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Exploring the phase space: fundamentals of statistical mechanics

Lars Pastewka

Johns Hopkins University
Baltimore
USA

Strada Costiera, 11 - 34151 - Trieste - Italy • Tel. +39 0402240111 • Fax. +39 040224163 • sci_info@ictp.it • www.ictp.it
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A note on notations in the different talks:

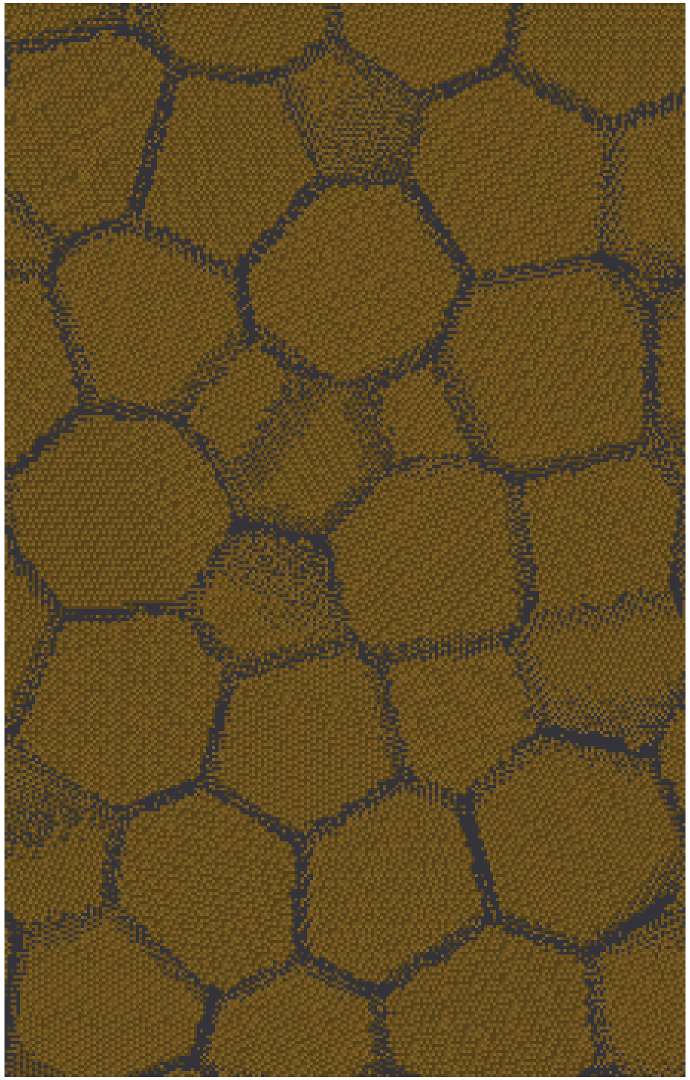
Quantity	This Talk	Alessandro	Julian
Free energy	A	F	G
Configuration, point in the space of relevant coordinates	$\vec{Q}$	x	x
Collective variables, order parameters	$\Phi, \phi(\vec{Q})$	$s, S(x)$	$s, S(x)$

Exploring the Phase Space

Fundamentals of Classical Statistical Mechanics

Lars Pastewka
Department of Physics and Astronomy
Johns Hopkins University

Microscopic view



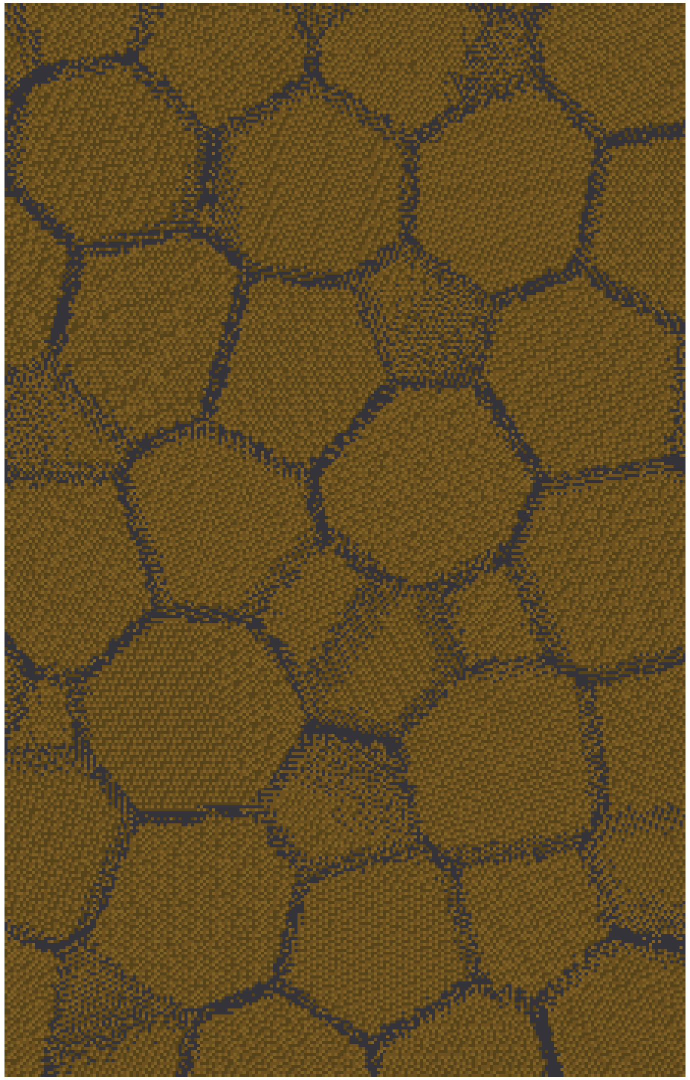
Macroscopic view

$\{\vec{\boldsymbol{r}}_i\}, \{\vec{\boldsymbol{p}}_i\} = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \dots\}, \{\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \dots\}$

$\boldsymbol{P}, \boldsymbol{V}$

Microscopic view

Macroscopic view



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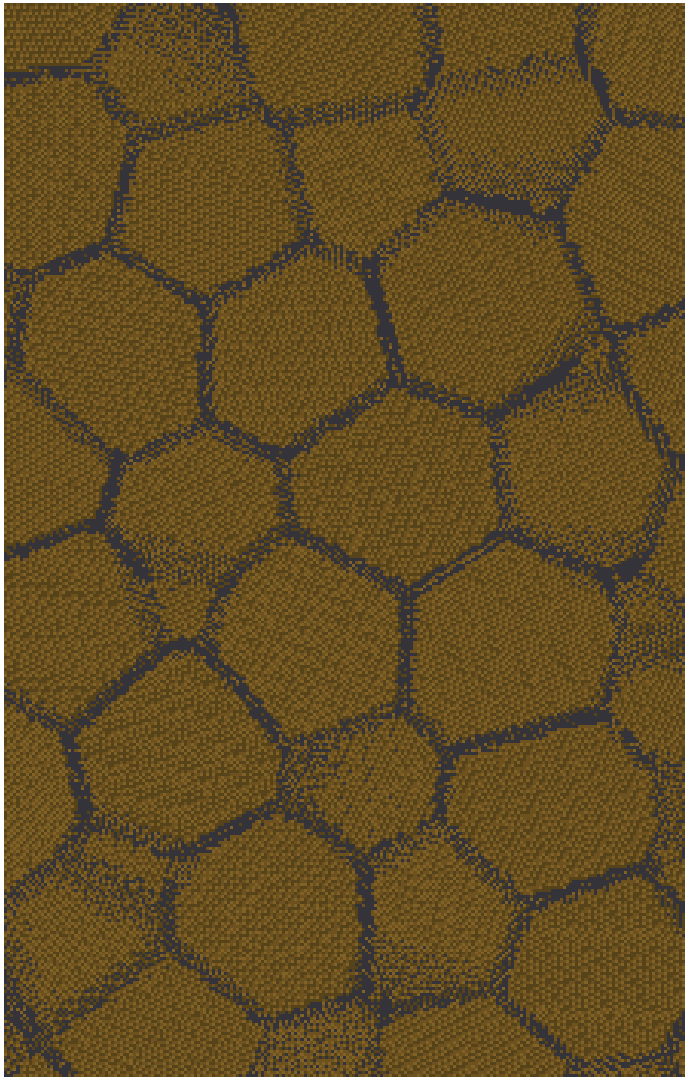
$\boldsymbol{P}, \boldsymbol{V}$

Microscopic view

Macroscopic view



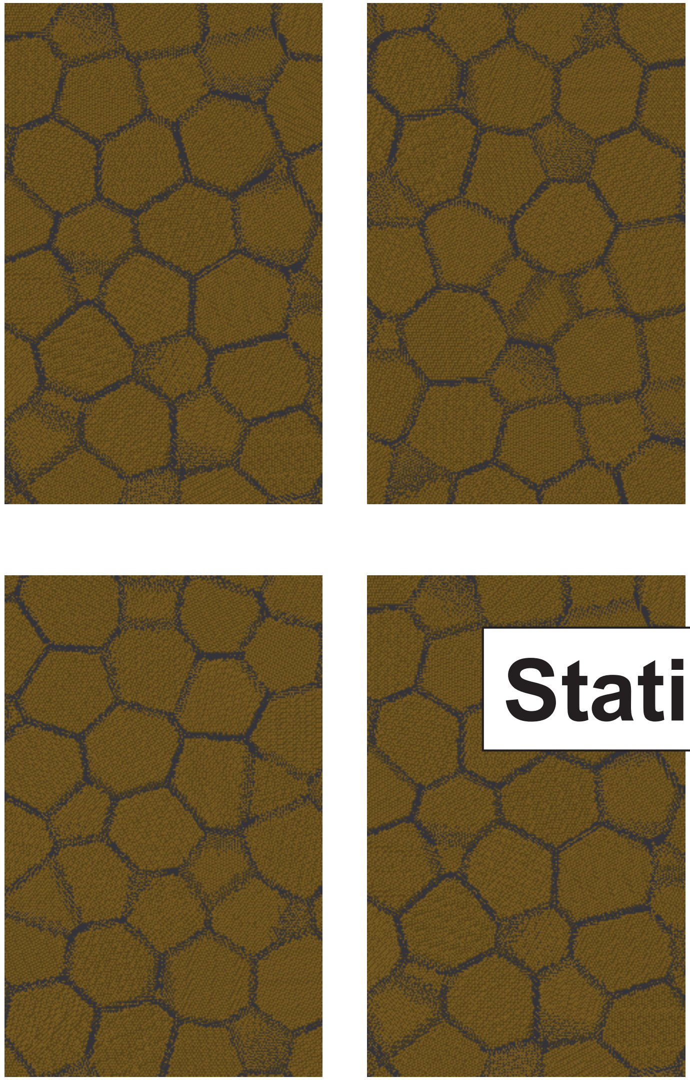
↔

$\{\boldsymbol{\vec{r}_i}\}, \{\boldsymbol{\vec{p}_i}\} = \{\boldsymbol{r_1}, \boldsymbol{r_2}, \boldsymbol{r_3}, \dots\}, \{\boldsymbol{p_1}, \boldsymbol{p_2}, \boldsymbol{p_3}, \dots\}$

$\boldsymbol{P}, \boldsymbol{V}$

Microstates

Macrostate



Statistical Mechanics

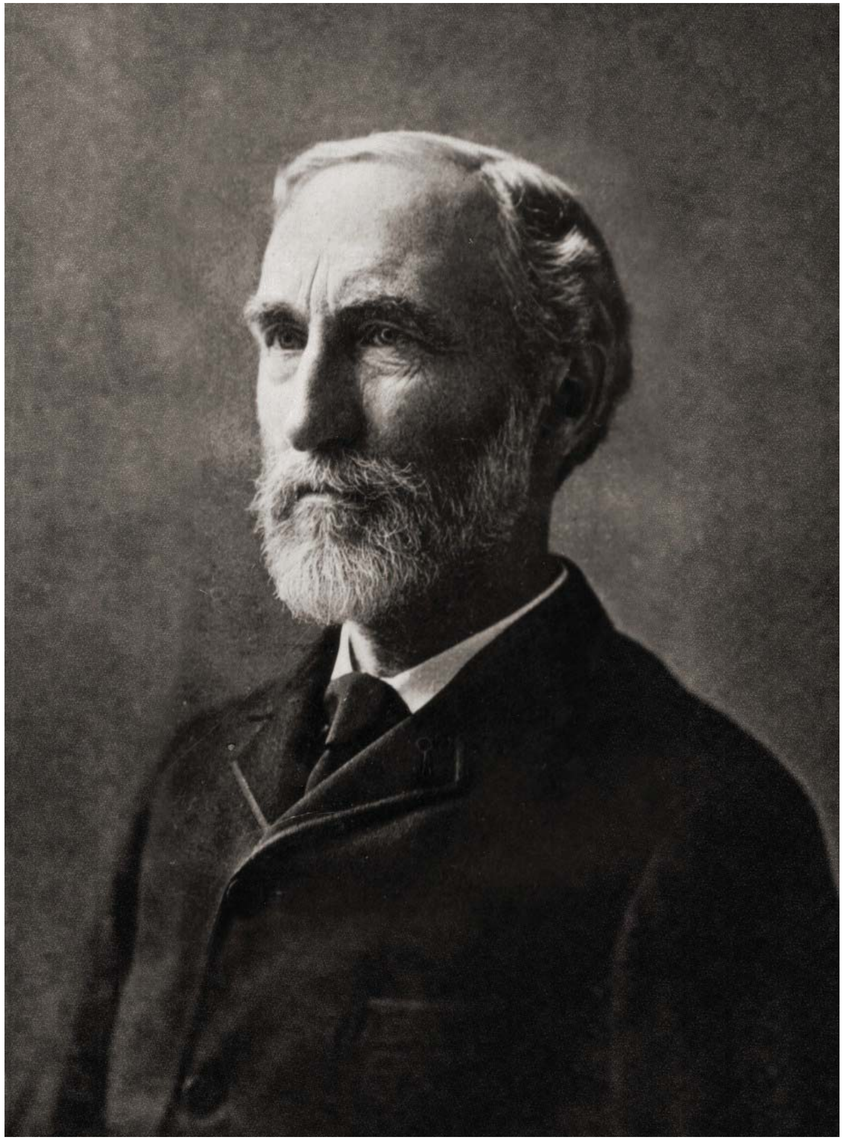
Ensemble of $\{\vec{r}_i\}$, $\{\vec{p}_i\}$

