \mathcal{E}_{\text{bulk}})^{-1}$.

Proof: Adapt Menz '14. Techniques from the realm of Poincaré inequalities, log-Sobolev inequalities... Builds on integration by parts and Helffer-Sjöstrand formula for covariances.

Uniform decay of correlations: full measure

. . . but only $m < \infty$.

Theorem

$m < \infty$, $p > 0$ small. There exists $\gamma > 0$ such that for all sufficiently large β, suitable $C(\beta)$, all $n \in \mathbb{N}$, all $f, g : \mathbb{R}_+ \to \mathbb{R}$,

$$\left|\mu_\beta(f_0 g_n) - \mu_\beta(f_0)\mu_\beta(g_n)\right| \leq C(\beta)\mathrm{e}^{-\gamma n}||f||_\infty ||g||_\infty.$$

For $m = 2$: $C(\beta) = 1$.

Proof: Gaussian approximation and perturbation theory for transfer operators.

Conclusion

Structure of energy functionals at zero temperature fits nicely with transfer operator formalism from statistical mechanics.

Proof of LDP via eigenmeasure of transfer operator $\mathcal{L}_\beta^* \nu_\beta = \lambda_0(\beta)\nu_\beta$.

Several bounds on decay of correlations, some of them uniform in β.

Missing: Uniform algebraic decay for $m = \infty$?

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