Thermodynamics of finite systems via molecular dynamics in generalized ensembles

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Outline of the Talk

- Motivation: thermodynamics of finite, classical systems
- A microcanonical system with constant heat capacity
- The superstatistical approximation
- System subject to total energy oscillations
- Concluding remarks

Thermodynamics of finite, classical systems

Finite (“small”) systems, even with short-range interactions, can manifest **non-canonical** statistics if:

- The system is isolated (microcanonical ensemble)
- The system is in contact with a finite reservoir

This means, for finite number of particles N

$$P(\boldsymbol{\Gamma}|S) \neq \frac{\exp\big(-\beta\mathcal{H}(\boldsymbol{\Gamma})\big)}{Z(\beta)} \tag{1}$$

but it converges to the canonical ensemble in the thermodynamic limit.

What is the appropriate framework to deal with non-canonical ensembles?

Superstatistics (C. Beck, E. G. D. Cohen, 2003)

In superstatistics, the inverse temperature $\beta := 1/(k_B T)$ is promoted from a constant to an unknown ("random") quantity with joint probability density

$$P(\mathbf{\Gamma}, \beta|S) = P(\mathbf{\Gamma}|\beta, S)P(\beta|S) = P(\beta|S)\left[\frac{\exp\big(-\beta\mathcal{H}(\mathbf{\Gamma})\big)}{Z(\beta)}\right]. \tag{2}$$

The probability (density) of observing a microstate $\mathbf{\Gamma}$ is given by the marginalization rule as

$$P(\mathbf{\Gamma}|S) = \int_0^\infty d\beta P(\beta|S)\left[\frac{\exp\big(-\beta\mathcal{H}(\mathbf{\Gamma})\big)}{Z(\beta)}\right]. \tag{3}$$

Superstatistical ensembles are then superpositions of canonical ensembles at different values of β. The canonical ensemble is a particular case, as

$$P(\beta|\beta_0) = \delta(\beta - \beta_0) \quad \Longrightarrow \quad P(\mathbf{\Gamma}|\beta_0) = \frac{\exp\big(-\beta_0\mathcal{H}(\mathbf{\Gamma})\big)}{Z(\beta_0)}$$

The microcanonical ensemble

Assuming a classical Hamiltonian of the form

$$\mathcal{H} = \underbrace{\sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i}}_{=K(\boldsymbol{P})} + \underbrace{\Phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)}_{=\Phi(\boldsymbol{R})} \tag{4}$$

the isolated system should be described by a microcanonical ensemble,

$$P(\boldsymbol{R}, \boldsymbol{P}|E) = \frac{1}{\Omega(E)}\delta\big(E - K(\boldsymbol{P}) - \Phi(\boldsymbol{R})\big), \tag{5}$$

where

$$\Omega(E) = \int d\boldsymbol{P} d\boldsymbol{R}\, \delta\big(E - K(\boldsymbol{P}) - \Phi(\boldsymbol{R})\big) \tag{6}$$

is the (total) density of states.

Microcanonical configurational ensemble

Let us take the microcanonical ensemble

$$P(\boldsymbol{R}, \boldsymbol{P}|E) = \frac{1}{\Omega(E)}\delta\big(E - K(\boldsymbol{P}) - \Phi(\boldsymbol{R})\big)$$

and define the kinetic density of states by

$$\Omega_K(K) := \int d\boldsymbol{P}\delta\big(K - K(\boldsymbol{P})\big) = W \cdot \big[K\big]_{+}^{\frac{3N}{2}-1}. \tag{7}$$

Then we can marginalize over $\boldsymbol{P}$ to obtain the configurational distribution

$$P(\boldsymbol{R}|E) = \int d\boldsymbol{P}P(\boldsymbol{R}, \boldsymbol{P}|E) = \frac{W}{\Omega(E)}\left[E - \Phi(\boldsymbol{R})\right]_{+}^{\frac{3N}{2}-1}. \tag{8}$$

Here, W is an uninteresting constant depending on the number of particles and their masses.