$\boldsymbol{P}, \boldsymbol{V}$

Microscopic view

Macroscopic view

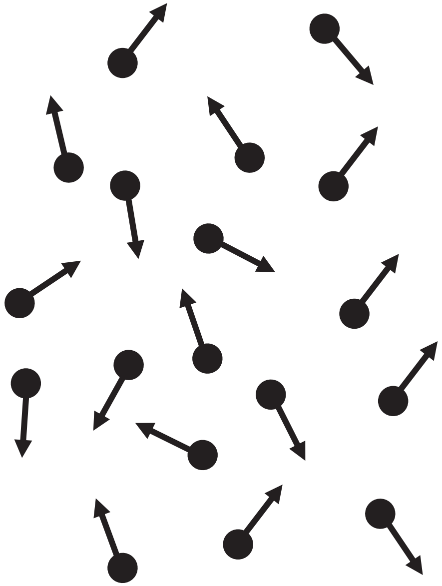
Ludwig Boltzmann
1844 – 1906



Josiah Willard Gibbs
1839 – 1903

Microstates

Macrostate



$\{\vec{r}_i\}, \{\vec{p}_i\}$

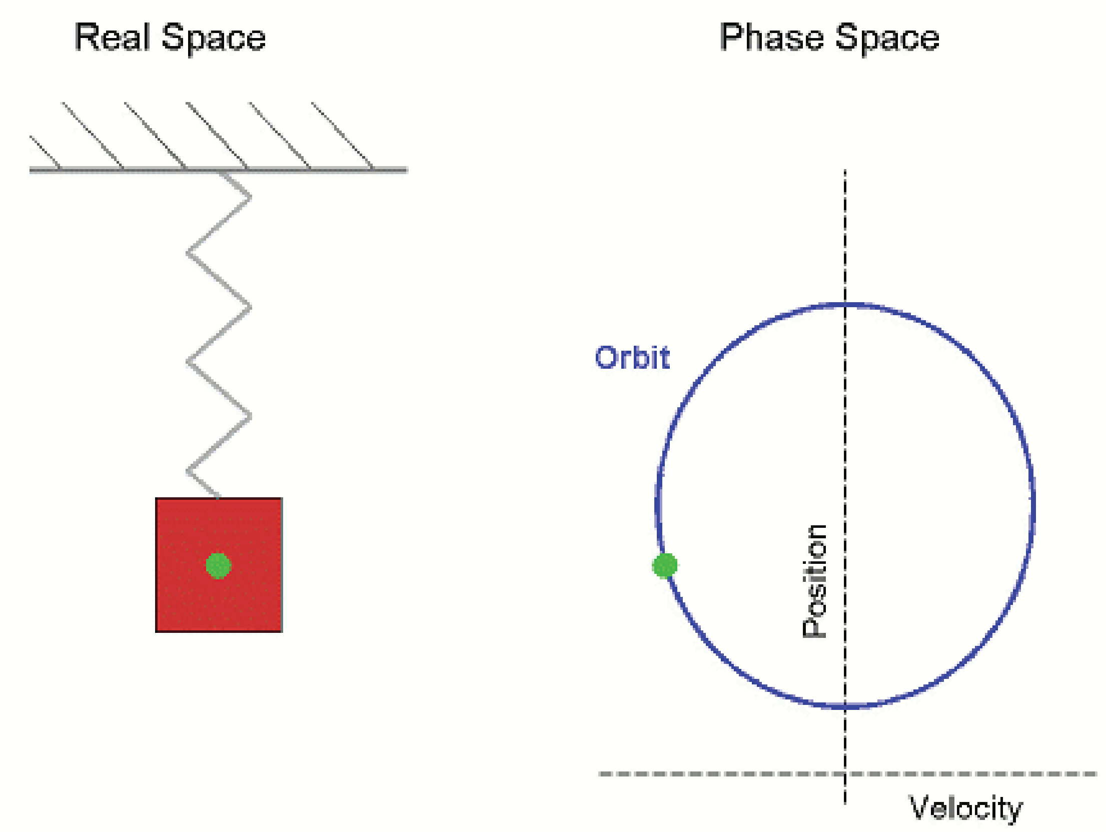
$\sim 10^{24}$ **degrees of freedom**

V, T

2 degrees of freedom

Characterizing a microstate

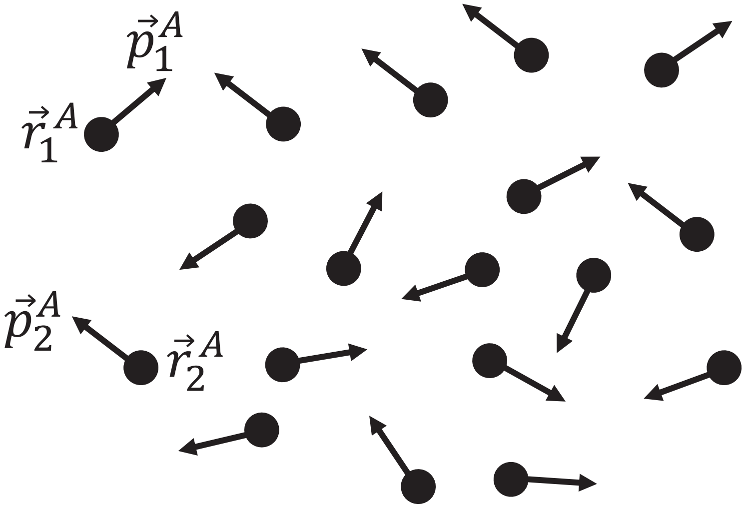
- Atom i has position $\vec{r}_i$ and momentum $\vec{p}_i$
- A system of N atoms is described by a point in $6N$ dimensional space Γ
- 1D Harmonic oscillator, 2D phase space: $\Gamma = (r, p);\ E = \frac{p^2}{2m} + \frac{1}{2} k r^2 = \text{const.}$



Source: Wikipedia

Characterizing a microstate

- Why is thinking in terms of the phase space useful?
- Phase space density ρ for a single microstate of N particles



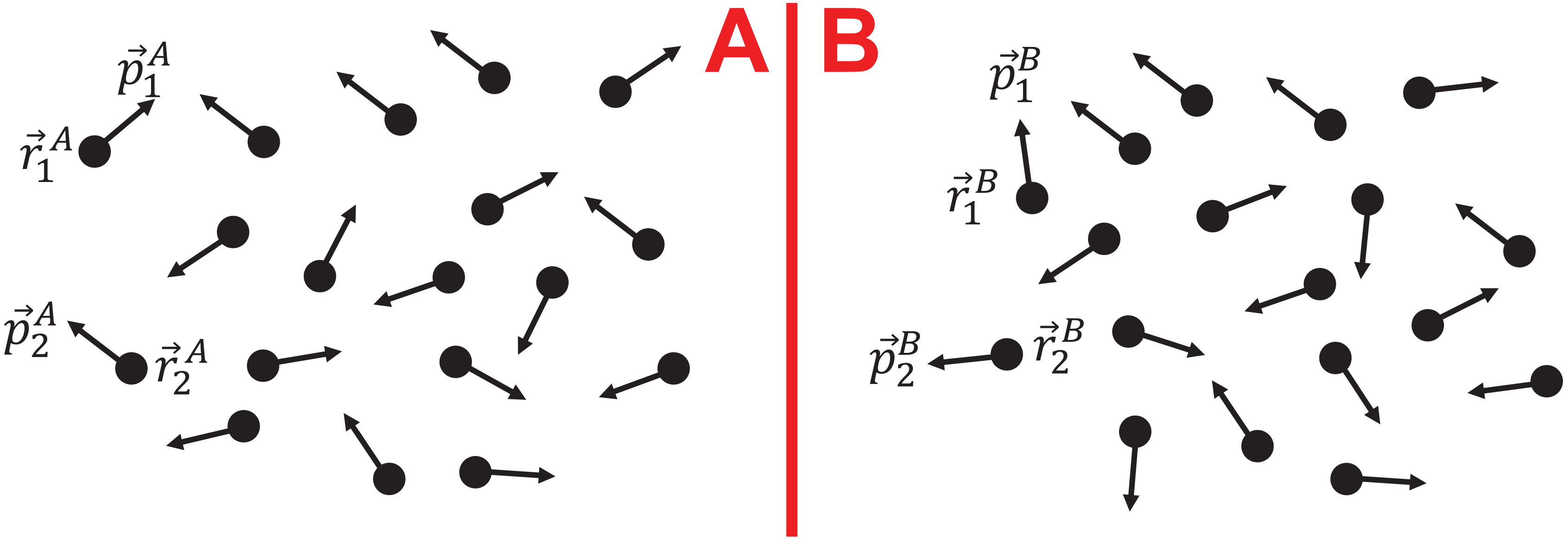
$$\rho(\vec{r}_1,\vec{r}_2,\ldots;\vec{p}_1,\vec{p}_2,\ldots;t)=\prod_i \delta(\vec{r}_i-\vec{r}_i^{\,A}(t))\delta(\vec{p}_i-\vec{p}_i^{\,A}(t))$$

Dirac δ function $\int \mathrm{d}x\,\delta(x-x_0)f(x)=f(x_0)$

Note that $\int \mathrm{d}\Gamma\,\rho\big(\vec{\Gamma}\big)=\int \mathrm{d}r^{3N}\mathrm{d}p^{3N}\,\rho(\{\vec{r}_i\},\{\vec{p}_i\})=1$

Characterizing two microstates

- Why is thinking in terms of the phase space useful?
- Mixture of two single microstates: a statistical ensemble



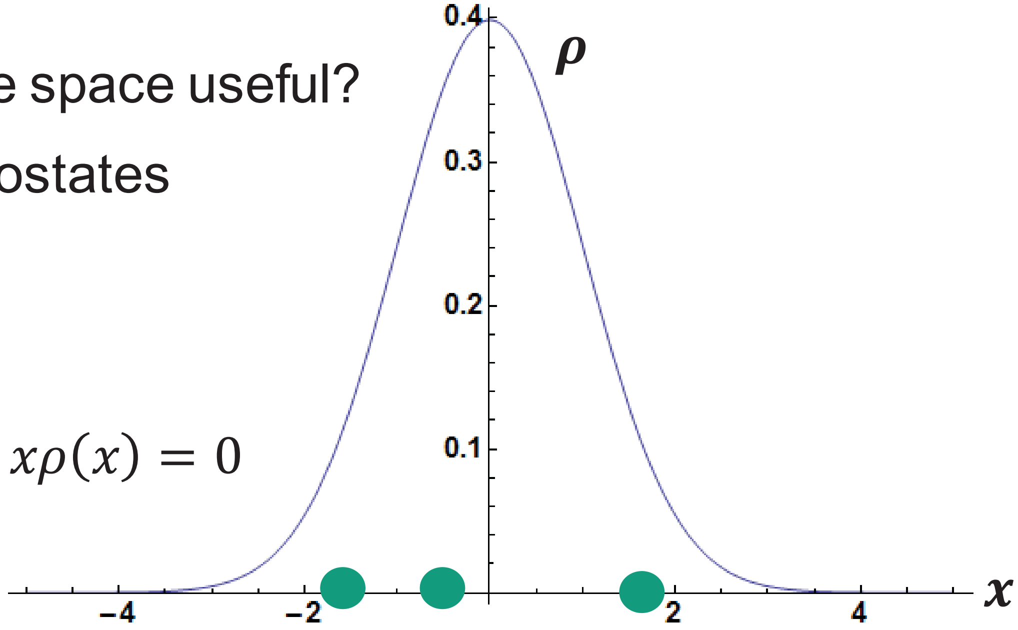
$$\rho(\vec{r}_1, \vec{r}_2, \dots; \vec{p}_1, \vec{p}_2, \dots; t) = w_A \prod_i \delta(\vec{r}_i - \vec{r}_i^{\,A}(t))\delta(\vec{p}_i - \vec{p}_i^{\,A}(t)) + w_B \prod_i \delta(\vec{r}_i - \vec{r}_i^{\,B}(t))\delta(\vec{p}_i - \vec{p}_i^{\,B}(t))$$

$$\boxed{w_A + w_B = 1}$$

Characterizing an ensemble of microstates

- Why is thinking in terms of the phase space useful?
- Mixture of an infinite number of microstates
- Useful to think about a single particle in 1 dimension first

$$\langle x \rangle = \int \mathrm{d}x \, x\rho(x) = 0$$



- Observables are obtained as phase-space (ensemble) averages

$$\boxed{\langle O \rangle_\rho(t) = \int \mathrm{d}^{6N}\Gamma \, O(\vec{\Gamma})\rho(\vec{\Gamma};t)}$$

$$\vec{\Gamma} = (\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots; \vec{p}_1, \vec{p}_2, \vec{p}_3, \ldots) = (\{\vec{r}_i\}, \{\vec{p}_i\})$$

$$\vec{\Gamma} = (\{r_\alpha\}, \{p_\alpha\})$$

- $O(\vec{\Gamma})$ is called a phase variable

Time evolution of ρ: the Liouville theorem

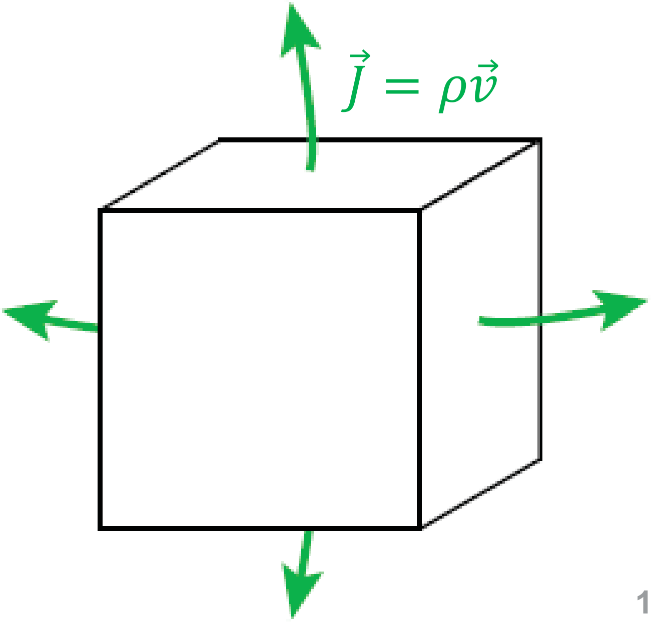
- Hamilton's equations of motion:

$$H(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots;\vec{p}_1,\vec{p}_2,\vec{p}_3,\ldots)=\sum_i \frac{\vec{p}_i^{\,2}}{2m}+U(\vec{r}_1,\vec{r}_2,\vec{r}_3,\ldots)$$

$$\frac{\partial\vec{r}_i}{\partial t}=\frac{\partial H}{\partial\vec{p}_i}\ \text{and}\ \frac{\partial\vec{p}_i}{\partial t}=-\frac{\partial H}{\partial\vec{r}_i}\qquad\left(\vec{v}=\frac{\vec{p}}{m}\ \text{and}\ m\vec{a}=\vec{F}\right)$$

