

# Density of states from microcanonical averages

Stefan Schnabel

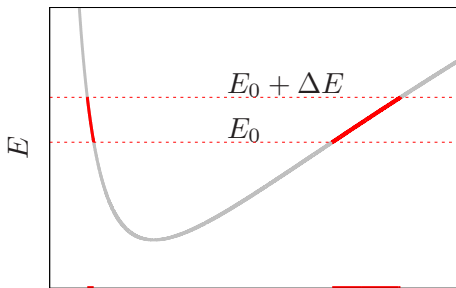
CompPhys23

# Density of states

- Density of states:

$$\begin{aligned}g(E_0) &= \int \delta(\mathcal{H}(\mathbf{X}) - E_0) d\mathbf{x}^N, \\ &= \int_{A_{E_0}} \frac{1}{|\nabla \mathcal{H}(\mathbf{X})|} d\mathbf{x}^{N-1}.\end{aligned}$$

$A_{E_0}$  : surface of constant energy



configuration space

# Density of states

- Density of states:

$$g(E) = \int_{A_E} \frac{1}{|\nabla \mathcal{H}(\mathbf{X})|} d\mathbf{x}^{N-1}.$$

- “Inverse Microcanonical temperature”:

$$\frac{d \ln g(E)}{dE} = \left\langle \frac{\Delta \mathcal{H}}{(\nabla \mathcal{H})^2} - 2 \frac{\nabla \mathcal{H} \mathcal{H} \nabla \mathcal{H}}{(\nabla \mathcal{H})^4} \right\rangle_E,$$

$$\Delta \mathcal{H}(\mathbf{X}) = \sum_i \frac{\partial^2 \mathcal{H}(\mathbf{X})}{(\partial x_i)^2} \quad \text{Laplacian,}$$

$$\mathcal{H}_{i,j} = \frac{\partial^2 \mathcal{H}(\mathbf{X})}{\partial x_i \partial x_j} \quad \text{Hessian.}$$

- G. Gilat, Solid State Communications **14**, 263 (1974).  
H. H. Rugh, Phys. Rev. Lett. **78**, 772 (1997).

## Alternative way

- Microcanonical average:

$$\langle Q \rangle_E = \frac{\int_{A_E} \frac{Q(\mathbf{x})}{|\nabla \mathcal{H}(\mathbf{x})|} d\mathbf{x}^{N-1}}{g(E)}.$$

- Derivative of microcanonical average:

$$\frac{d}{dE} \langle Q \rangle_E = \left\langle \nabla \left( \frac{Q \nabla \mathcal{H}}{(\nabla \mathcal{H})^2} \right) \right\rangle_E - \langle Q \rangle_E \frac{d \ln g(E)}{dE}.$$

- In particular for  $Q(\mathbf{x}) = (\nabla \mathcal{H}(\mathbf{x}))^2$ :

$$\frac{d}{dE} \langle (\nabla \mathcal{H})^2 \rangle_E = \langle \Delta \mathcal{H} \rangle_E - \langle (\nabla \mathcal{H})^2 \rangle_E \frac{d \ln g(E)}{dE}.$$

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$$\frac{d}{dE} \langle (\nabla \mathcal{H})^2 \rangle_E = \langle \Delta \mathcal{H} \rangle_{E'} - \langle (\nabla \mathcal{H})^2 \rangle_E \frac{d \ln g(E)}{dE}$$

- leads to

$$\frac{d \ln g(E)}{dE} = \frac{\langle \Delta \mathcal{H} \rangle_{E'}}{\langle (\nabla \mathcal{H})^2 \rangle_E} - \frac{d}{dE} \ln \langle (\nabla \mathcal{H})^2 \rangle_E$$

- or

$$g(E) \propto \frac{1}{\langle (\nabla \mathcal{H})^2 \rangle_E} \exp \left[ \int_{E_0}^E \frac{\langle \Delta \mathcal{H} \rangle_{E'}}{\langle (\nabla \mathcal{H})^2 \rangle_{E'}} dE' \right]$$

# Flat-histogram (MUCA) Monte Carlo sampling

- Often the density of states is not known at the start of the simulation.
- Usually estimates  $\tilde{g}_i(E)$  of the density of states are obtained from histograms  $h(E)$ :

$$\tilde{g}_{i+1}(E) = \tilde{g}_i(E)h_i(E)$$

- or the Wang-Landau technique is used

$$\tilde{g}_{t+1}(E_t) = f\tilde{g}_t(E_t), \quad \tilde{g}_{t+1}(E)|_{E \neq E_t} = \tilde{g}_t(E).$$

- However, histograms carry relatively large statistical errors and correlations and Wang-Landau violates detailed balance.
- Can we get the information directly from the geometry of the energy-landscape?