The assumption of constant heat capacity

Now we use the condition of constant heat capacity $E = \alpha k_B T$ to determine

$$\Omega(E) = \Omega_0 E^\alpha. \tag{9}$$

Introducing the configurational density of states

$$\mathcal{D}(\phi) := \int d\boldsymbol{R}\,\delta\big(\phi - \Phi(\boldsymbol{R})\big) = \frac{\Omega_0}{W}\frac{\Gamma(\alpha+1)}{\Gamma(3N/2)\Gamma(\alpha - 3N/2 + 1)}\phi^{\alpha - \frac{3N}{2}} \tag{10}$$

we obtain, after normalization,

$$P(\phi|E) = \frac{\phi^{\alpha - \frac{3N}{2}}\left[E - \phi\right]_+^{\frac{3N}{2}-1}}{B\left(\frac{3N}{2}, \alpha + 1 - \frac{3N}{2}\right)E^\alpha}$$

which is a Beta distribution for the "reduced" variable $\varphi := \phi/E \in [0,1]$.

Its mean and relative variance are given by

$$\big\langle \phi \big\rangle_E = \left(1 - \frac{3N}{2(\alpha+1)}\right)E, \qquad \frac{\big\langle (\delta\phi)^2 \big\rangle_E}{\big\langle \phi \big\rangle_E^2} = \frac{3N}{2(\alpha+2)\left(\alpha - \frac{3N}{2} + 1\right)} \tag{11}$$

Convergence to the canonical ensemble

Taking the microcanonical configurational ensemble

$$P(\boldsymbol{R}|E) = \frac{W}{\Omega(E)}\,[E - \Phi(\boldsymbol{R})]_+^{\frac{3N}{2}-1}$$

and rewriting the factor $\mathcal{M}(\phi; E) := \big[E - \phi\big]_+^{\frac{3N}{2}-1}$ as

$$\mathcal{M}(\phi; E) = (E - \phi_E)^{\frac{3N}{2}-1}\Big[1 + (q-1)\beta_E\,\phi\Big]_+^{\frac{1}{1-q}} \tag{12}$$

with ϕ_E a reference potential energy (to be determined) and

$$q := 1 - \frac{2}{3N-2}, \qquad \beta_E := \frac{3N-2}{2(E-\phi_E)}$$

we have, in the limit $N \to \infty$ that $\mathcal{M}(\phi; E) \approx (E - \phi_E)^{\frac{3N}{2}-1}\exp\big(-\beta_E\,\phi\big)$ and

$$P(\boldsymbol{R}|E) \approx \frac{\exp\big(-\beta_E\,\Phi(\boldsymbol{R})\big)}{Z(\beta_E)} \tag{13}$$

Steady states: the superstatistical approximation

If the system is no longer microcanonical but has an energy distribution $P(E|S)$, then

$$P(\boldsymbol{R}|S) = \int_0^\infty dE\, P(E|S) P(\boldsymbol{R}|E) \approx \int_0^\infty dE\, P(E|S) \frac{\exp\left(-\beta_E\, \Phi(\boldsymbol{R})\right)}{Z(\beta_E)} \tag{14}$$

But this looks suspiciously like superstatistics!

It is actually revealed to be superstatistics by introducing a factor of 1 as

$$P(\boldsymbol{R}|S) \approx \int_0^\infty d\beta \underbrace{\left[\int_0^\infty dE\, P(E|S)\delta(\beta - \beta_E)\right]}_{=P(\beta|S)} \frac{\exp(-\beta\Phi(\boldsymbol{R}))}{Z(\beta)}, \tag{15}$$

thus arriving at a superstatistical inverse temperature distribution given by

$$\boxed{P(\beta|S) = \Big\langle \delta(\beta - \beta_E) \Big\rangle_S}$$

The superstatistical approximation

We can conclude that, in the limit $N \to \infty$,

$$P(\boldsymbol{R}|S) = \int_0^\infty d\beta P(\beta|S) \frac{\exp(-\beta\Phi(\boldsymbol{R}))}{Z(\beta)}$$

We can use the ensemble equivalence condition

$$\langle \phi \rangle_{\beta=\beta_E} = \langle \phi \rangle_E \quad (16)$$

to fix the value of β_E. In our case, this reads

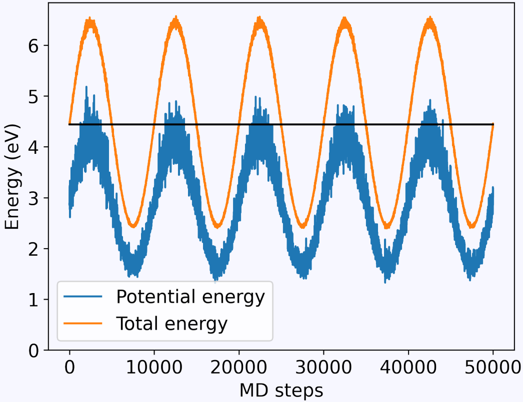
$$\frac{2\alpha - 3N}{2\beta_E} = \left(1 - \frac{3N}{2\alpha}\right) E \quad (17)$$