- Probability conservation $\int \mathrm{d}^{6N}\Gamma\,\rho(\vec{\Gamma})=1$ gives rise to the continuity equation

$$\frac{\partial\rho}{\partial t}=-\nabla\cdot\vec{J}$$



- From this we can derive the Liouville theorem

$$\frac{\partial\rho}{\partial t}+\frac{\partial\rho}{\partial\vec{r}_i}\cdot\frac{\partial H}{\partial\vec{p}_i}-\frac{\partial\rho}{\partial\vec{p}_i}\cdot\frac{\partial H}{\partial\vec{r}_i}\equiv 0$$

The microcanonical ensemble: Equilibrium ρ^{eq}

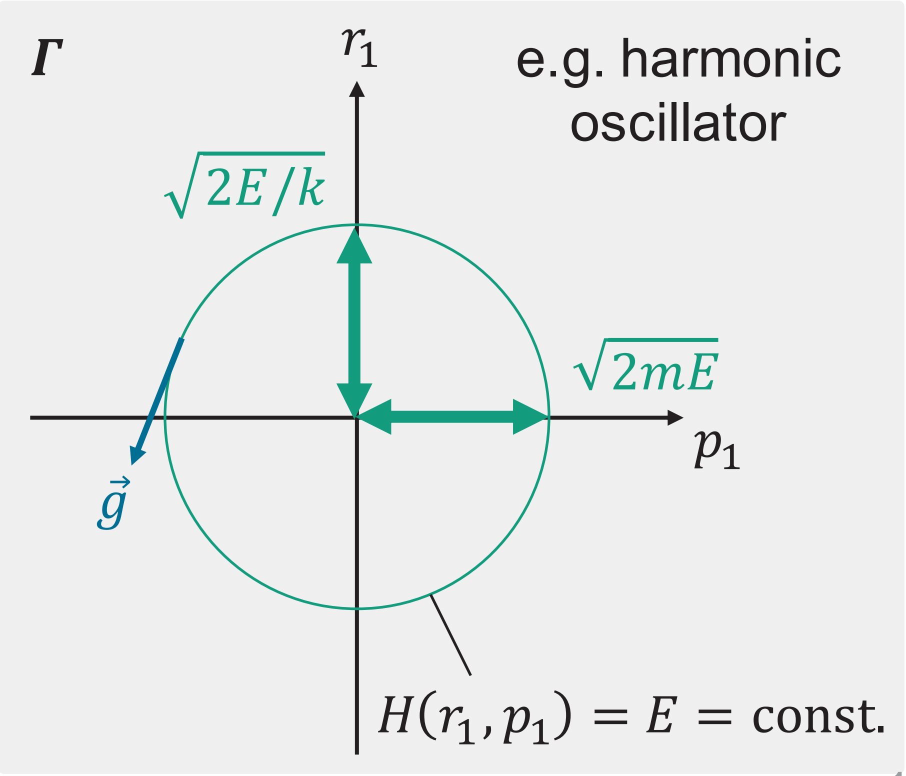
- Equilibrium is stationary: $\frac{\partial \rho^{\mathrm{eq}}}{\partial t} \equiv 0$

$$\frac{\partial \rho^{\mathrm{eq}}}{\partial \vec{r}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho^{\mathrm{eq}}}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{r}_i} = \underbrace{\frac{\partial \rho^{eq}}{\partial \vec{\Gamma}} \cdot \vec{g}}_{\textbf{Derivative, projected onto the surface of constant energy}} \equiv 0 \quad \Bigg| \quad \vec{g} = \begin{pmatrix} \partial H / \partial \vec{p}_i \\ -\partial H / \partial \vec{r}_i \end{pmatrix} \quad \Bigg| \quad \vec{g} \cdot \frac{\partial H}{\partial \vec{\Gamma}} = 0$$

- Derivative vanishes if phase-space density is constant on

$$\boxed{\boldsymbol{H(\vec{\Gamma}) = E}}$$

- **All points in phase-space have equal weight**



The microcanonical ensemble: Equilibrium ρ^{eq}

- Equilibrium is stationary: $\frac{\partial \rho^{\mathrm{eq}}}{\partial t} \equiv 0$
- This means: **All points in phase-space have equal weight**

$$\rho^{\mathrm{eq}}(\vec{\Gamma}; E) = \begin{cases} 1/\Omega(E), & H(\vec{\Gamma}) = E \\ 0, & \text{else} \end{cases}$$

Phase space volume

$$\Omega(E) = \int_{H(\vec{\Gamma})=E} \mathrm{d}^{6N}\Gamma$$

Entropy

- All points in phase space have equal weight because we do not know anything about our system, except the total energy E
- Is it possible to quantify our amount of knowledge?
- Entropy

$$\boxed{S[\rho] = -k \int \mathrm{d}^{6N}\Gamma \; \rho \ln(\rho)}$$

- Properties: 1) Maximum for equal probabilities, 2) Not affected by states with zero probability, 3) Conditional probabilities

nonequilibrium

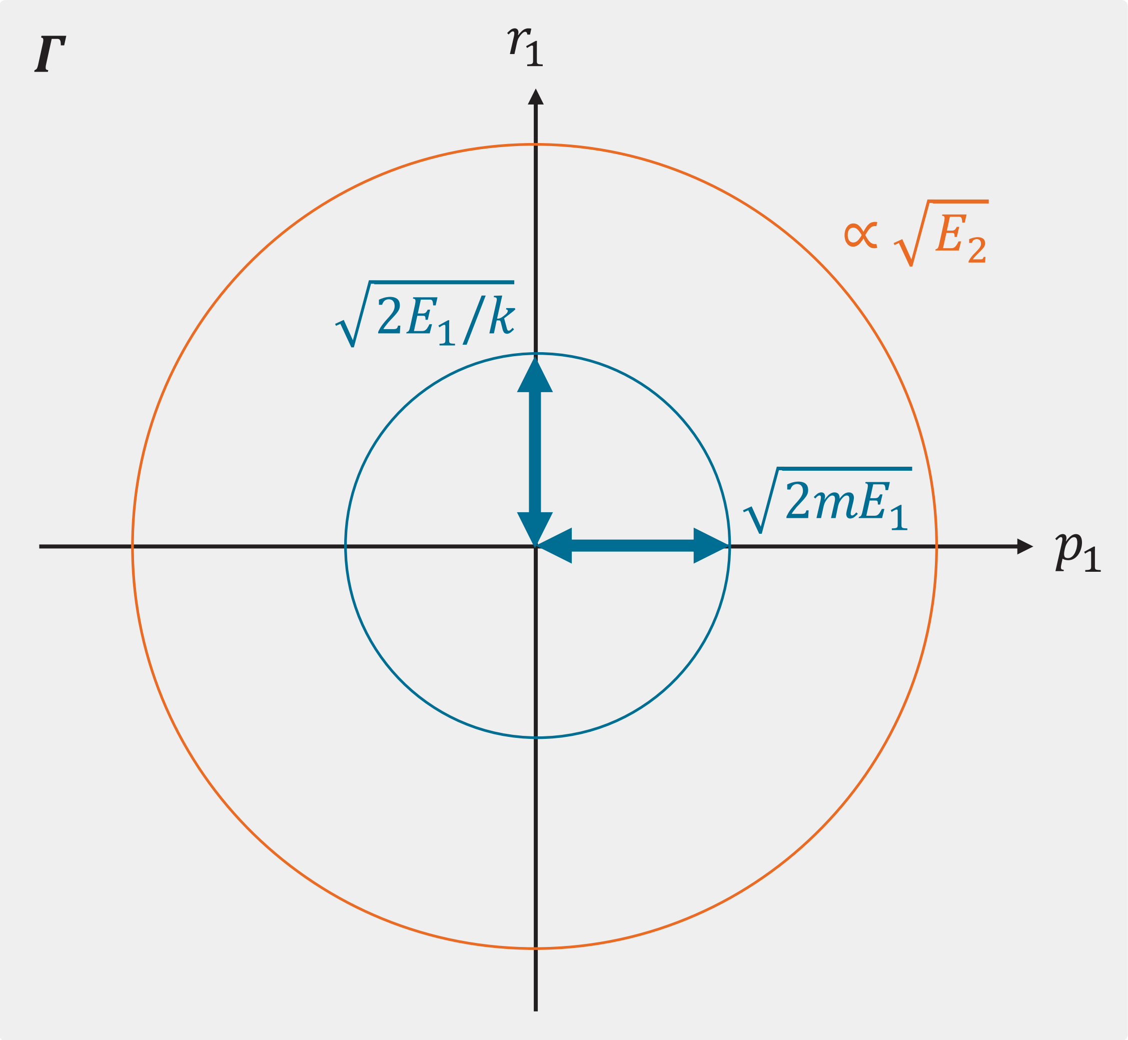
- Equilibrium phase-space density maximizes S under the constraint $H(\vec{\Gamma}) = E$
- Equilibrium entropy: $S^{\mathrm{eq}}(E) = -k \int_{H(\vec{\Gamma})=E} \mathrm{d}^{6N}\Gamma \; \frac{1}{\Omega(E)} \ln\left(\frac{1}{\Omega(E)}\right)$

$$\boxed{S^{\mathrm{eq}}(E) = k \ln \Omega(E)}$$

equilibrium

Entropy

- Ensemble of a single harmonic oscillator $E = \frac{p^2}{2m} + \frac{1}{2}kr^2 = \text{const.}$

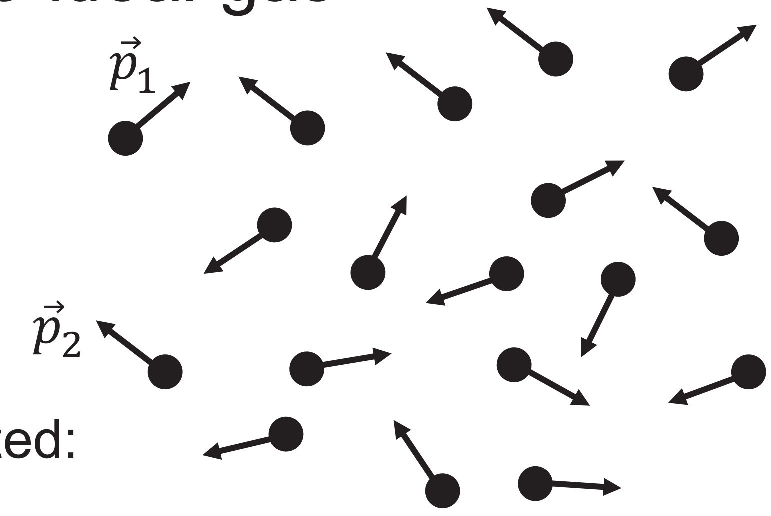


$$S^{\text{eq}}(E) = k \ln \Omega(E)$$

$$\Omega(E) \propto \sqrt{E}$$

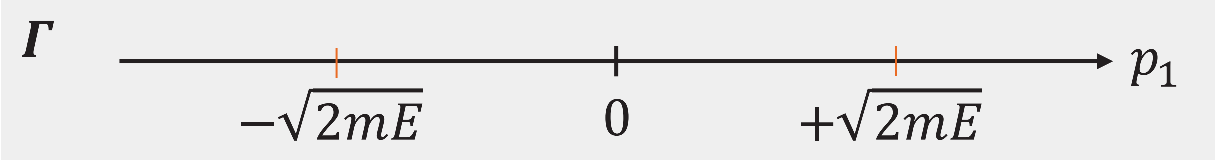
$$S^{\text{eq}}(E) \propto \ln E$$

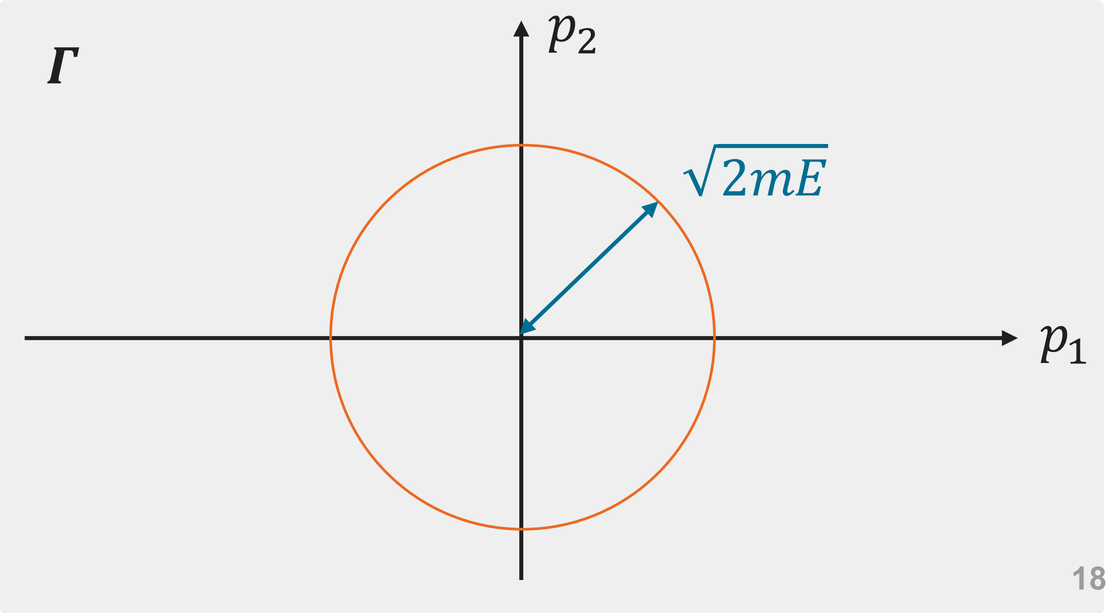
The microcanonical ensemble: The ideal gas



