Limitations of statistical mechanics:
Hints from large deviation theory

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Limits, limitations and boundaries

Experimental limits - incompleteness
- Relativistic phenomena not described by Newtonian mechanics
- Photoelectric effect not explained by classical EM theory

Theoretical limitations
- QM does not describe nonlinear evolutions (if any)
- Classical EM theory does not explain particle-like phenomena

Conditions of validity / boundaries
- Thermodynamics apply to large systems
- QM applies when action $\sim \hbar$
Questions and approach

Questions

1. Are there any phenomena not explained by statistical mechanics? (Boltzmann-Gibbs equilibrium statistical mechanics = ESM)
2. What are the conditions of validity of ESM?
3. What are the boundaries of ESM?

Approach

- ESM = Large deviation theory (LDT)
- Study known boundaries of LDT
- Derive boundaries of ESM

Plan

- Recap on LDT / Limits of LDT
- ESM = LDT / Limits of ESM
- Conclusions

Large deviation theory


- Random variable: $A_n$
- Probability distribution: $P(A_n = a)$

Large deviation principle (LDP)

$$P(A_n = a) \approx e^{-nI(a)}, \quad n \to \infty$$

- Meaning of $\approx$:
  $$\lim_{n \to \infty} -\frac{1}{n} \ln P(a) = I(a)$$
- Rate function: $I(a) \geq 0$

Goals of large deviation theory

- Prove that a large deviation principle exists
- Calculate the rate function
Two important results

- Scaled cumulant generating function (SCGF):
  \[
  \lambda(k) = \lim_{n \to \infty} \frac{1}{n} \ln \langle e^{nkA_n} \rangle, \quad k \in \mathbb{R}
  \]

Varadhan (1966)
If \( A_n \) satisfies an LDP with rate function \( I(a) \), then
\[
\lambda(k) = \max_a \{ ka - I(a) \}
\]

- \( \lambda = I^* \)
- \( \lambda(k) \) always convex

If \( \lambda(k) \) is differentiable, then
1. \( P(A_n = a) \approx e^{-nI(a)} \)
2. \( I(a) = \max_k \{ ka - \lambda(k) \} \)

- \( I = \lambda^* \)
- \( I(a) \) is convex in this case
- Not applicable when \( I \) is nonconvex

Applications

- Sum of random variables
  - Cramér 1938
- Product of random variables
- Markov processes
  - Donsker & Varadhan
- Stochastic differential equations
  - Freidlin & Wentzell 1970s
- Stochastic field equations
- ...
Example: Exponential random variables

\[ S_n = \frac{1}{n} \sum_{i=1}^{n} X_i, \quad p(X_i = x) = \frac{1}{\mu} e^{-x/\mu}, \quad x > 0, \quad \text{IID} \]

- SCGF:
  \[ \lambda(k) = -\ln(1 - \mu k), \quad k < \frac{1}{\mu} \]

- Rate function:
  \[ I(s) = \frac{s}{\mu} - 1 - \ln \left( \frac{s}{\mu} \right), \quad s > 0 \]

- Concentration point: \( s^* = \langle X \rangle = \mu \)
- Gaussian fluctuations around \( s^* \)
- Non-Gaussian fluctuations away from \( s^* \)

General properties

- Law of Large Numbers
  - Typical points = concentration points = zeros of \( I(a) \)
- Central Limit Theorem
  - Quadratic minima = Gaussian fluctuations
  - Small deviations
- Large deviations
  - Fluctuations away from typical points

General theory of typical states and fluctuations
Boundaries of LDT

- LDP:
  \[ P(A_n = a) \approx e^{-nI(a)} \]

- SCGF:
  \[ \lambda(k) = \sup_a \{ ka - I(a) \} \]

- Rate function:
  \[ I(a) = \sup_k \{ ka - \lambda(k) \} \]

Boundary cases

- no LDP
- \( I = 0 \) or \( \infty \)
- \( \lambda \) not differentiable (smoothness problem)
- \( \lambda \) does not exist (existence problem)

Smoothness problem: Nonconvex rate functions


- \( \lambda(k) \) always convex
- \( I(a) \) not necessarily convex

### Convex

\[ \lambda = I^* \text{ and } I = \lambda^* \]

### Nonconvex

\[ \lambda = I^* \text{ but } I \neq \lambda^* \]