therefore

$$\beta_E = \frac{\alpha}{E} = \frac{1}{k_B T(E)}. \quad (18)$$

System subject to total energy oscillations

Molecular dynamics simulations



$$E(t) = E_0 + A \sin(\omega t)$$

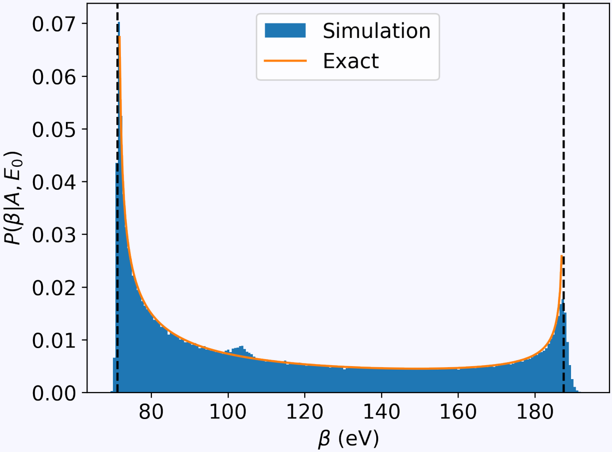
$$P(E|S) = \frac{1}{\pi} \frac{1}{\sqrt{A^2 - (E - E_0)^2}}$$

for $|E - E_0| \leq A$.

We will use a Lennard-Jones (LJ) crystal with N = 108 atoms, lattice constant a = 5.256 Å and with parameters ϵ = 120 $k_B \cdot$ K and σ = 3.4 Å .

Inverse temperature distribution

$$P(\beta|A,E_0) = \frac{1}{\pi\beta_0}\frac{1}{\sqrt{\gamma^2(\beta/\beta_0)^4 - (\beta/\beta_0)^2(1-\beta/\beta_0)^2}}, \qquad \beta_0 = \frac{\alpha}{E_0}$$



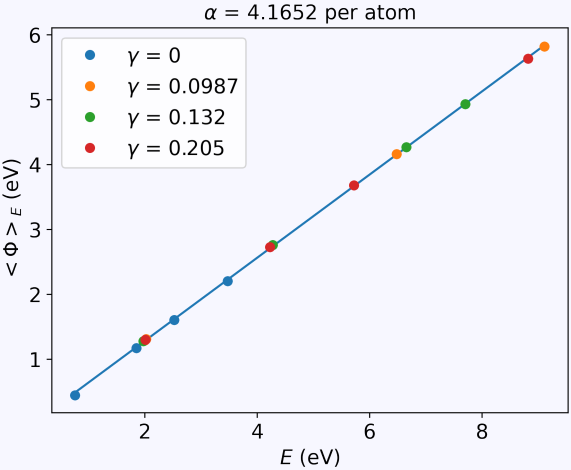
$$\gamma := \frac{A}{E_0}, \qquad 0 \leq \gamma \leq 1$$

$$\langle\beta\rangle_{A,E_0} = \frac{\beta_0}{\sqrt{1-\gamma^2}}$$

$$\frac{\beta_0}{1+\gamma} \leq \beta \leq \frac{\beta_0}{1-\gamma}$$

The caloric curve

$$\langle\phi\rangle_{A,E_0} = \left\langle \left(\alpha - \frac{3N}{2}\right)\frac{1}{\beta}\right\rangle_{A,E_0} = R\,E_0 = \langle\phi\rangle_{E_0} \quad \text{with} \quad R := 1 - \frac{3N}{2\alpha} \tag{19}$$

