Limitations of statistical mechanics: Hints from large deviation theory

Hugo Touchette

School of Mathematical Sciences
Queen Mary, University of London

3rd International Conference on Statistical Physics
Larnaca, Cyprus, July 2011

Supported by the European Physical Society

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

Ellis (1985), Touchette Phys Rep 178 (2009)

- 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

1. Prove that a large deviation principle exists
2. Calculate the rate function

Two important results

- Scaled cumulant generating function (SCGF):

$$\lambda(k) = \lim_{n\to\infty} \frac{1}{n} \ln\langle e^{nkA_n}\rangle, \qquad k \in \mathbb{R}$$

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

Gärtner (1977), Ellis (1984)

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

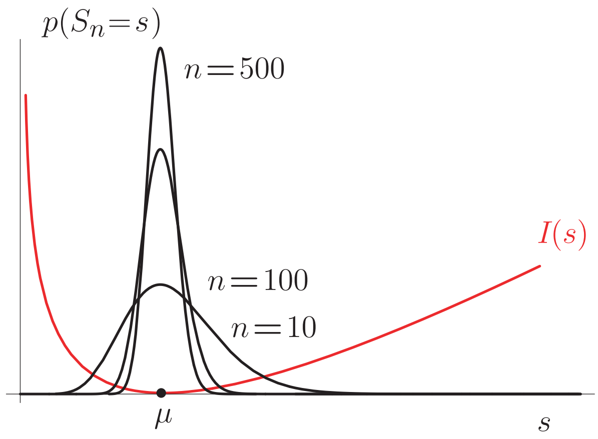
$$S_n = \frac{1}{n}\sum_{i=1}^{n} X_i, \qquad p(X_i = x) = \frac{1}{\mu}e^{-x/\mu}, \quad x > 0, \quad \text{IID}$$

- SCGF:

$$\lambda(k) = -\ln(1-\mu k), \qquad k < \frac{1}{\mu}$$

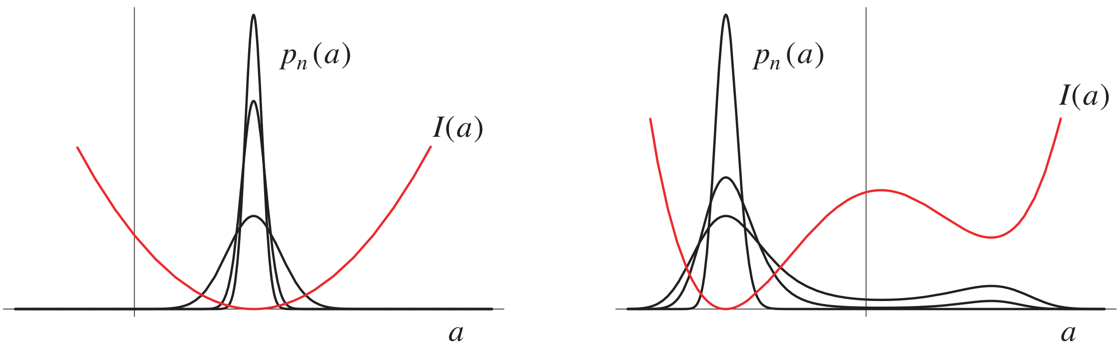
- Rate function:

$$I(s) = \frac{s}{\mu} - 1 - \ln\frac{s}{\mu}, \qquad s > 0$$



- 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:

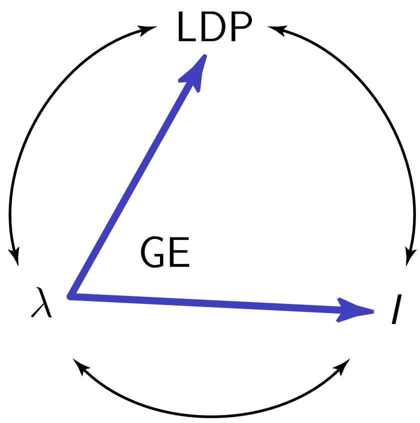
$$P(A_n = a) \approx e^{-nI(a)}$$

- SCGF:

$$\lambda(k) = \sup_a \{ka - I(a)\}$$

- Rate function:

$$I(a) = \sup_k \{ka - \lambda(k)\}$$



Boundary cases

- no LDP
- $I = 0$ or ∞
- λ not differentiable (smoothness problem)
- λ does not exist (existence problem)

Smoothness problem: Nonconvex rate functions

Dinwoodie (1993), Ellis (1995)

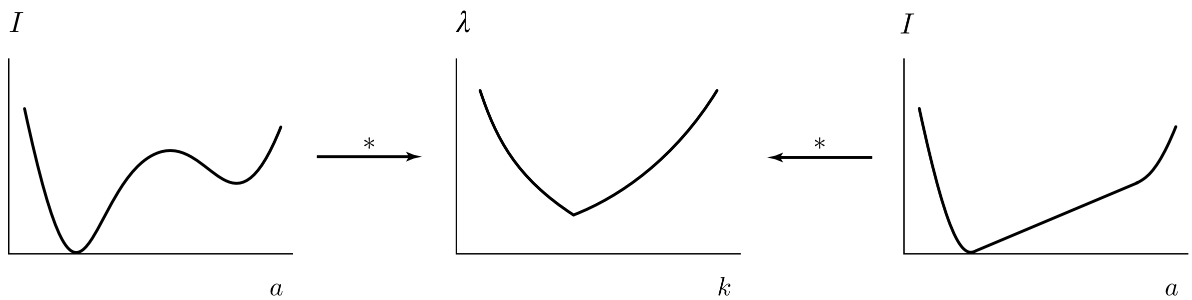
- $\lambda(k)$ always convex
- $I(a)$ not necessarily convex