- \( \lambda \) differentiable \( \Rightarrow I = \lambda^* \)
- \( \lambda \) nondifferentiable \( \Rightarrow I \) is nonconvex or affine

Legendre structure only if \( I \) is convex
Existence problem: Non-exponential LDs

Existence of \( \lambda(k) \) \iff \text{Existence of LDP}

Sub-exponential

\[
\lambda = \infty \quad \text{if} \quad P(A_n) \sim n^{-\alpha} \\
l = 0
\]

Super-exponential

\[
\lambda = 0 \quad \text{if} \quad P(A_n) \sim e^{-e^n} \\
l = \infty
\]

Example: Cauchy sample mean

\[
S_n = \frac{1}{n} \sum_{i=1}^{n} X_i, \quad p(X_i = x) = \frac{1}{\pi} \frac{1}{x^2 + 1}, \quad x \in \mathbb{R}
\]

- SCGF: \( \lambda(k) = \begin{cases} 0 & k = 0 \\ \infty & k \neq 0 \end{cases} \)

No LDP – LDT does not apply

Applications in statistical physics


- Equilibrium statistical mechanics
  - Lanford (1973)
  - Ruelle (1960s)
  - Ellis (1984)
- Noise-perturbed dynamical systems, SDEs
  - Freidlin & Wentzell (1970s)
  - Onsager-Machlup (1953)
  - Graham (1980s)
- Nonequilibrium systems
  - Derrida, Bodineau (1990s-2000s)
  - Bertini, Gabrielli, Jona-Lasinio (2000s)
  - ...

LDT is the mathematical language of statistical mechanics
Entropy and free energy

- Microstate: $\omega = \omega_1, \omega_2, \ldots, \omega_N$
- Energy: $U_N(\omega)$
- Density of states: $\Omega(U_N = u)$
- LDP: $\Omega(U_N = u) \approx e^{Ns(u)}$

Gärtner-Ellis Theorem

$$s(u) = \min_\beta \{ \beta u - \varphi(\beta) \}$$

- Free energy:
  $$\varphi(\beta) = \lim_{N \to \infty} -\frac{1}{N} \ln \Omega(u_N, \beta), \quad \Omega(u_N, \beta) = \int e^{-\beta U_N(\omega)} d\omega$$

- $\Omega(u_N, \beta)$ = partition function = generating function
- $\varphi(\beta)$ = free energy = SCGF
- $s(u)$ = entropy = rate function
- Basis of Legendre transform in thermo

Boundaries of ESM

- LDT:
  $$P_n(a) \approx e^{-nI(a)}$$
  - LDP
  - No LDP

- Exponential
  - Non-exponential

- ESM:
  $$\Omega_N(u) \approx e^{Ns(u)}$$
  - Exponential
  - Non-exponential
Nonconcave entropies


- Concave entropy
  \[ \varphi = s^* \]
  \[ s = \varphi^* \]

- Nonconcave entropy
  \[ \varphi = s^* \]
  \[ s \neq \varphi^* \]

- Long-range systems (mean-field, gravitation, etc.)
- Generalized canonical ensemble recovers equivalence [HT PRE 2009]

No Legendre transform for nonconcave entropy systems

Non-exponential density of states

Accepted idea

Free energy does not exist \( \Rightarrow \) no ESM

- True for canonical ensemble
- Not true for microcanonical ensemble

Sub-exponential

\[ \varphi = \infty \text{ if } \Omega_N(u) \sim N^\alpha \]
\[ s = 0 \]

Super-exponential?

Use probabilities

- Are there systems with non-exponential density of states?
- Described by microcanonical ensemble
- Possible generalization of canonical ensemble?
Conclusions

Statistical mechanics ⇔ Large deviation theory

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<tr>
<td>ESM based on LDP</td>
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<td>$\Omega_N(u)$ and $Z_N(\beta)$ exponential in $N = \text{LDP}$</td>
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<td>Entropy $s(u) = \text{rate function}$</td>
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<td>Free energy $\varphi(\beta) = \text{SCGF}$</td>
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<td>Legendre transform $\leftarrow \text{Gärtner-Ellis Theorem}$</td>
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Limitations

1. $s(u)$ may be nonconcave
2. $\varphi(\beta)$ may not exist
   - $\Omega_N(u)$ not exponential
   - Physically possible / observable?
   - Systems with: long-range interaction / correlation / order