- For the ideal gas $H(\{\vec{r}_i\};\{\vec{p}_i\}) = \sum_i \frac{\vec{p}_i^{\,2}}{2m}$
- In 1 dimension $p_1 = \pm\sqrt{2mE}$ equally weighted:

$$\rho^{\mathrm{eq}}(r_1;p_1;E) \propto \delta\left(p_1 - \sqrt{2mE}\right) + \delta(p_1 + \sqrt{2mE})$$





- In 2 dimensions $p_1^2 + p_2^2 = 2mE$

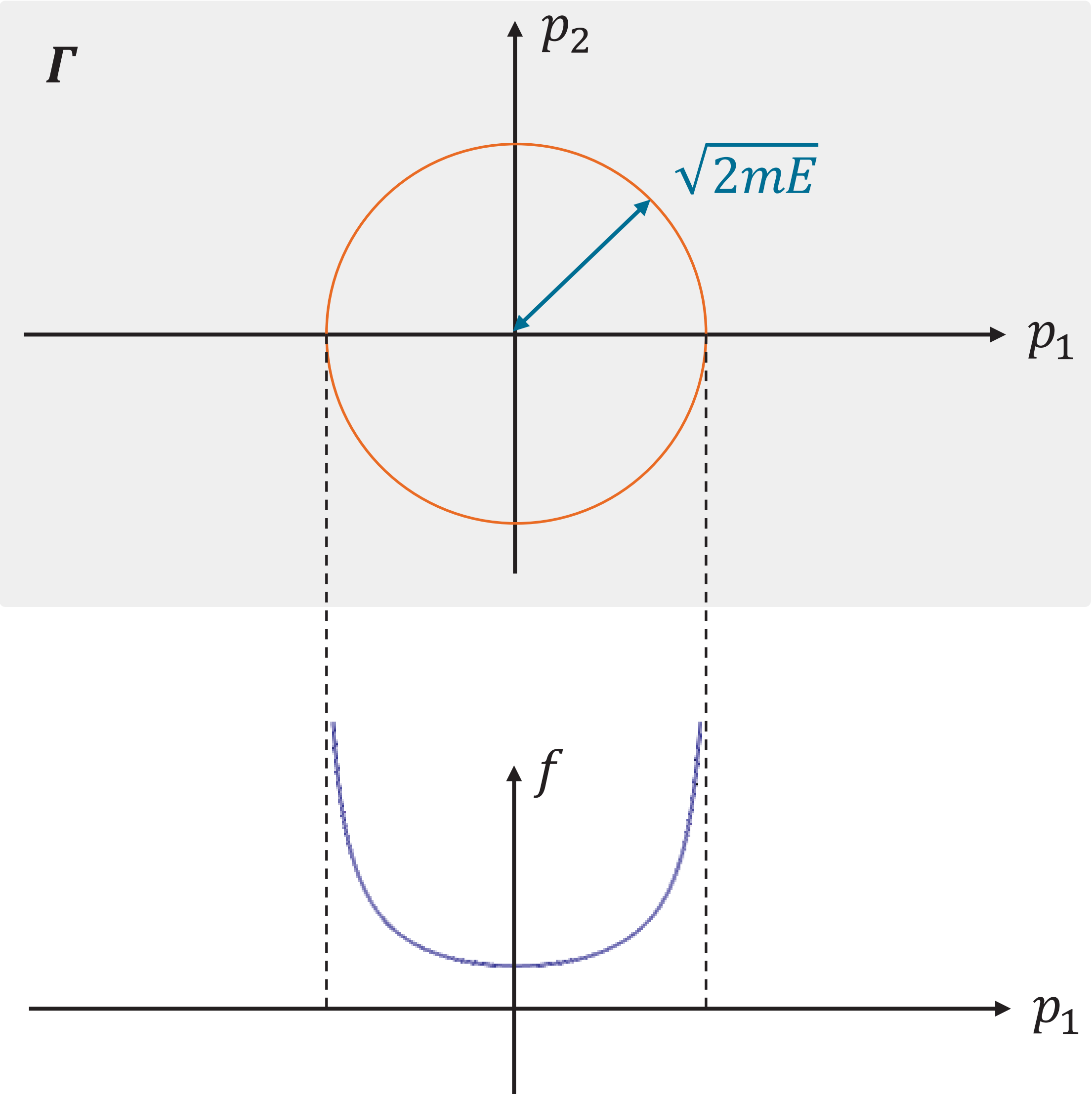
The microcanonical ensemble: The ideal gas

- Two particles:
  Integrate out p_2

- $f(p_1) = \int \mathrm{d}p_2 \, \rho^{\mathrm{eq}}(p_1, p_2; E)$

- $f(p_1) \propto \frac{1}{\sqrt{2mE - p_1^2}}$

- Not extremely useful for few degrees of freedom



The microcanonical ensemble: Coarse graining

- N particles: $\rho^{\mathrm{eq}}(\{\vec{p}_i\}; E) \propto \frac{1}{\sqrt{2mE}^{3N-2}} \delta\left(\sum_i \vec{p}_i^{\,2} - 2mE\right)$

- Find the probability distribution for p_1
- Average over $p_2, p_3, \ldots$; compute marginal probability distribution

$$f(p_1; E) = \int \prod_{\alpha>1} \mathrm{d}p_\alpha \, \rho^{\mathrm{eq}}(\{p_\alpha\}; E)$$

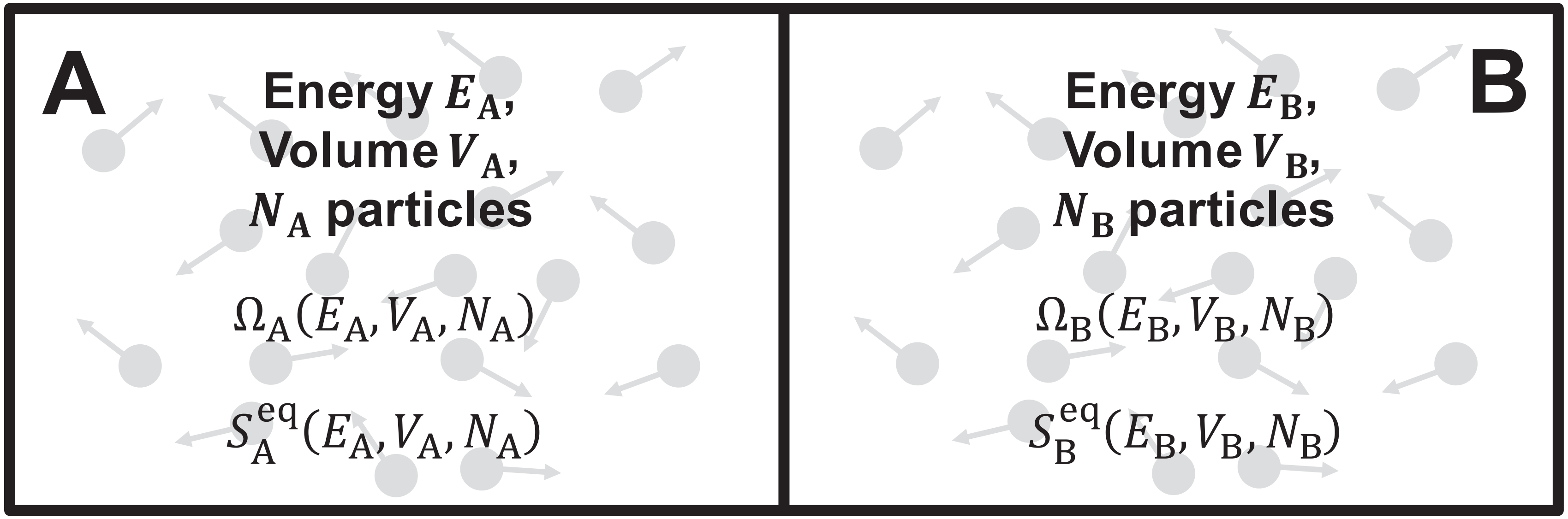
- We get $f(p_1; E) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(-\frac{{p_1}^2}{2m} \frac{3N}{2E}\right)$

$$= \frac{1}{\sqrt{2\pi m k_{\mathrm{B}} T}} \exp\left(-\frac{{p_1}^2}{2m k_{\mathrm{B}} T}\right)$$

$$\boxed{k_{\mathrm{B}} T = \frac{2}{3} \frac{E}{N}}$$

Temperature, pressure, and chemical potential

- Entropy depends on the observer! Divide the system into two parts



A

Energy E_A, Volume V_A, N_A particles

$\Omega_\mathrm{A}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A})$

$S_\mathrm{A}^\mathrm{eq}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A})$

B

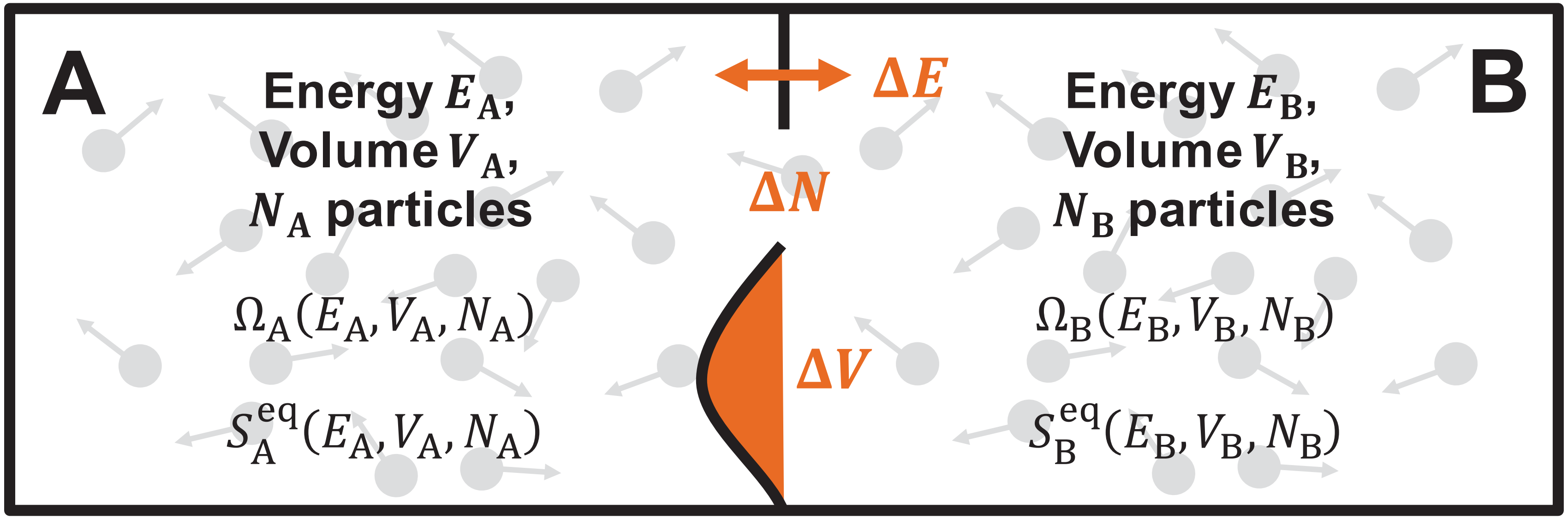
Energy E_B, Volume V_B, N_B particles

$\Omega_\mathrm{B}(E_\mathrm{B}, V_\mathrm{B}, N_\mathrm{B})$

$S_\mathrm{B}^\mathrm{eq}(E_\mathrm{B}, V_\mathrm{B}, N_\mathrm{B})$

Temperature, pressure, and chemical potential

- Entropy depends on the observer! Divide the system into two parts



A

Energy E_A, Volume V_A, N_A particles

$\Omega_\mathrm{A}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A})$

$S_\mathrm{A}^\mathrm{eq}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A})$