# Flat-histogram (MUCA) Monte Carlo sampling

- To achieve a uniform distribution in energy the acceptance probability of a proposed move is

$$\ln \Pi_{\text{acc}}(E_{\text{old}} \rightarrow E_{\text{new}}) = \min \left( 0, \ln \frac{g(E_{\text{old}})}{g(E_{\text{new}})} \right).$$

- With the two methods this becomes

$$\begin{aligned} \ln \frac{g(E_{\text{old}})}{g(E_{\text{new}})} &= \int_{E_{\text{new}}}^{E_{\text{old}}} \left\langle \frac{\Delta \mathcal{H}}{(\nabla \mathcal{H})^2} - 2 \frac{\nabla \mathcal{H} \mathcal{H} \nabla \mathcal{H}}{(\nabla \mathcal{H})^4} \right\rangle_{E'} dE', \\ \ln \frac{g(E_{\text{old}})}{g(E_{\text{new}})} &= \int_{E_{\text{new}}}^{E_{\text{old}}} \frac{\langle \Delta \mathcal{H} \rangle_{E'}}{\langle (\nabla \mathcal{H})^2 \rangle_{E'}} dE' - \ln \frac{\langle (\nabla \mathcal{H})^2 \rangle_{E_{\text{old}}}}{\langle (\nabla \mathcal{H})^2 \rangle_{E_{\text{new}}}}. \end{aligned}$$

# How to integrate

- Polynomials are not a good fit for  $f(E) = \frac{d}{dE} \ln g(E)$ .
- We use the ansatz  $g(E) \propto |E - \eta|^\mu$  corresponding to a system with
  - ▶ Ground state energy  $\eta : (E \geq \eta)$
  - ▶ Constant specific heat  $C(T) = k_B(\mu + 1)$
- Leading to  $f(E) = \mu/(E - \eta)$
- And with two points  $(E_i, f_i)$  and  $(E_{i+1}, f_{i+1})$  one finds
  - ▶  $\mu_i = (E_i - E_{i+1})/(f_i^{-1} - f_{i+1}^{-1})$
  - ▶  $\eta_i = (E_i f_i - E_{i+1} f_{i+1})/(f_i - f_{i+1})$
- Finally

$$\int_{E_k}^{E_l} f(E) dE \approx \sum_{i=k}^{l-1} \mu_i \ln \left| \frac{E_{i+1} - \eta_i}{E_i - \eta_i} \right|.$$

# Vector spin model

- Hamiltonian

$$\mathcal{H} = - \sum_{\langle ij \rangle} \boldsymbol{\sigma}_i \boldsymbol{\sigma}_j, \quad \boldsymbol{\sigma} \in \mathbb{R}^n, |\boldsymbol{\sigma}| = 1, n \geq 2,$$

- local field and spin energy

$$\mathbf{h}_i = \sum_{\langle ij \rangle} \boldsymbol{\sigma}_j, \quad \varepsilon_i = -\mathbf{h}_i \boldsymbol{\sigma}_i,$$

- gradient squared

$$\langle (\nabla \mathcal{H})^2 \rangle_E = N(\langle \mathbf{h}^2 \rangle_E - \langle \varepsilon^2 \rangle_E),$$

