Infinite Ergodic Theory meets Boltzmann-Gibbs statistics

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Bad Wildbad
• Non-normalized Boltzmann-Gibbs states.
• Ensemble and time averages.
• Thermodynamics relations virial theorem.

Infinite ergodic theory formulated by: Aaronson, Thaler, Zweimüller,...

Non-normalises states are found in an increasing number of physical works: Fermi... (Hydrogen atom paradox) Bouchaud (trap model) Klages, Kantz, Korabel, Akimoto (non-linear dynamics) Kessler, Lutz, Aghion (cold atoms) Rebenshtok, Denisov, Hänggi, Fouxon, Radons (Lévy walks, Lorentz gas) Leibovich, Deng (multiplicative noise), Farago (periodic potentials), Ryabov (unstable fields), Burioni, Vezzani, Wang (Big Jump).

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Normalizable and non-Normalizable fields

\[ x^3 \]

\[ \log(x) \]

\[ -x^2 \]
BG for non-binding potential $Z = \infty$
Entropy extremum principle

\[ S[P(x, t)] = -k_B \int_0^\infty P(x, t) \ln P(x, t) \, dx - \]
\[ \beta k_B \left( \int_0^\infty V(x) P(x, t) \, dx - \langle V \rangle \right) - \lambda k_B \left( \int_0^\infty P(x, t) \, dx - 1 \right) \]
\[ -\zeta k_B \left( \int_0^\infty x^2 P(x, t) \, dx - 2Dt \right). \]

- Equal probability.
- Averaged energy fixed, Canonical like ensemble.
- Normal diffusion.

\[ P(x, t) = \frac{\exp \left[ -V(x)/k_BT - x^2/(4Dt) \right]}{Z_t}. \]

\[ \lim_{t \to \infty} Z_t P(x, t) = \exp \left( -\frac{V(x)}{k_BT} \right). \]
The Langevin equation with fluctuation dissipation $D = k_B T / \gamma$

\[
\dot{x}(t) = -\frac{V'(x)}{\gamma} + \sqrt{2D \Gamma(t)}.
\]

The Fokker-Planck equation

\[
\frac{\partial P_t(x)}{\partial t} = D \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial x} \frac{V'(x)}{k_B T} \right] P_t(x).
\]

In illustration we will consider the Lennard Jones potential $V_{LJ}(x)$. 
Towards a non normalized state

- Let us consider fixed point solutions \( \frac{\partial P_t(x)}{\partial t} = 0 \).

- A mathematical solution of the Fokker-Planck equation

\[
P_{fp}(x) = \text{Const} \exp[-V(x)/k_BT]
\]

- If the potential is normalising then this is a Boltzmann state. If not trash the non-normalised solution?
We consider the Fokker-Planck equation for asymptotically flat potential $V(\infty) = 0$. e.g. the LJ potential.

The force field is non binding, the density close to the minimum of the potential decays in time.

At long times and finite $x << \sqrt{2Dt}$

$$P_t(x) \propto t^{-\alpha} \exp[-V(x)/k_B T]$$

Since $V(x)$ is small for $x >> 1$

$$P_t(x) \simeq t^{-1/2} \exp(-x^2/4Dt)/\sqrt{\pi D}.$$  

Ahhh...  $\alpha = 1/2$, normal diffusion.

The uniform solution, found by matching or by eigenfunction expansion

$$P_t(x) \simeq \frac{1}{\sqrt{\pi D t}} \exp \left[ -V(x)/k_B T - x^2/(4Dt) \right]$$
From normalized density to non-normalized BG state

- In the long time limit \( \lim_{t \to \infty} \exp(-x^2/4Dt) = 1 \).
- For asymptotically flat potentials
  \[
  \lim_{t \to \infty} Z_t P_t(x) = \exp[-V(x)/k_B T]
  \]
  where \( Z_t = \sqrt{\pi Dt} \).
- This solution is independent of the initial state.
- All force fields in nature decay at large distances, so asymptotically flat potentials are common.
Ensemble averages

- The ensemble average, by definition
  \[ \langle \mathcal{O}(x) \rangle_t = \int_0^\infty \mathcal{O}(x) P_t(x) \, dx. \]

- In the long time limit,
  \[ \langle \mathcal{O}(x) \rangle_t \sim \frac{1}{Z_t} \int_0^\infty \mathcal{O}(x) e^{-V(x)/k_BT} \, dx. \]

- Averages are obtained with respect to the Boltzmann factor.