ΔE

ΔN

ΔV

B

Energy E_B, Volume V_B, N_B particles

$\Omega_\mathrm{B}(E_\mathrm{B}, V_\mathrm{B}, N_\mathrm{B})$

$S_\mathrm{B}^\mathrm{eq}(E_\mathrm{B}, V_\mathrm{B}, N_\mathrm{B})$

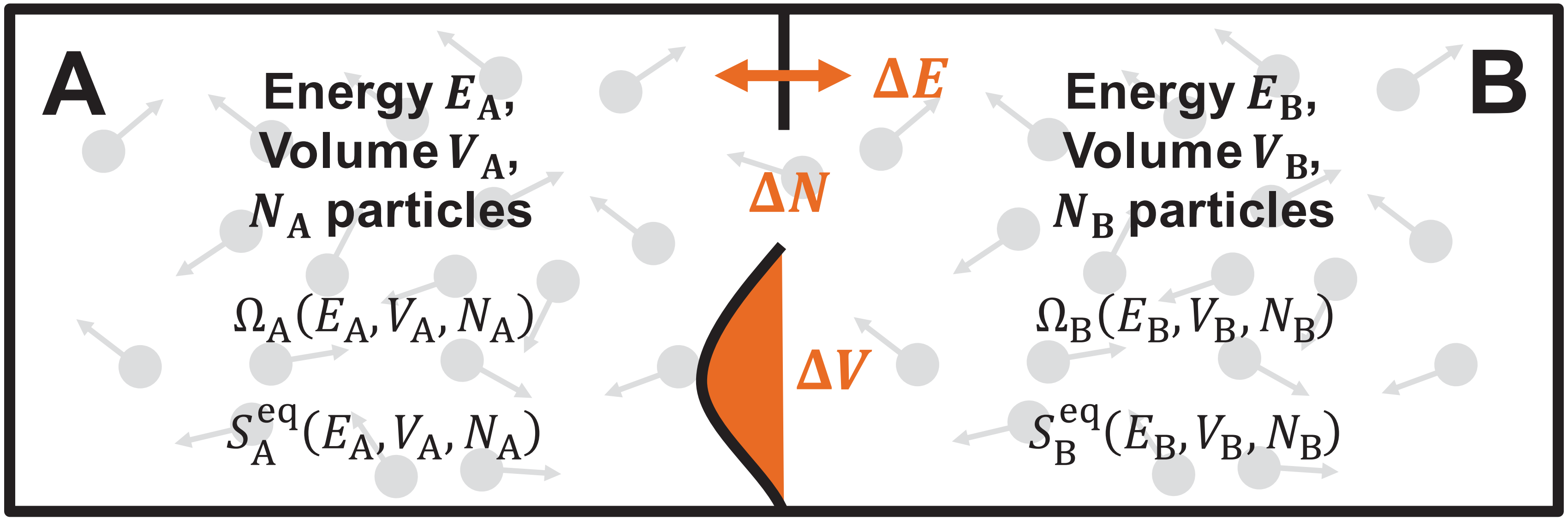
- Generally:

$$\Omega_\mathrm{A}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A})\Omega_\mathrm{B}(E_B, V_B, N_\mathrm{B}) < \Omega(E, V, N)$$

$$S_\mathrm{A}^\mathrm{eq}(E_\mathrm{A}, V_\mathrm{A}, N_\mathrm{A}) + S_\mathrm{B}^\mathrm{eq}(E_\mathrm{B}, V_\mathrm{B}, N_\mathrm{B}) < S^\mathrm{eq}(E, V, N)$$

Temperature, pressure, and chemical potential

- Entropy depends on the observer! Divide the system into two parts



- Maximize $S_A^{eq}(E_A, V_A, N_A) + S_B^{eq}(E - E_A, V - V_A, N - N_A)$ with respect to E, V, N

$$\frac{1}{T_A} = \frac{1}{T_B} \qquad \boxed{\frac{1}{T} = \frac{\partial S}{\partial E}} \qquad \frac{P_A}{T_A} = \frac{P_B}{T_B} \qquad \boxed{\frac{P}{T} = \frac{\partial S}{\partial V}} \qquad \frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \qquad \boxed{-\frac{\mu}{T} = \frac{\partial S}{\partial N}}$$

Probability densities

- Important: Carefully distinguish

$$\begin{tikzcd}
\rho(\{r_\alpha\},\{p_\alpha\},t) \arrow[d, "\text{eq.}"'] \\
\rho^{\mathrm{eq}}(\{r_\alpha\},\{p_\alpha\};E) \arrow[d, "\int\prod_{\alpha>1}\mathrm{d}p_\alpha\,\cdot"'] \\
f(p_1;E)
\end{tikzcd}$$

$\rho(\{r_\alpha\},\{p_\alpha\},t)$

Phase space density

Probability density that the system is in the particular state given by positions r_α and momenta p_α

$\rho^{\mathrm{eq}}(\{r_\alpha\},\{p_\alpha\};E)$

Equilibrium phase space density

Probability density that a system with energy E is in the state given by positions r_α and momenta p_α

$f(p_1;E)$

Marginal probability distribution

Probability density that system is in any of the many states where the first particle has momentum p_1

Probability densities and entropies

- Important: Carefully distinguish

$$\begin{tikzcd} \rho(\{r_\alpha\},\{p_\alpha\},t) \arrow[d, "\text{eq.}"'] \\ \rho^{\mathrm{eq}}(\{r_\alpha\},\{p_\alpha\};E) \arrow[d, "\int \prod_{\alpha>1} \mathrm{d}p_\alpha \cdot"'] \\ f(p_1;E) \end{tikzcd}$$

Nonequilibrium entropy

$$S[\rho] = -k_B \int \mathrm{d}^{6N}\Gamma\, \rho \ln(\rho)$$

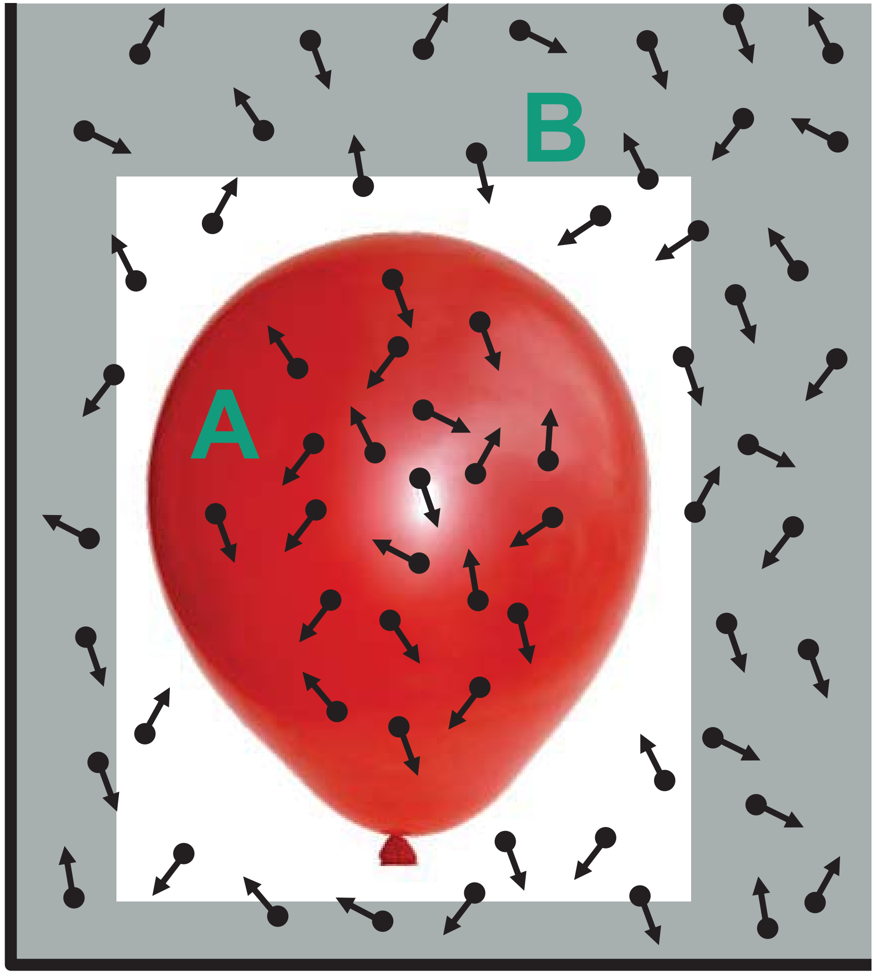
Equilibrium entropy

$$S^{\mathrm{eq}}(E) = k_B \ln \Omega(E)$$

Marginal probability distribution

$$S^{\mathrm{eq}}(E) = -k_B \int \mathrm{d}p_1\, f(p_1;E) \ln f(p_1;E)$$

The canonical ensemble



- Consider just a small part **A** of a large system **A** ∪ **B** (i.e. $N_A \ll N_B$)
- Average over the boring part **B**

$$\mathcal{P}_\mathrm{A} \cdot = \frac{1}{N_A!} \int \prod_{\alpha \in \mathrm{B}} \mathrm{d}r_\alpha \mathrm{d}p_\alpha \cdot$$

- Ideal gas: Marginal probability density for **A**

$$f\left(p_1, p_2, p_3, \dots, p_{N_A}; T\right) = \mathcal{P}_\mathrm{A} \rho^\mathrm{eq}$$

$$\propto \exp\left(-\beta H\left(p_1, p_2, p_3, \dots, p_{N_A}\right)\right)$$

$\frac{1}{\beta} = k_\mathrm{B} T = \frac{2}{3} \frac{E_B}{N_B}$, **B** is the heat bath

- Possible to show that generally $f(\{r_\alpha\}, \{p_\alpha\}; T) \propto \exp\left(-\beta H(\{r_\alpha\}, \{p_\alpha\})\right)$

Canonical ensemble averages

- $f(\vec{Q};T) = \frac{1}{Z}\exp\left(-\beta H(\vec{Q})\right)$ where $\vec{Q} = \{\vec{r}_i\},\{\vec{p}_i\}$ is a **marginal prob. density**

- Canonical ensemble averages: Average with weight $f(\vec{Q};T)$

$$\langle O\rangle_f(T,V,N) = \int \mathrm{d}^{6N}Q\; O(\vec{Q})f(\vec{Q}) = \frac{1}{Z}\int \mathrm{d}^{6N}Q\; O(\vec{Q})\,\exp\left(-\beta H(\vec{Q})\right)$$

with $\boxed{Z = \int \mathrm{d}^{6N}Q\,\exp\left(-\beta H(\vec{Q})\right)}$ the partition function

- Why is the normalization factor Z useful? Can be used to compute many statistical quantities.

Canonical ensemble: The free energy

- Canonical probability density $f(\vec{Q};T)$
- Canonical entropy $S[f] = -k_B \int \mathrm{d}^{6N}Q\ f(\vec{Q}) \ln f(\vec{Q})$
- Maximize $S[f]$, constraints $E = \langle H\rangle_f \equiv \int \mathrm{d}^{6N}\,Q\ H(\vec{Q}) f(\vec{Q})$ and $\int \mathrm{d}^{6N}Q\ f(\vec{Q}) = 1$

$$F[f] = -\int \mathrm{d}^{6\mathrm{N}}Q\ f(\vec{Q}) \ln f(\vec{Q}) + \beta\left(\int \mathrm{d}^{6N}Q\ H(\vec{Q}) f(\vec{Q}) - E\right) + \alpha\left(\int \mathrm{d}^{6N}Q\ f(\vec{Q}) - 1\right)$$

$$f(\vec{Q}) = \frac{1}{Z}\exp\left(-\beta H(\vec{Q})\right) \qquad \text{with } Z = \exp(1-\alpha)$$

- Identical to minimizing $\boxed{A = \min_f\left(\langle H\rangle_f - TS[f]\right)}$ subject to $\int \mathrm{d}Q\ f(\vec{Q}) = 1$

This is the free energy $A = E - TS \equiv -k_B T \ln Z$

Example: Ideal gas

- Hamiltonian:

$$H(\{\vec{r}_i\},\{\vec{p}_i\}) = \sum_i \frac{\vec{p}_i^{\,2}}{2m}$$

- Partition function:

$$Z^{\mathrm{id}} = \frac{1}{N!}\left(\frac{L}{\lambda}\right)^{3N}$$ with $\lambda = \frac{h}{2m\pi kT}$, the de Broglie wavelength

- Free energy:

$$A^{\mathrm{id}}(T,V,N) = NkT(\ln\rho\lambda^3 - 1)$$

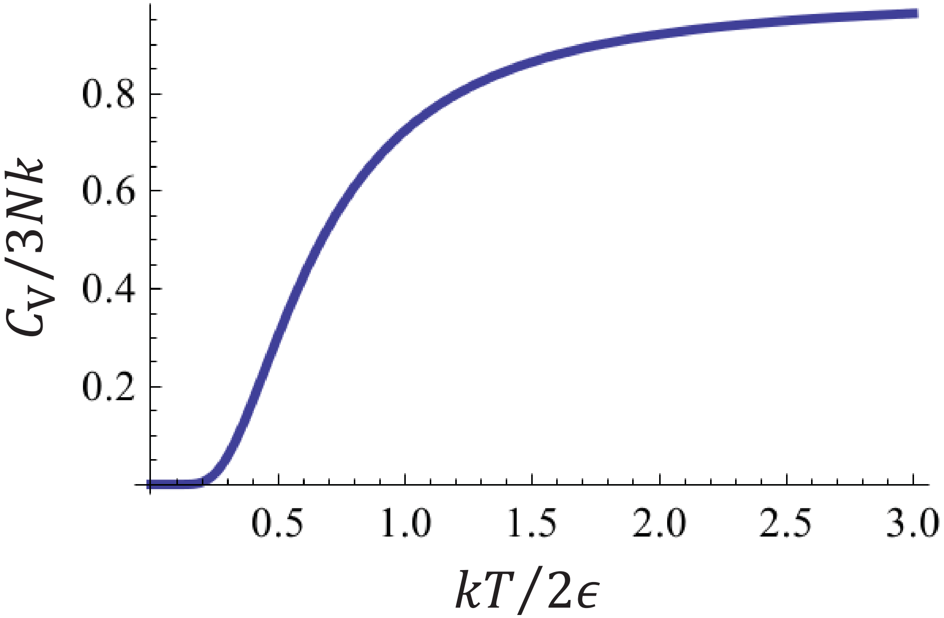
- Important because for many Hamiltonians $H(\{\vec{r}_i\},\{\vec{p}_i\}) = T(\{\vec{p}_i\}) + U(\{\vec{r}_i\})$:

$$Z = \frac{1}{h^{3N}N!}\int \mathrm{d}^{3N}p\, \exp\bigl(-\beta T(\{\vec{p}_i\})\bigr)\int \mathrm{d}^{3N}r\, \exp\bigl(-\beta U(\{\vec{r}_i\})\bigr) = Z^{\mathrm{id}}Z^{\mathrm{conf}}$$