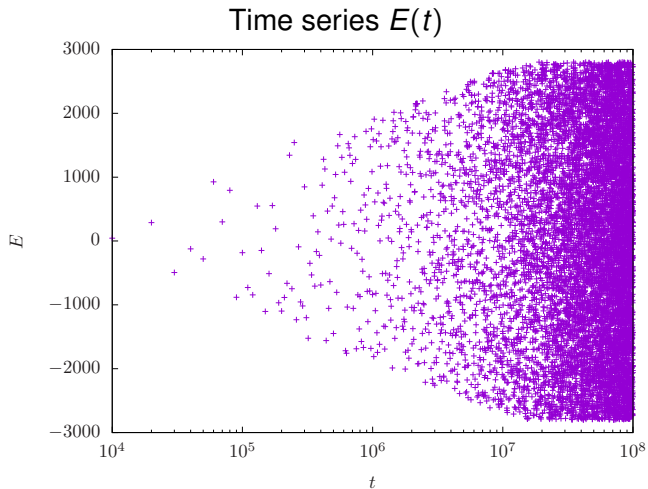
- Laplacian

$$\langle \Delta \mathcal{H} \rangle_E = -2(n-1)E,$$

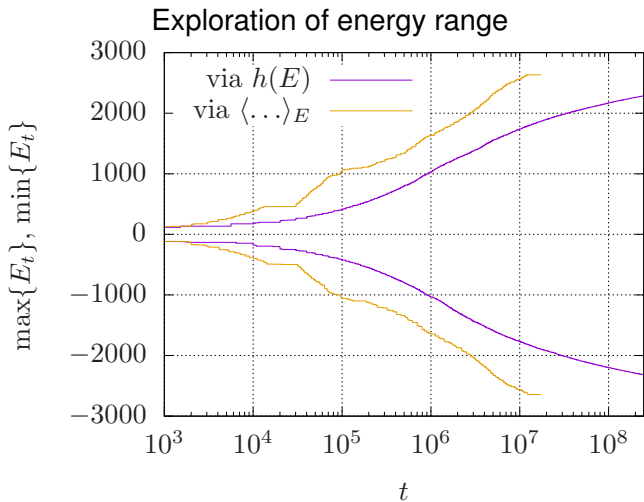
- Hessian term

$$\langle \nabla \mathcal{H} \mathcal{H} \nabla \mathcal{H} \rangle_E = \left\langle \sum_i \varepsilon_i (\varepsilon_i^2 - \mathbf{h}_i^2) - \sum_{\langle ij \rangle} (\mathbf{h}_i + \varepsilon_i \boldsymbol{\sigma}_i) (\mathbf{h}_j + \varepsilon_j \boldsymbol{\sigma}_j) \right\rangle_E.$$

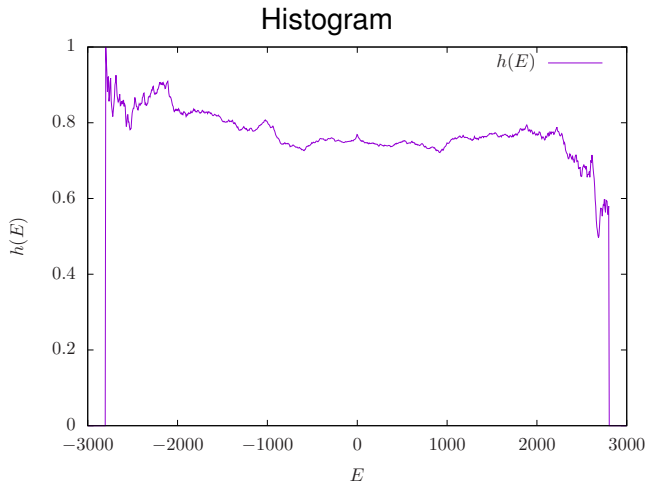
# Vector spin model ( $n = 3, N = 10^3$ )



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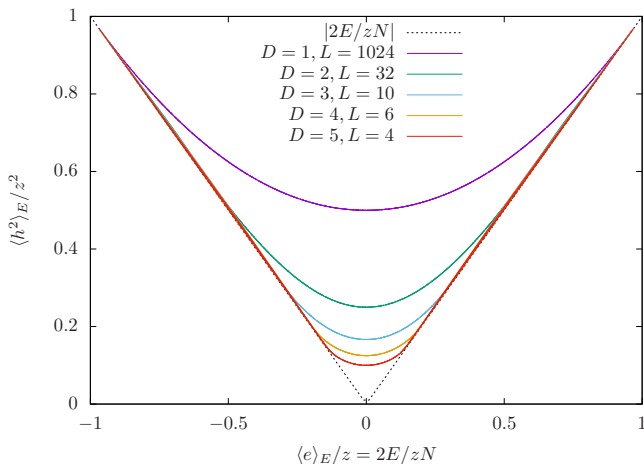