- Provided that the integral is finite. And then \( \mathcal{O} \) is called integrable.

- Integrable observables are common, for example: the occupation fraction, energy, and the virial theorem.
Simulation in LJ potential

Non-normalizable Boltzmann-Gibbs state

\[ \exp\left(-V_{LJ}(x)/k_B T\right) \]
Mean of the time average is obtained with the non-normalized state

\[ \langle \mathcal{O}[x(t)] \rangle \sim \frac{1}{t} \int_0^t \langle \mathcal{O}(x) \rangle_{t'} dt' = 2 \langle \mathcal{O}(x) \rangle \]

A doubling effect is found from a time integration of \( 1/Z_t \sim t^{-1/2} \).

More generally \( \langle \mathcal{O} \rangle / \langle \mathcal{O} \rangle = 1/\alpha \), where \( 0 < \alpha < 1 \).

More on \( \alpha \) soon.
Ratio between time and ensemble average is $\frac{\langle E_p \rangle}{\langle E_p \rangle} = 2$

Infinite-ergodic theory

\[ \langle E_p \rangle / \langle E_p \rangle = 2 \]

$\times 10^5$
Distribution of time average

- Time averages remain random even in the long time limit.
- Let $\xi = \overline{O} / \langle \overline{O} \rangle$.
- For example consider the indicator $\theta(\chi_a < x(t) < \chi_b) = 1$ if condition holds, otherwise zero.
- The sequence $1, 0, 1, 0, \ldots$ with $\tau_{in}, \tau_{out}, \tau_{in}, \ldots$

\[
\text{PDF}(\tau_{out}) \propto (\tau_{out})^{-(1+\alpha)}
\]

- $\alpha$ is the first return exponent.
- Mean return time diverges.
- The process is recurrent.
- $\alpha = 1/2$ for asymptotically flat potentials in dimension one.
Aaronson-Darling-Kac in a thermal setting

Then $\xi = \overline{O}/\langle O \rangle = n/\langle n \rangle$.

Number of returns/renewals yield the fluctuations of $\overline{O}$.

Lévy statistics describes the distribution of time averages.

The magic: this holds true for any integrable observable.

$$\text{PDF}(\xi) = \frac{\Gamma^{1/\alpha (1+\alpha)}}{\alpha \xi^{1+1/\alpha}} L_{\alpha} \left[ \frac{\Gamma^{1/\alpha (1+\alpha)}}{\alpha \xi^{1/\alpha}} \right]$$

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The energy resembles a renewal process!
Virial Theorem

- The machinery of stat. mech. can be extended to infinite ergodic theory.
- The virial theorem:
  \[ \lim_{t \to \infty} \mathcal{Z}_t \langle x F(x) \rangle = l_0 k_B T. \]
- \( l_0 \) is the second virial coefficient

\[ l_0 = \int_0^\infty \left\{ 1 - \exp\left[-V(x)/k_B T \right] \right\} \, dx. \]

- To see this:

\[ \langle x F(x) \rangle = \frac{k_B T \int_0^\infty x \partial_x [\exp(-V(x)/k_B T) - 1] \, dx}{\mathcal{Z}_t}. \]
The importance of the virial

\[
P(x, t) = \frac{e^{-x^2/4Dt}}{\sqrt{\pi Dt}} \left[ 1 - \frac{l_0 x}{2Dt} + \cdots \right].
\]

for large \(x\).
Virial Theorem

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Eigen function expansion, $U(x) = V(x)/k_B T$

- Eigen function expansion

$$P_t(x) = e^{-U(x)/2+U(x_0)/2} \sum N_k^2 \Psi_k(x_0) \Psi_k(x)e^{-Dk^2t}.$$  

- The Schrödinger like equation

$$\hat{H}\Psi(x) = Dk^2\Psi(x)$$

- The energy spectrum, is $k^2$, as for a free particle. $k = 0$ ground state.

- Explicitly

$$-\frac{\partial^2}{\partial x^2}\Psi_k(x) + \left[ U'(x)^2 \frac{1}{4} - U''(x) \frac{1}{2} \right] \Psi_k(x) = k^2 \Psi_k(x).$$

- Standard: Ground state is $\exp[-U(x)/2]$. It is not normalized.