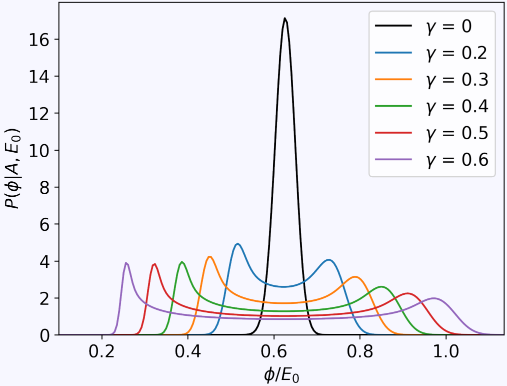


$$\left\langle \frac{1}{\beta} \right\rangle_{A,E_0} = \frac{E_0}{\alpha}$$

Potential energy distribution

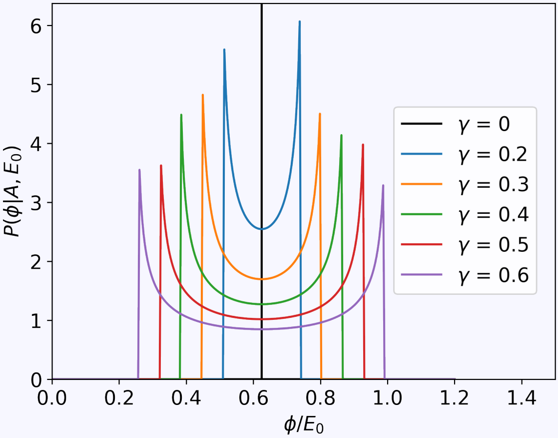
$$P(\phi|A,E_0) = \frac{\left(\frac{\phi}{E_0}\right)^{\alpha-\frac{3N}{2}}\mathcal{K}\left(\frac{\phi}{E_0};\gamma,\alpha,N\right)}{E_0\,\pi\,B\left(\frac{3N}{2},\alpha+1-\frac{3N}{2}\right)},$$

$$\mathcal{K}(z;\gamma,\alpha,N) := \int_{\max(z,1-\gamma)}^{1+\gamma} \frac{dx\,x^{-\alpha}(x-z)^{\frac{3N}{2}-1}}{\sqrt{x-(1-\gamma)}\sqrt{(1+\gamma)-x}} \tag{20}$$



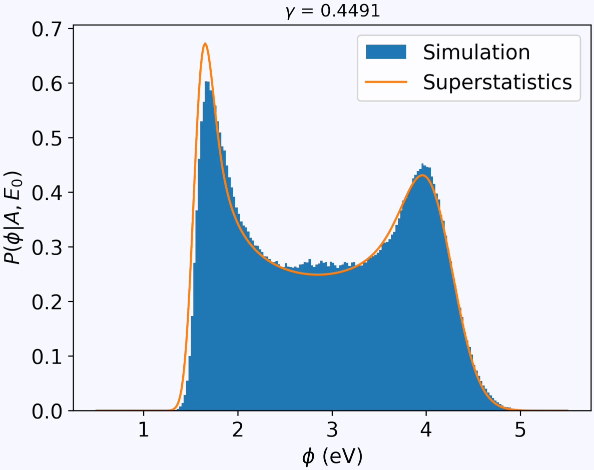
Potential energy distribution (asymptotic limit)

$$P(\phi|A,E_0) \approx \frac{1}{\pi R E_0} \frac{1}{\sqrt{z-(1-\gamma)}\sqrt{1+\gamma-z}}, \quad z := \frac{\phi}{RE_0}, \quad 1-\gamma \leq z \leq 1+\gamma$$

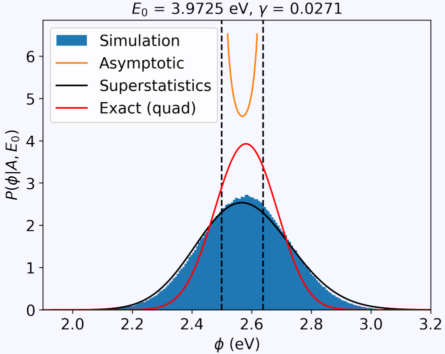


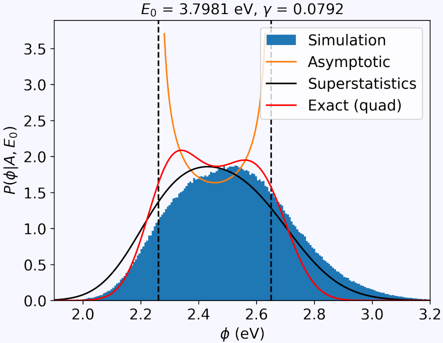
Superstatistical potential energy distribution

$$P(\phi|A, E_0) = \frac{1}{\pi\beta_0\Gamma(\alpha - 3N/2 + 1)} \int_0^{\infty} \frac{d\beta\,\beta\,(\beta\phi)^{\alpha-\frac{3N}{2}}\exp(-\beta\phi)}{\sqrt{\gamma^2(\beta/\beta_0)^4 - (\beta/\beta_0)^2(1-\beta/\beta_0)^2}}$$