# Vector spin model ( $n = 3, N = 10^3$ )

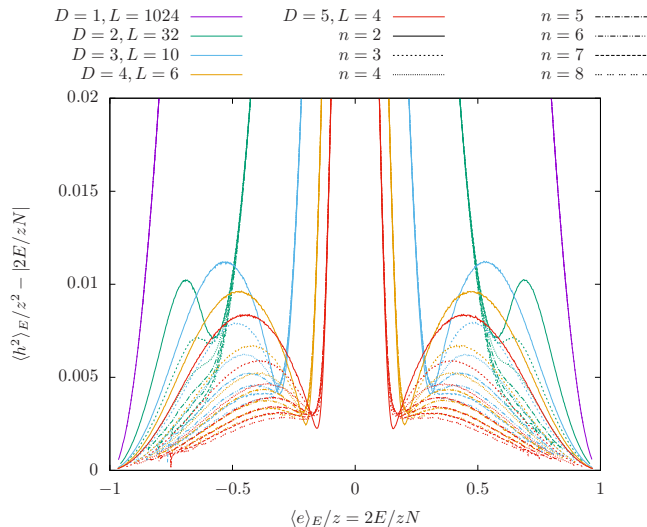


# Vector spin model

$$g(E) \propto \frac{1}{\langle \mathbf{h}^2 \rangle_E - \langle \mathbf{e}^2 \rangle_E} \exp \left( \int_{E_0}^E \frac{-2(n-1)E'/N}{\langle \mathbf{h}^2 \rangle_{E'} - \langle \mathbf{e}^2 \rangle_{E'}} dE' \right).$$

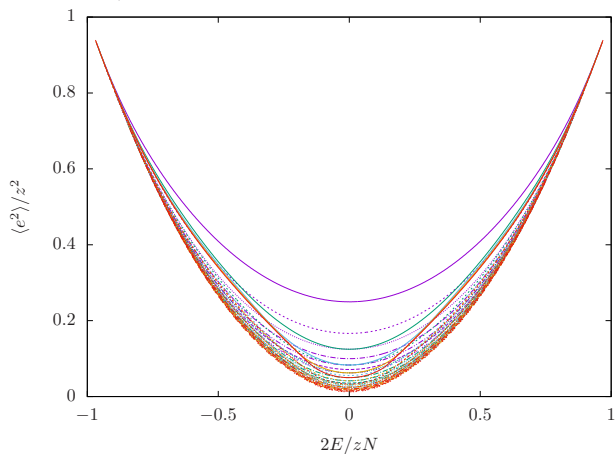


# Vector spin model

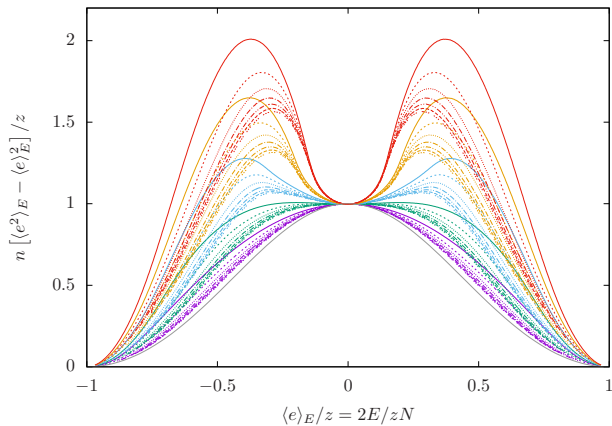
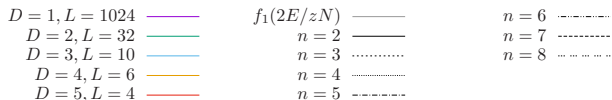


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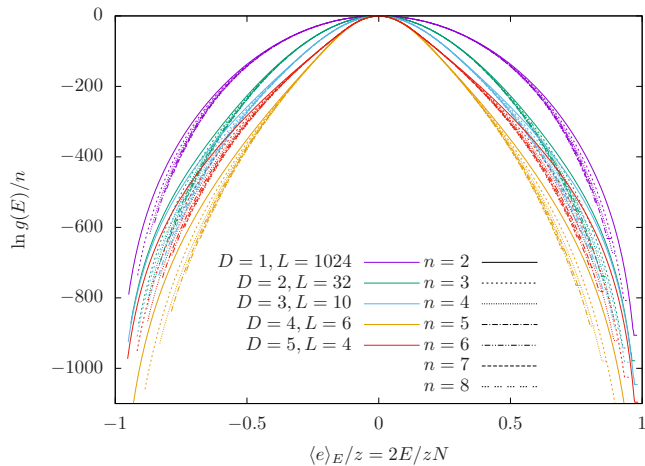
$D = 1, L = 1024$  — purple —  $D = 5, L = 4$  — red —  $n = 5$  - - - - -  
 $D = 2, L = 32$  — green —  $n = 2$  — black —  $n = 6$  - · - · -  
 $D = 3, L = 10$  — cyan —  $n = 3$  ······  $n = 7$  - · - · -  
 $D = 4, L = 6$  — orange —  $n = 4$  ······  $n = 8$  - · - · -