Example: Heat capacity of solids

- Einstein solid: Independent 3D quantum harmonic oscillators
- Quantum harmonic oscillator: $E_n = \epsilon\left(n + \frac{1}{2}\right)$
- Partition function: $Z = z^{3N}$ with $z = \sum_{n=0}^{\infty} \exp(-\beta E_n) = 1/2\sinh\left(\frac{1}{2}\beta\epsilon\right)$
- Energy $\langle E\rangle = 3N\frac{\epsilon}{2}\coth\left(\frac{1}{2}\beta\epsilon\right)$
- Heat capacity

$$C_\mathrm{V} = \frac{\partial\langle E\rangle}{\partial T} = 3N\,k\left(\frac{\epsilon}{2kT}\right)^2/\sinh^2\left(\frac{\epsilon}{2kT}\right)$$



Microcanonical and canonical ensembles

$$\Omega(E) = \int\limits_{H(\vec{\Gamma})=E} \mathrm{d}^{6N}\Gamma$$

$$S^{\mathrm{eq}}(E) = k \ln \Omega(E, V, N)$$

$$\rho^{\mathrm{eq}}(\vec{\Gamma}; E) = \frac{1}{\Omega(E)} \begin{cases} 1, & H(\vec{\Gamma}) = E \\ 0, & \text{else} \end{cases}$$

$$Z(T) = \int \mathrm{d}^{6N}Q \exp\left(-\frac{H(\vec{Q})}{k_{\mathrm{B}}T}\right)$$

$$A(T) = -kT \ln Z(T, V, N)$$

$$f(\vec{Q}; T) = \frac{1}{Z(T)} \mathrm{e}^{-\frac{H(\vec{Q})}{k_{\mathrm{B}}T}}$$

$$\xrightarrow{\quad \frac{1}{N!}\int \prod_{\alpha\in\mathrm{bath}} \mathrm{d}r_\alpha \mathrm{d}p_\alpha \cdot \quad}$$

The canonical ensemble: Alternative derivation

- Probability for small part **A** of **A** ∪ **B** to be in state with energy E_A

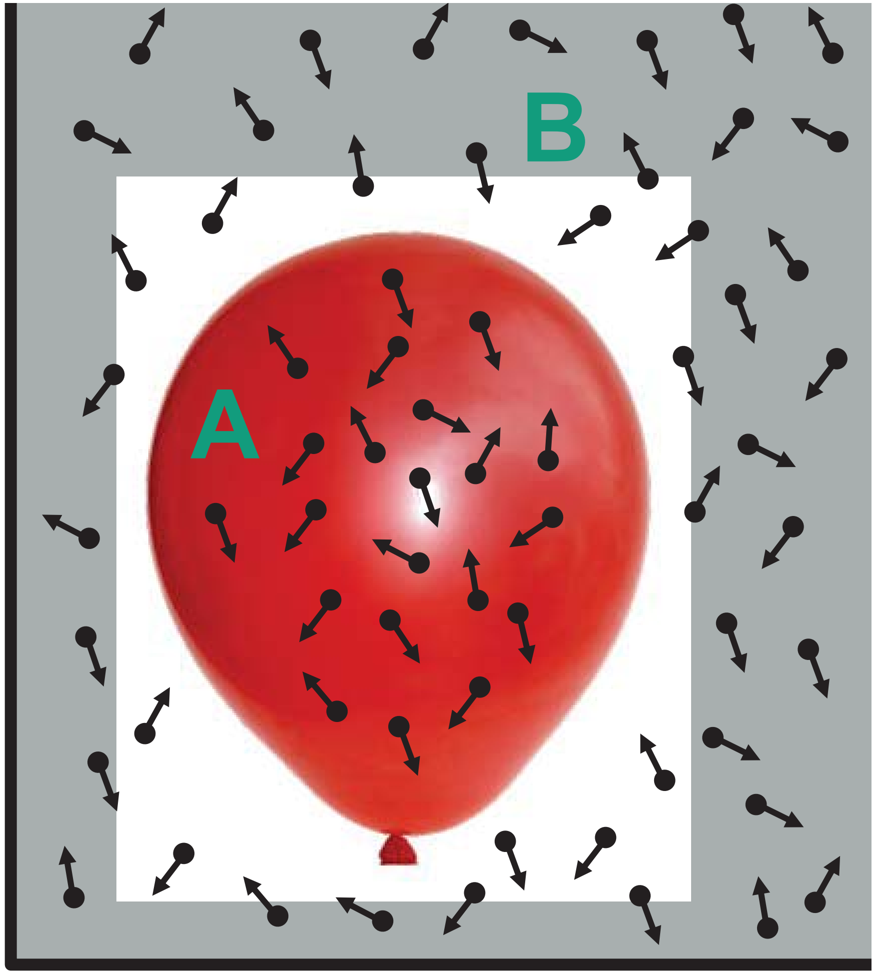
$$f(E_\mathrm{A}) \propto \Omega_\mathrm{B}(E - E_\mathrm{A})$$

$$= \exp\left(\frac{S_\mathrm{B}(E - E_\mathrm{A})}{k}\right)$$

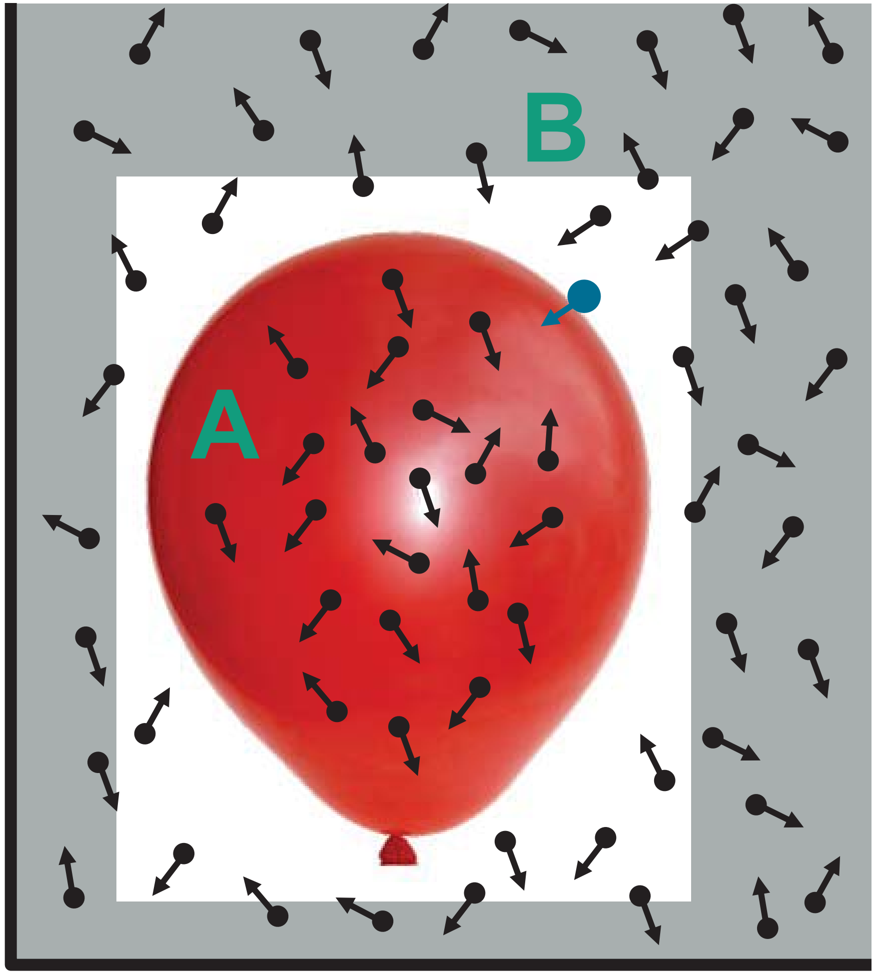
$$\propto \exp\left(-\frac{1}{k}\frac{\partial S_\mathrm{B}}{\partial E}E_\mathrm{A}\right)$$

if $E_\mathrm{A} \ll E$

$$f(E_\mathrm{A}) = \frac{1}{Z}\exp\left(-\frac{E_\mathrm{A}}{kT_\mathrm{B}}\right)$$



The grand canonical ensemble



- Allow variation in the number of particles N

$$f(E_\mathrm{A},N_A) \propto \Omega_\mathrm{B}(E-E_\mathrm{A},N-N_A)$$

$$= \exp\left(\frac{S_\mathrm{B}(E-E_\mathrm{A},N-N_\mathrm{A})}{k}\right)$$

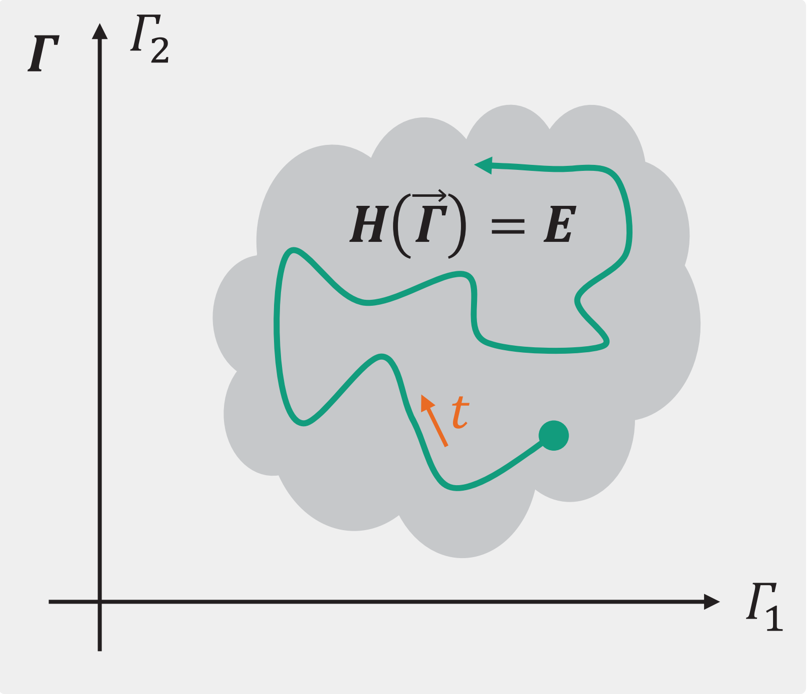
$$\propto \exp\left(-\frac{1}{k}\frac{\partial S_\mathrm{B}}{\partial E}E_\mathrm{A}-\frac{1}{k}\frac{\partial S_\mathrm{B}}{\partial N}N_\mathrm{A}\right)$$

if $E_\mathrm{A} \ll E$ and $N_\mathrm{A} \ll N$

$$f(E_\mathrm{A},N_\mathrm{A}) = \frac{1}{\mathcal{Z}}\exp\left(-\frac{E_\mathrm{A}-\mu N_\mathrm{A}}{kT_\mathrm{B}}\right)$$

- Grand canonical partition function $\mathcal{Z}(T,V,\mu) = \sum_N \int \mathrm{d}^{6N}Q \exp\left(-\frac{H(\vec{Q})-\mu N}{kT}\right)$

Ergodicity

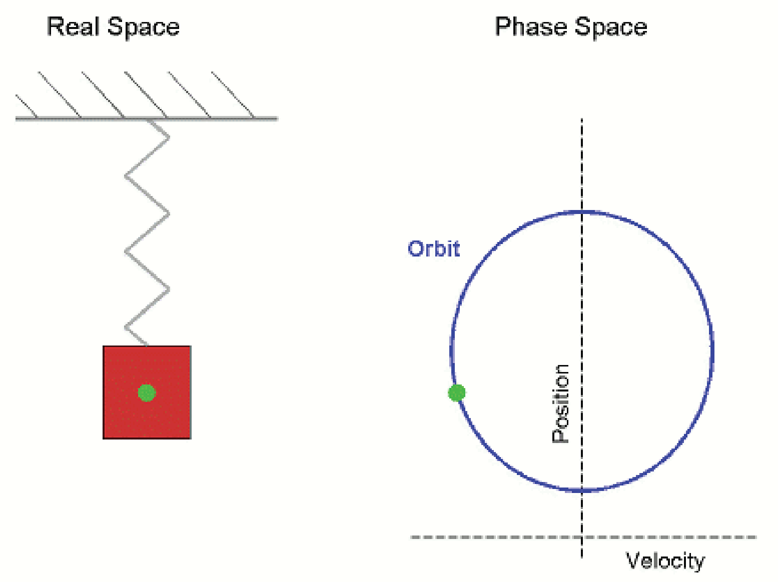


- Ergodicity: “The trajectory of almost every point in phase space passes arbitrarily close to every other point on the surface of constant energy.”[1]

- This implies: Time averages equal microcanonical ensemble averages

$$\boldsymbol{\bar{O} = \langle O \rangle}$$

where $\bar{O} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_0^\tau \mathrm{d}t\, O\left(\vec{\Gamma}(t)\right)$



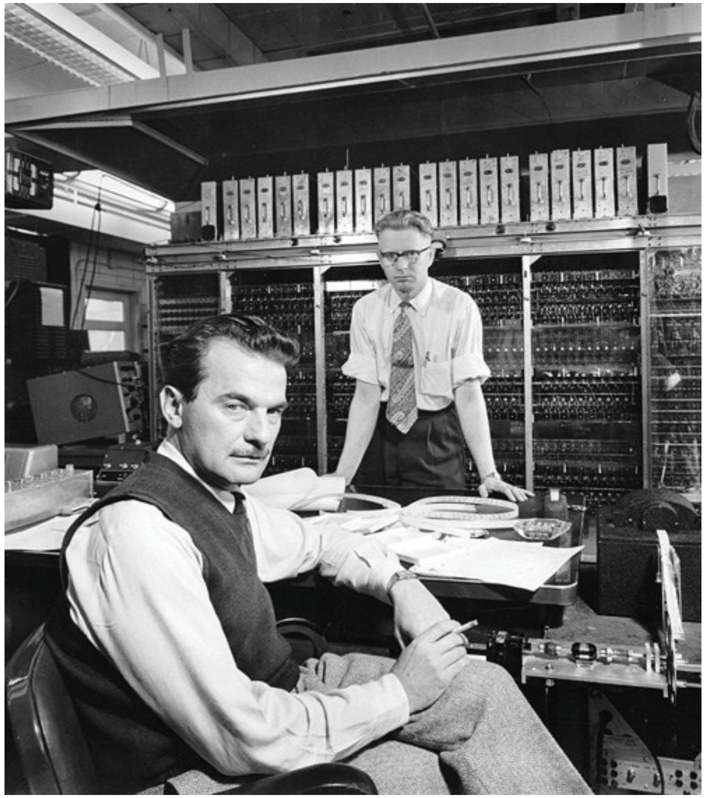
- Difficult (impossible?) to show for most system, it’s usually assumed.