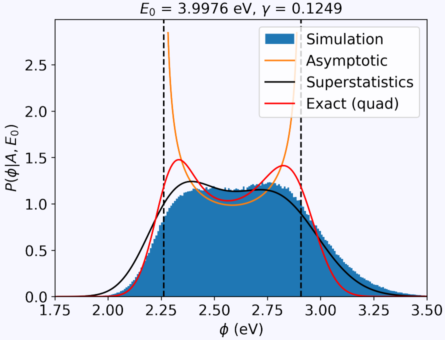


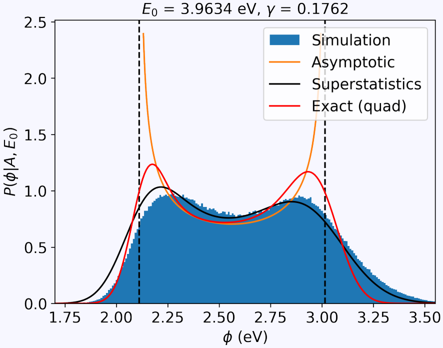
Potential energy distributions



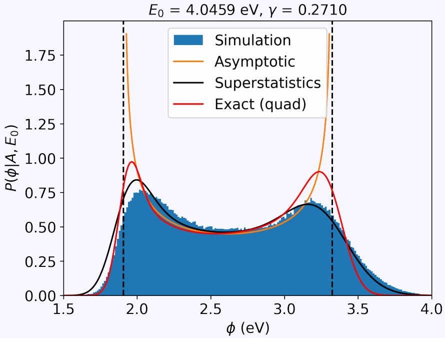


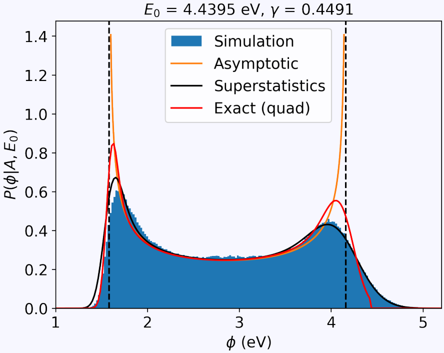
Potential energy distributions





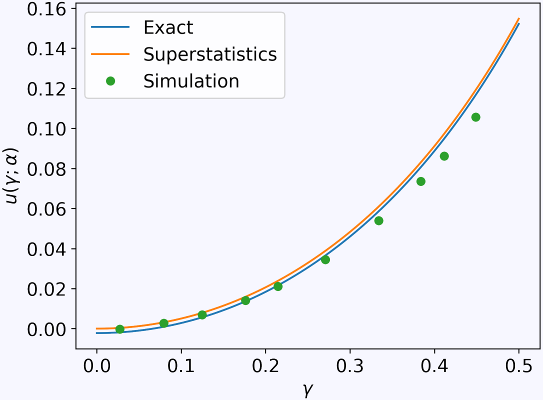
Potential energy distributions





Inverse temperature uncertainty

$$u := \frac{\mathcal{U}}{{\beta_S}^2}, \qquad \mathcal{U} := \left\langle (\delta\beta)^2 \right\rangle_{A,E_0} = \left\langle \big(\delta b(\phi)\big)^2 \right\rangle_{A,E_0} + \left\langle b(\phi)' \right\rangle_{A,E_0} \tag{21}$$



$$u = \frac{\alpha - 1}{\alpha\sqrt{1-\gamma^2}} - 1 \tag{22}$$

$$u \approx u_{\text{sup}} = \frac{1}{\sqrt{1-\gamma^2}} - 1$$

$$b(\phi) = \frac{2\alpha - 3N}{2\phi} \tag{23}$$

Concluding Remarks

- We have shown that a large enough classical system under a total energy distribution can be described by superstatistics in some cases
- We have tested this result by studying an energy-driven Lennard-Jones system using molecular dynamics simulations
- Our results suggest that the superstatistical approximation not only improves with increasing N but also when increasing the amplitude γ

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Superstatistics as the thermodynamic limit of driven classical systems

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Superstatistics is an elegant framework for the description of steady-state thermodynamics, mostly used for systems with long-range interactions such as plasmas. In this work, we show that the potential energy distribution of a classical system under externally imposed energy fluctuations can also be described by superstatistics in the thermodynamic limit. As an example, we apply this formalism to the thermodynamics of a finite Lennard-Jones crystal with constant microcanonical heat capacity driven by sinusoidal energy oscillations. Our results show that molecular dynamics simulations of the Lennard-Jones crystal are in agreement with the provided theoretical predictions.

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