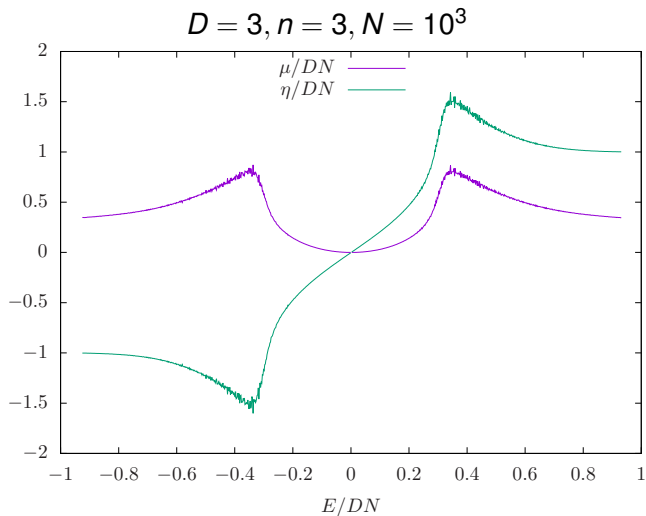
# Vector spin model



# Vector spin model



# Vector spin model



# Lennard-Jones atoms

- Hamiltonian with standard 12-6 Lennard-Jones potential

$$\mathcal{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N U(|\mathbf{x}_i - \mathbf{x}_j|), \quad U(r) = \frac{1}{r^{12}} - \frac{2}{r^6}.$$

- Gradient

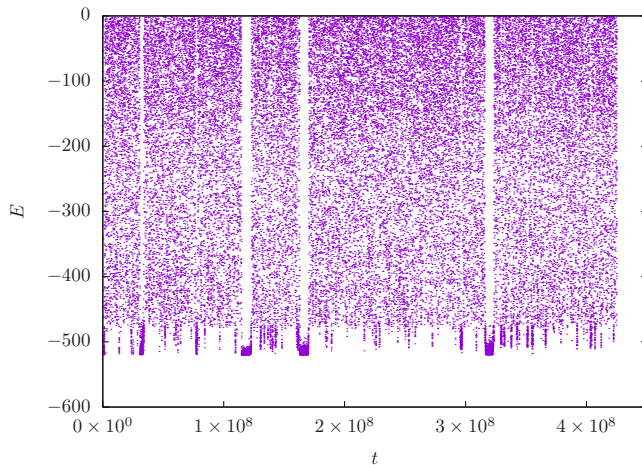
$$\nabla_i \mathcal{H} = -12 \sum_{j \neq i} (\mathbf{x}_i - \mathbf{x}_j) \left( \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|^{14}} - \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|^8} \right),$$

$$(\nabla \mathcal{H})^2 = \left( \sum_{i=1}^N \nabla_i \mathcal{H} \right)^2.$$

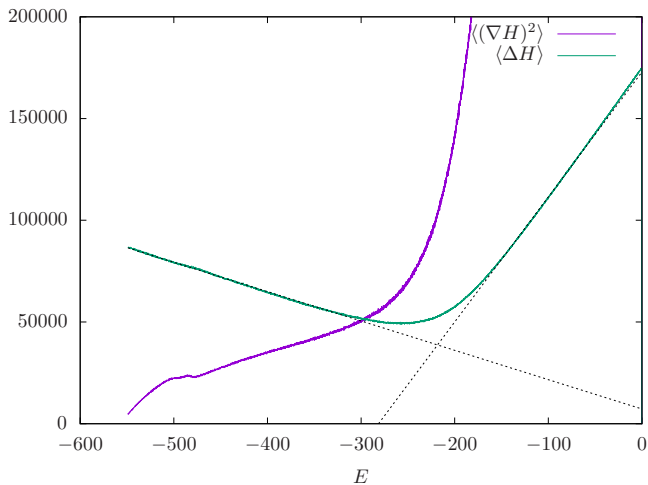
- Laplacian

$$\Delta \mathcal{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N 24 \left( \frac{11}{|\mathbf{x}_i - \mathbf{x}_j|^{14}} - \frac{5}{|\mathbf{x}_i - \mathbf{x}_j|^8} \right).$$