Convex

$$\lambda = I^* \quad \text{and} \quad I = \lambda^*$$

Nonconvex

$$\lambda = I^* \quad \text{but} \quad I \neq \lambda^*$$



- λ differentiable $\Rightarrow I = \lambda^*$
- λ nondifferentiable $\Rightarrow I$ is nonconvex or affine

Legendre structure only if I is convex

Existence problem: Non-exponential LDs

Existence of $\lambda(k)$ $\Longleftrightarrow$ Existence of LDP

Sub-exponential

$$\lambda = \infty \quad \text{if } P(A_n) \sim n^{-\alpha}$$
$$I = 0$$

Super-exponential

$$\lambda = 0 \quad \text{if } P(A_n) \sim e^{-e^n}$$
$$I = \infty$$

Example: Cauchy sample mean

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

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

No LDP – LDT does not apply

Applications in statistical physics

Oono Prog Theoret Phys Suppl (1989), HT Phys Rep (2009)

- Equilibrium statistical mechanics
  - Lanford (1973)
  - Ruelle (1960s)
  - Ellis (1984)
- Noise-perturbed dynamical systems, SDEs
  - Freidlin & Wentzell (1970s)
  - Onsager-Machlup (1953)
  - Graham (1980s)
- Nonequilibrium systems
  - Gallavotti & Cohen (1995)
  - 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:

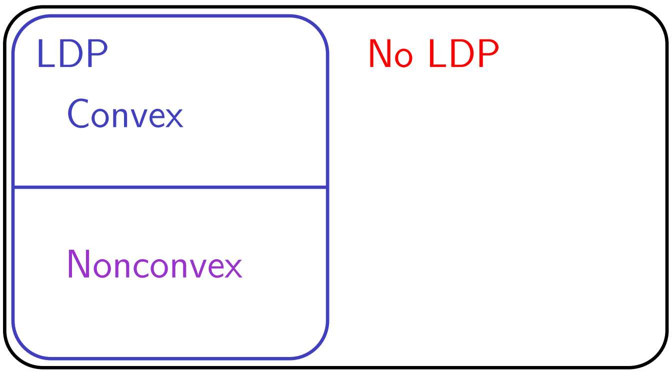
$$\varphi(\beta) = \lim_{N\to\infty} -\frac{1}{N} \ln Z_N(\beta), \qquad Z_N(\beta) = \int e^{-\beta U_N(\omega)} d\omega$$

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

Boundaries of ESM

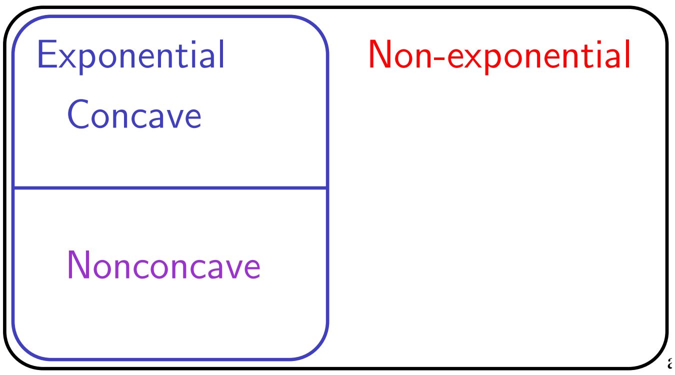
- LDT:

$$P_n(a) \stackrel{?}{\approx} e^{-nI(a)}$$



- ESM:

$$\Omega_N(u) \stackrel{?}{\approx} e^{Ns(u)}$$

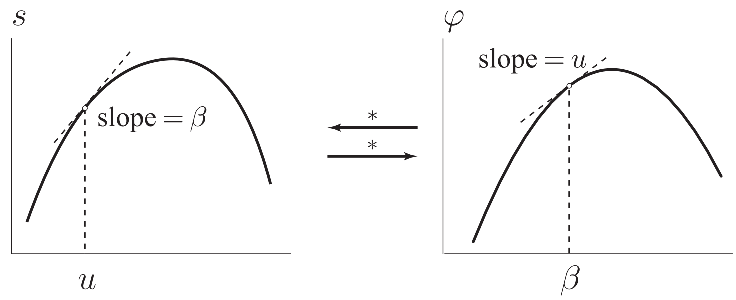


Nonconcave entropies

Campa, Dauxois & Ruffo Phys Rep (2009); HT Phys Rep (2009)

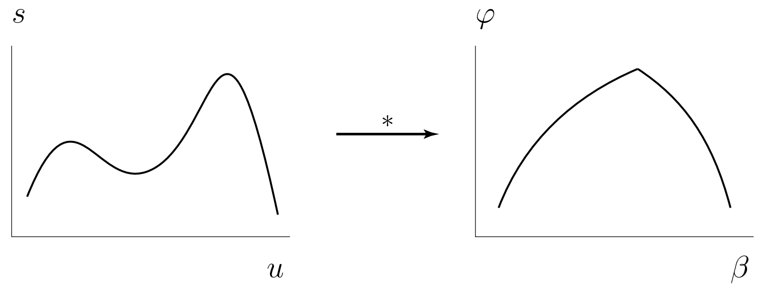
- Concave entropy

$$\varphi = s^*$$
$$s = \varphi^*$$



- 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

Existence of $\varphi(\beta)$ $\iff$ $\Omega_N(u)$ exponential

Sub-exponential

$\varphi = \infty$ 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 $\Leftrightarrow$ Large deviation theory

ESM

- ESM based on LDP
- $\Omega_N(u)$ and $Z_N(\beta)$ exponential in N = LDP
- Entropy $s(u)$ = rate function
- Free energy $\varphi(\beta)$ = SCGF
- Legendre transform $\Leftarrow$ Gärtner-Ellis Theorem

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