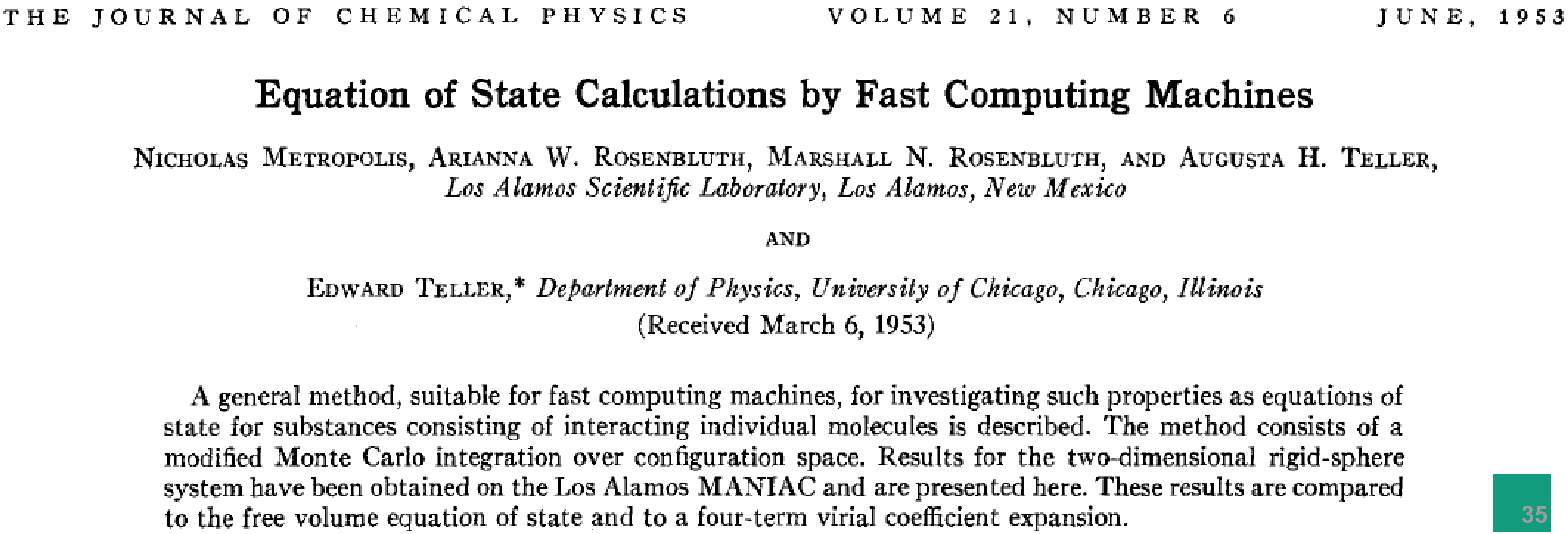
---

[1] see e.g. Sethna p. 66

Computing free energies

- Oldest: Monte-Carlo sampling of $\int \mathrm{d}^{6N}\Gamma \, f(\vec{\Gamma})$ ...
- i.e. Metropolis algorithm





THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 6 JUNE, 1953

Equation of State Calculations by Fast Computing Machines

NICHOLAS METROPOLIS, ARIANNA W. ROSENBLUTH, MARSHALL N. ROSENBLUTH, AND AUGUSTA H. TELLER,
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

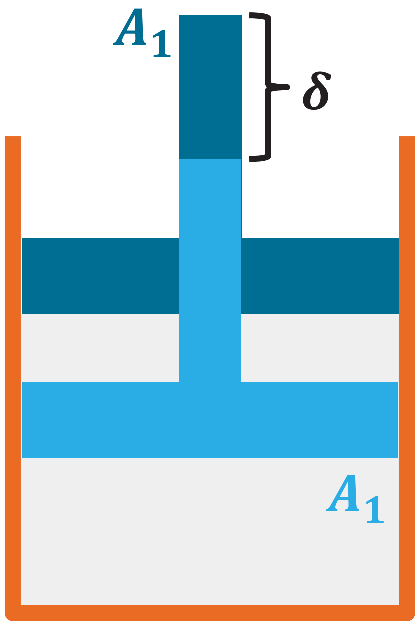
AND

EDWARD TELLER,* *Department of Physics, University of Chicago, Chicago, Illinois*

(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

The Jarzynski equation



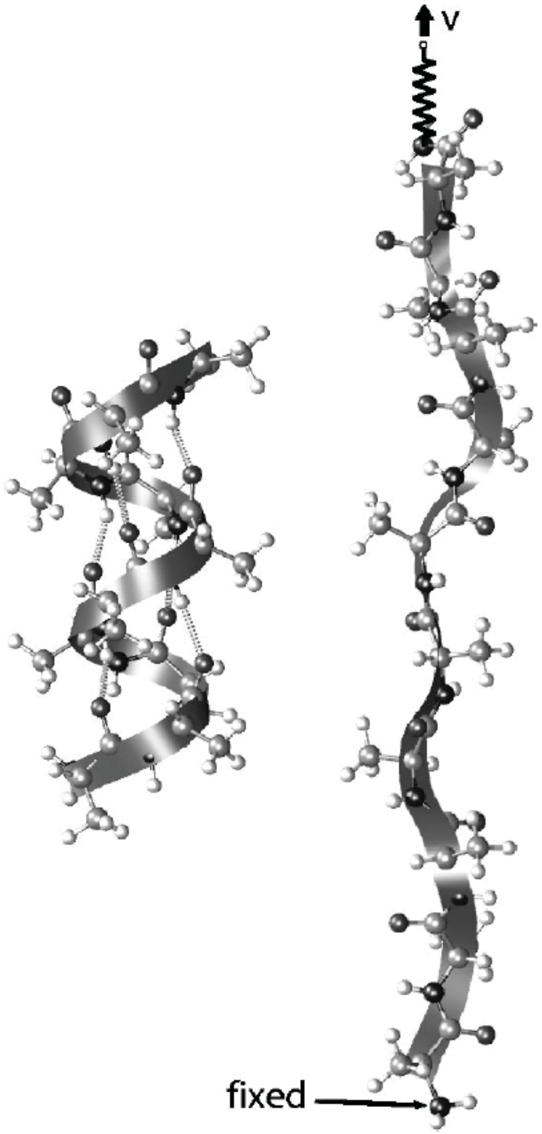
- Perform work W on system, ask how free energy changes ΔA

$$\langle W \rangle \geq \Delta A$$

- But

$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta A)$$

- Work is easy to measure, computations are usually not adiabatic



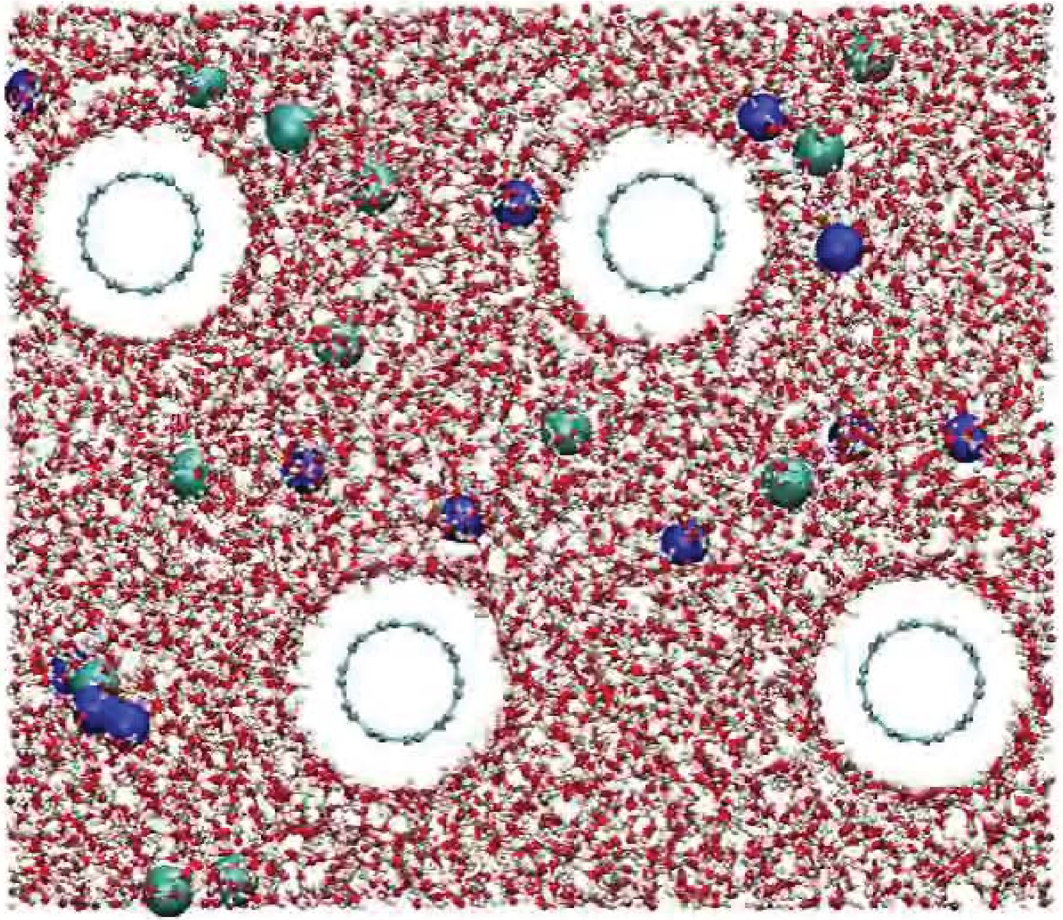
Park, Khalili-Araghi, Tajkhorshid, Schulten, J. Chem. Phys. 119, 3559 (2003)

Jarzynski, Phys. Rev. Lett. 78, 2690 (1997)

Internal constraints: Free energy landscapes

- Remember: Integrating out the bath variables

$$\frac{1}{N!}\int \prod_{\alpha\in\mathrm{bath}} \mathrm{d}r_\alpha \mathrm{d}p_\alpha \cdot$$



- “Bath” can be anything

  e.g. integrate out water,
  keep ions

- M ions: $A(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_M; T)$

Constraints and order parameters: Free energy landscapes

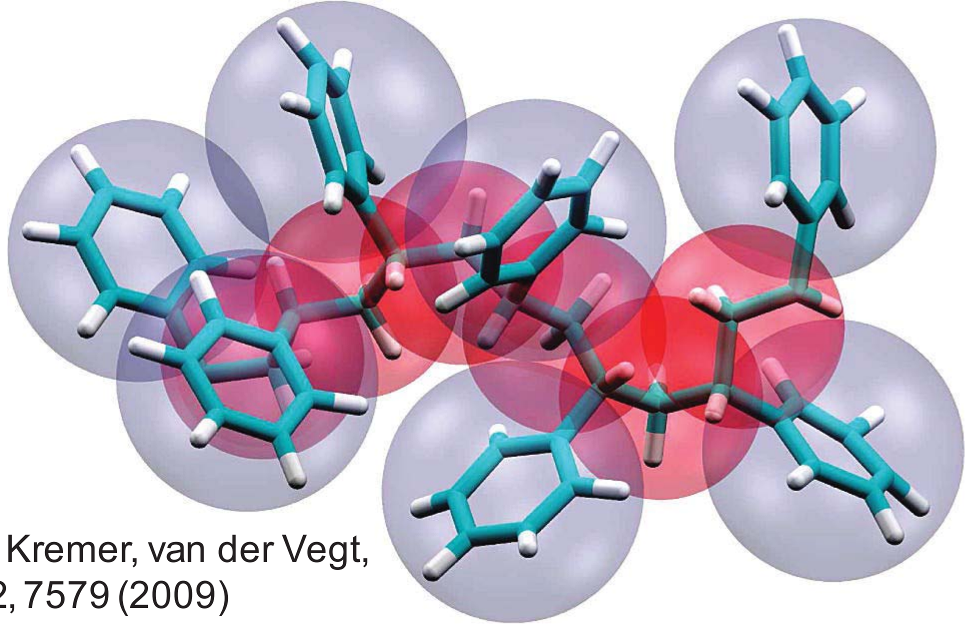
- Formally: $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M$ are constraints, usually called **order parameters** Φ_i or **phase variable** or **collective variable**

- Minimize $A[f] = \langle H \rangle_c - TS[f]$ with $\int \mathrm{d}Q\, f(\vec{Q}) = 1$ and $\Phi_1 = \phi_1(\vec{Q}), \ldots$

- $A(\Phi_1, \Phi_2, \ldots; T) = -k_\mathrm{B}T \ln \int \mathrm{d}^{6N}Q \exp\left(-\beta H(\vec{Q})\right) \delta(\Phi_1 - \phi_1(\vec{Q}))\, \delta(\Phi_2 - \phi_2(\vec{Q})) \ldots$