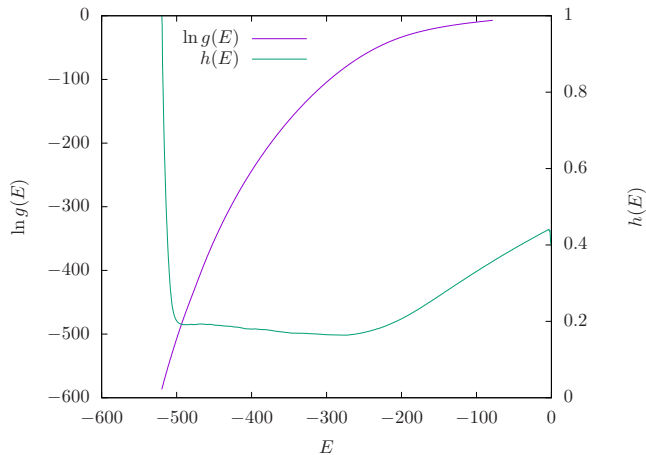
# Lennard-Jones atoms $N = 100$



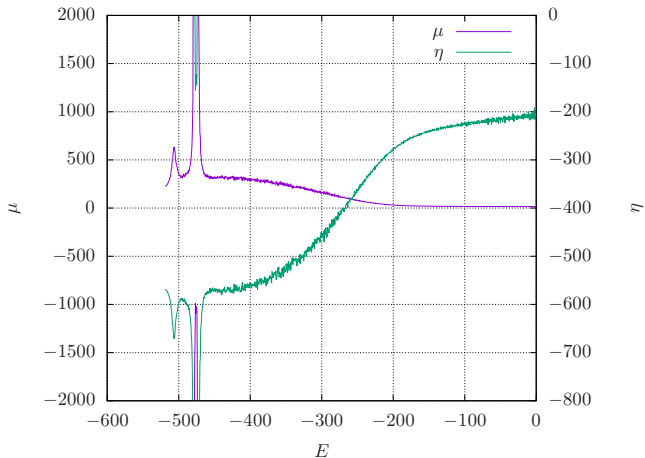
# Lennard-Jones atoms $N = 100$



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# Conclusions

- We can calculate the density of states from microcanonical averages of Laplacian and squared gradient alone.
- Numerical integration is relatively simple.
- Flat-histogram is faster than histogram-based (if it works).
- First-order phase transitions are challenging.
- For the  $O(n)$  vector spin model everything is easily obtainable.
- Lennard-Jones system can also be simulated.
- Average of Laplacian linear?
- S. Schnabel, and W. Janke, Surveying an energy landscape, *Front. Phys.* **11**, 1218107 (2023).

# Conclusions



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Deutsche  
Forschungsgemeinschaft

German Research Foundation

## Thanks for your attention

# Density of states

$$\begin{aligned}g(E) &= \int_{A_E} \frac{1}{|\nabla \mathcal{H}(\mathbf{X})|} dx^{N-1}, \\ &= \int_{A_E} \frac{\nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} \cdot \mathbf{n}(\mathbf{X}) dx^{N-1},\end{aligned}$$

with the unit vector perpendicular to  
the surface of cons.  $E$ :

$$\mathbf{n}(\mathbf{X}) = \nabla \mathcal{H}(\mathbf{X}) / |\nabla \mathcal{H}(\mathbf{X})|.$$