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• In that sense the infinite density is the ground states of the system.

• Here all the states $k$ are non-normalizable (basic QM).

• Small $k$ corrections

\[ \Psi_k(x) \simeq e^{-U(x)/2} \left[ \cos(kx)(1 - k^2 g(x)) - kl_0 \sin(kx) \right]. \]
- For $x \approx 1$

$$P(x, t) = \frac{\exp [-U(x)]}{\sqrt{\pi Dt}} \left[ 1 - \frac{h(x, x_0)}{t} \ldots \right]$$

- Small $k$ large $t$ so $\int_0^\infty dk \exp(-k^2t) \sim 1/t^{1/2}$.

- The correction are non-universal: they depend on $x_0$.

- For $x \gg 1$

$$P(x, t) = \frac{e^{-x^2/4Dt}}{\sqrt{\pi Dt}} \left[ 1 - \frac{l_0x}{2Dt} + \cdots \right].$$

- Corrections are universal.

- Leading term $\int_0^\infty e^{-k^2t} \cos(kx) \propto \exp(-x^2/4t)$. 

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Aghion, Kessler, Barkai PRL (2019).

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Summary

Stochastic thermodynamics of single particle trajectories in the presence of asymptotically flat (or log) potential fields, uses non-normalised Boltzmann-Gibbs statistics. Both time and ensemble averages of integrable observables are calculated using the non-normalised Boltzmann state. If the process is recurrent, with an infinite mean return time, standard ergodic theories obviously fail, however the resampling of the phase space implies that we may still construct a stat. mech. framework which is independent of the initial condition. Lévy statistics describes the fluctuations of the time averages (ADK theorem). An extremum principle yields a new ensemble, where the Gaussian central limit describes the dynamics for $x >> 1$. This leads to non-equilibrium thermodynamic relations, e.g. between entropy and energy, the virial theorem etc.

Thermodynamic relation: \( S(t) = k_B \ln(Z_t) + E_p/T + k_B \zeta \langle x^2 \rangle \)

Entropy-energy relation:

\[
S(t) = k_B \ln (\pi D t)/2 + \langle E_p \rangle/T + k_B \langle x^2 \rangle /4Dt.
\]

\[\frac{\partial S}{\partial E_p} \bigg|_t = \frac{1}{T} \] so fixed volume is replaced with \( t \)
Particle immersed in a bath with temperature $T$. Force field vanishes for large $x$. 

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• $V(x) = 0.5 \ln(1 + x^2)$, $P_{BG}(x) = (1 + x^2)^{-1/2T}/Z$ for $T < 1$.

• The normal BG phase Kessler Barkai PRL 2010.

• Transition point $T = 1$. 

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Transition from BG to NNBG

First return calculation

$$V(x) = \left(\frac{1}{2}\right) \log(1 + x^2)$$

- When $\alpha < 1$: i) mean return time ii) $Z$ and iii) $S_{BG}$, blow up.
Ratio between time and ensemble averages is $1/\alpha$

- Infinite-ergodic theory $\Rightarrow \langle \mathcal{O}[x(t)] \rangle / \langle \mathcal{O}(x) \rangle_t \to 1/\alpha$
Higher dimensions?

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Normalized BG in log potential

\[ P(x) \]

\[ BG \]

\[ ICD \]

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Trajectory

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Distribution of generalized Lyapunov Exp.

\[ \zeta = \frac{\lambda_\alpha}{\langle \lambda_\alpha \rangle}. \]

Renewal Theory: distribution of \( \lambda_\alpha \) is Mittag-Leffler.

Aaronson-Darling-Kac Theorem.


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Consider an inverted harmonic potential field $V(x) = -x^2/2$.

Also here fixed point solution is non-normalized.

However

$$P(x, t) = \sqrt{\frac{1}{2\pi(1-e^{-2t})}} \exp \left[ -\frac{(xe^{-t}-x_0)^2}{2(1-e^{-2t})} \right] e^{-t}$$

So

$$\lim_{t \to \infty} \sqrt{2\pi} \exp(t) P(x, t) = \exp \left[ -(x_0)^2/2 \right].$$

Here initial conditions remain for ever.

No Boltzmann Gibbs state.