# Density of states

$$g(E) = \int_{A_E} \frac{\nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} \cdot \mathbf{n}(\mathbf{X}) \, dx^{N-1},$$

$$\frac{dg(E)}{dE} = \lim_{\varepsilon \rightarrow 0} \frac{g(E + \varepsilon) - g(E)}{\varepsilon},$$

$$= \int_{A_E} \frac{1}{|\nabla \mathcal{H}(\mathbf{X})|} \nabla \frac{\nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} \, dx^{N-1},$$

$$= \int_{A_E} \left[ \frac{\Delta \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} - 2 \frac{\nabla \mathcal{H}(\mathbf{X}) \cdot \mathcal{H}(\mathbf{X}) \nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^4} \right] dx^{N-1}.$$

$$\Delta \mathcal{H}(\mathbf{X}) = \sum_i \frac{\partial^2 \mathcal{H}(\mathbf{X})}{(\partial x_i)^2} \quad \text{Laplacian,}$$

$$\mathcal{H}_{ij} = \sum_i \frac{\partial^2 \mathcal{H}(\mathbf{X})}{\partial x_i \partial x_j} \quad \text{Hessian.}$$

# Density of states

$$\begin{aligned}\frac{d \ln g(E)}{dE} &= \frac{1}{g(E)} \frac{dg(E)}{dE}, \\ &= \left\langle \frac{\Delta \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} - 2 \frac{\nabla \mathcal{H}(\mathbf{X}) \mathcal{H}(\mathbf{X}) \nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^4} \right\rangle_E.\end{aligned}$$

It follows

$$\ln g(E) = \int_{E_0}^E \left\langle \frac{\Delta \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} - 2 \frac{\nabla \mathcal{H}(\mathbf{X}) \mathcal{H}(\mathbf{X}) \nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^4} \right\rangle_{E'} dE' + c.$$

# Density of states

- Microcanonical average:

$$\langle Q \rangle_E = \frac{\int_{A_{E_0}} \frac{Q(\mathbf{X})}{|\nabla \mathcal{H}(\mathbf{X})|} d\mathbf{x}^{N-1}}{\int_{A_{E_0}} \frac{1}{|\nabla \mathcal{H}(\mathbf{X})|} d\mathbf{x}^{N-1}}.$$

- Derivative of a microcanonical average:

$$\frac{d}{dE} \langle Q(\mathbf{X}) \rangle_E = \left\langle \nabla \left( \frac{Q(\mathbf{X}) \nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} \right) \right\rangle_E - \langle Q(\mathbf{X}) \rangle_E \frac{d \ln g(E)}{dE}.$$

- Especially for  $Q(\mathbf{X}) = (\nabla \mathcal{H}(\mathbf{X}))^2$ :

$$\frac{d}{dE} \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E = \langle \Delta \mathcal{H}(\mathbf{X}) \rangle_E - \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E \frac{d \ln g(E)}{dE}.$$

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$$\frac{d \ln g(E)}{dE} = \frac{\langle \Delta \mathcal{H}(\mathbf{X}) \rangle_E}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E} - \frac{\frac{d}{dE} \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E},$$

$$\ln g(E) = \int_{E_0}^E \frac{\langle \Delta \mathcal{H}(\mathbf{X}) \rangle_{E'}}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_{E'}} dE' - \ln \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E + c.$$

# Density of states

$$\frac{d}{dE} \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E = \langle \Delta \mathcal{H}(\mathbf{X}) \rangle_E - \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E \frac{d \ln g(E)}{dE},$$

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# Density of states

$$\begin{aligned}\frac{d}{dE} \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E &= \langle \Delta \mathcal{H}(\mathbf{X}) \rangle_E - \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E \frac{d \ln g(E)}{dE}, \\ \frac{d \ln g(E)}{dE} &= \frac{\langle \Delta \mathcal{H}(\mathbf{X}) \rangle_E}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E} - \frac{\frac{d}{dE} \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E}, \\ \ln g(E) &= \int_{E_0}^E \frac{\langle \Delta \mathcal{H}(\mathbf{X}) \rangle_{E'}}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_{E'}} dE' - \ln \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E + c.\end{aligned}$$

# Density of states

$$\ln g(E) = \int_{E_0}^E \left\langle \frac{\Delta \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^2} - 2 \frac{\nabla \mathcal{H}(\mathbf{X}) \mathcal{H}(\mathbf{X}) \nabla \mathcal{H}(\mathbf{X})}{(\nabla \mathcal{H}(\mathbf{X}))^4} \right\rangle_{E'} dE' + c.$$

$$\ln g(E) = \int_{E_0}^E \frac{\langle \Delta \mathcal{H}(\mathbf{X}) \rangle_{E'}}{\langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_{E'}} dE' - \ln \langle (\nabla \mathcal{H}(\mathbf{X}))^2 \rangle_E + c.$$