- Constraints can be complex,
  e.g. center of mass of polymer beads

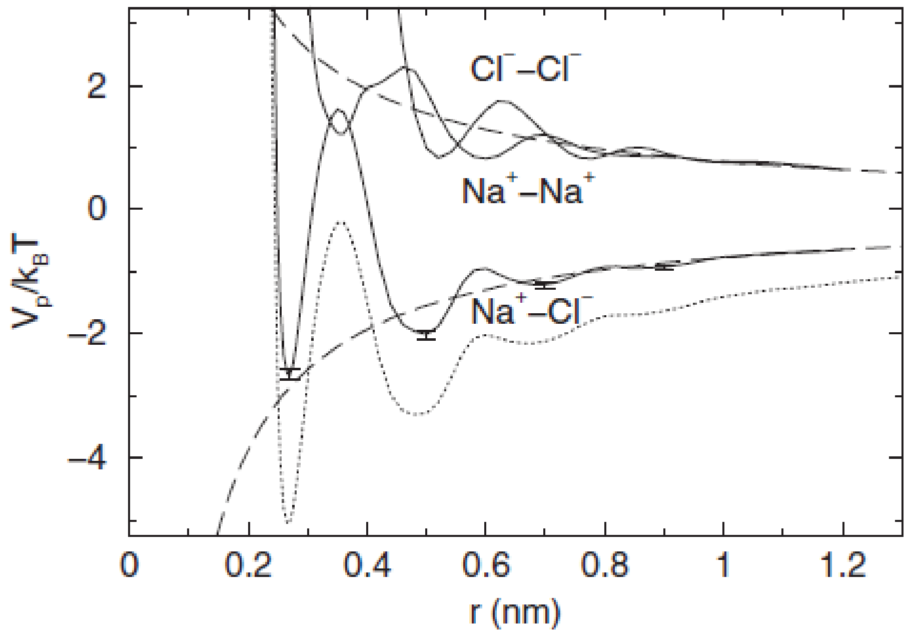
- Actual computation of
  $A(\Phi_1, \Phi_2, \ldots; T)$ is complex

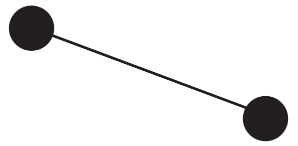


Fritz, Harmandaris, Kremer, van der Vegt, Macromolecules 42, 7579 (2009)

Free energy landscapes

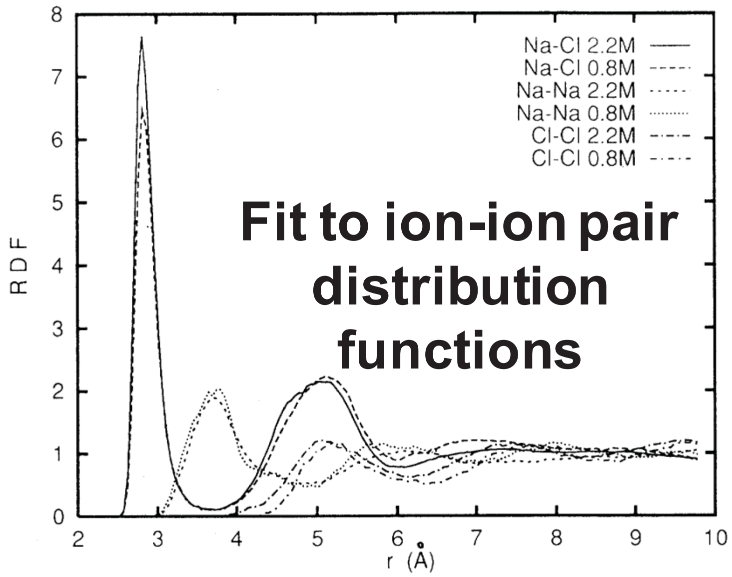
- Example: Na-Cl in water
- Assume pair potential:
  $A(\{\vec{R}_i\};T) = \sum_{I,J} V_\mathrm{p}(|\vec{R}_I - \vec{R}_J|;T)$





Constrain ion-ion distance, measure constraint force

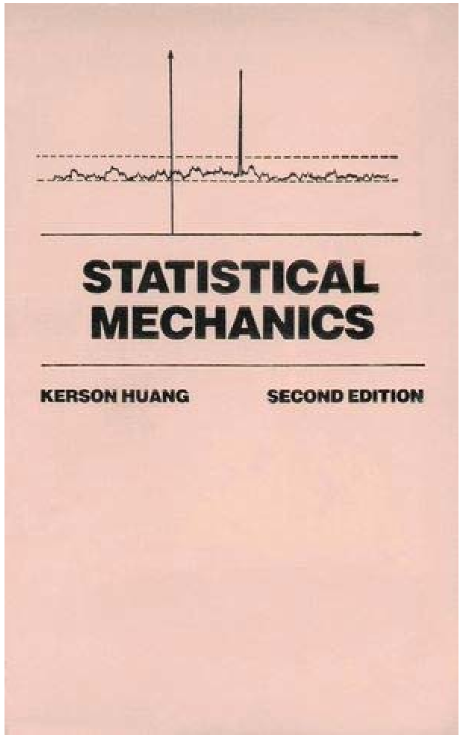
Hess, Holm, van der Vegt, PRL 96, 147801 (2006)

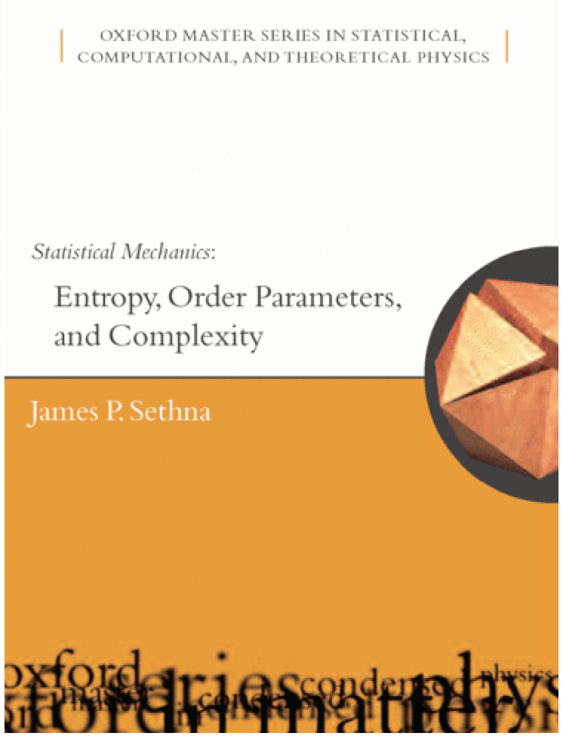


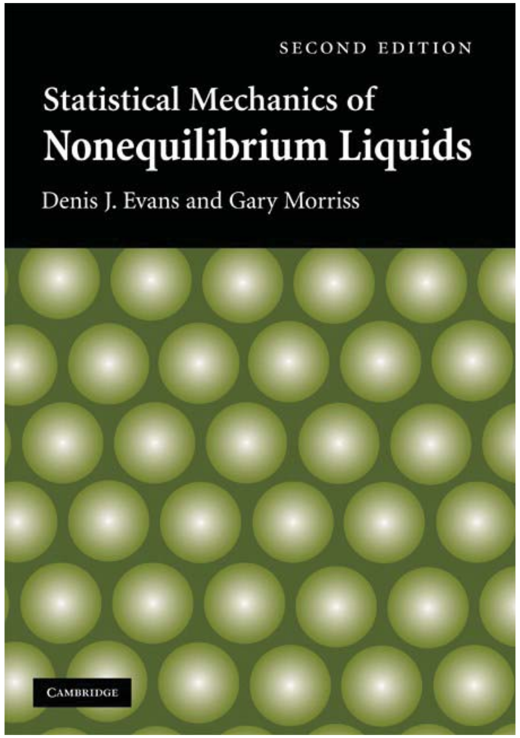
Fit to ion-ion pair distribution functions

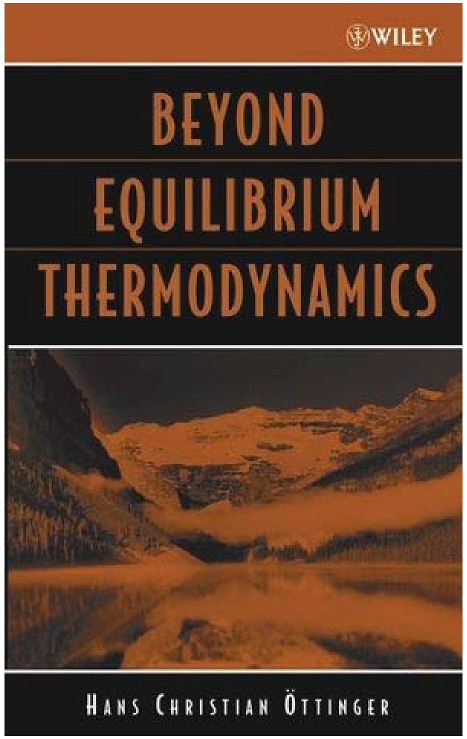
Lyubartsev, Laaksonen, PRE 52, 3730 (1995)

Free electronic version at:
http://pages.physics.cornell.edu/~sethna/StatMech/









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Slide 12:

- Local current $\vec{J} = \rho\vec{v}$
- Total current J_V out of volume V with surface A: $J_V = \int_A \mathrm{d}A\,\vec{J}\cdot\hat{n}$ where $\hat{n}$ is surface normal
- Gauss theorem: $J_V = \int_V d^3r\,\nabla\cdot\vec{J}$
- But: $\frac{\partial\rho_V}{\partial t} = -J_V = -\nabla\cdot\rho\vec{v}$
- But $\nabla\cdot\rho\vec{v} = \frac{\partial}{\partial\vec{r}}\cdot\rho\frac{\partial\vec{r}}{\partial t} + \frac{\partial}{\partial\vec{p}}\cdot\rho\frac{\partial\vec{p}}{\partial t} = \frac{\partial\rho}{\partial\vec{r}}\cdot\frac{\partial H}{\partial\vec{p}} - \frac{\partial\rho}{\partial\vec{p}}\cdot\frac{\partial H}{\partial\vec{r}} + \rho\frac{\partial^2 H}{\partial\vec{r}\partial\vec{p}} - \rho\frac{\partial^2 H}{\partial\vec{p}\partial\vec{r}}$
- Liouville theorem follows

Slide 13:

- The Liouville operator:
$$i\mathcal{L} = \frac{\partial H}{\partial\vec{p}_i}\cdot\frac{\partial}{\partial\vec{r}_i} - \frac{\partial H}{\partial\vec{r}_i}\cdot\frac{\partial}{\partial p_i}$$
- Time evolution:
$$\frac{\partial}{\partial t}\rho = -i\mathcal{L}\rho$$
with formal solution
$$\rho(t) = \exp\big(-i\mathcal{L}(t-t_0)\big)\rho(t_0)$$
- Time evolution of a point $\vec{\Gamma}$ in space-space:
$$\frac{\partial}{\partial t}\vec{\Gamma} = i\mathcal{L}\vec{\Gamma}$$
reduces to Hamilton's equation of motion

Slide 15:

- Property 1): Maximize $S[\rho] = -k\int \mathrm{d}^{6N}\Gamma\,\rho\ln\rho$ with constraint $\int \mathrm{d}^{6N}\,\rho = 1$
$$\frac{\delta\left(\frac{S}{k} - \alpha\int \mathrm{d}^{6N}\,\rho\right)}{\delta\rho} = -(1-\ln\rho) - \alpha$$
$$\rho = \exp(-1-\alpha)$$
- Property 2) trivial
- Property 3): see Sethna p. 89

Slide 18:

- Equilibrium phase space density: $\rho^{eq}(p_1,p_2;E) \propto \delta(p_1^2 + p_2^2 - 2mE)$
- If x_i are the roots of $g(x)$, then
$$\delta\big(g(x)\big) = \sum_i \frac{\delta(x-x_i)}{|g'(x_i)|}$$
- $g(p_2) = p_1^2 + p_2^2 - 2mE = 0$ if $p_2 = \pm\sqrt{2mE - p_1^2}$
- Hence
$$f(p_1) = \int \mathrm{d}p_2\,\rho^{\mathrm{eq}}(p_1,p_2;E)$$

$$\begin{aligned}
&\propto \int \mathrm{d}p_2\, \delta(p_1^2 + p_2^2 - 2mE) \\
&= \int \mathrm{d}p_2\, \frac{\delta\left(p_2 \pm \sqrt{2mE - p_1^2}\right)}{|2p_2|} \\
&= \frac{1}{\sqrt{2mE - p_1^2}}
\end{aligned}$$

Slide 19:

- In N dimensions: Equilibrium phase-space density
$$\rho^{\mathrm{eq}}(p_1, p_1; E) = \rho_0 \delta(\sum_i p_i^2 - 2mE)$$
- Integration with rotational symmetry: $\int \mathrm{d}^M p = M\, \pi^{M/2}/\Gamma(M/2+1) \int \mathrm{d}p\; p^{M-1}$ (Note that Γ here is the Γ-function and not a phase-space coordinate).
- Normalization:
$$\int d^{3N}p\, \rho^{\mathrm{eq}} = \rho_0 \frac{3N\, \pi^{3N/2}}{\Gamma(3N/2+1)} \int dp\, p^{3N-1}\, \delta(p^2 - 2mE) = \rho_0 \frac{\pi^{3N/2}}{\Gamma(3N/2)} (2mE)^{\frac{3N-2}{2}} \equiv 1$$
- Prefactor:
$$\rho_0 = \frac{\Gamma(3N/2)}{\pi^{3N/2}(2mE)^{\frac{3N-2}{2}}}$$
- Marginal distribution:
$$f(p_1; E) = \int \mathrm{d}p_2 \ldots dp_{3N}\, \rho^{eq}(p_1, \ldots, p_N; E) = \rho_0 \int \mathrm{d}p\, p^{3N-2} \delta(p_1^2 + p^2 - 2mE)$$
- Hence
$$\begin{aligned}
f(p_1; E) &= \rho_0 \frac{(3N-1)\, \pi^{\frac{3N-1}{2}}}{\Gamma((3N-1)/2+1)} \int dp\, p^{3N-2} \frac{\delta\left(p \pm \sqrt{2mE - p_1^2}\right)}{|2p|} \\
&= \rho_0 \frac{\pi^{\frac{3N-1}{2}}}{\Gamma((3N-1)/2+1)} (2mE - p_1^2)^{\frac{3N-3}{2}} \\
&= \frac{1}{\sqrt{2mE}} \frac{\pi^{\frac{3N-1}{2}}}{\Gamma((3N-1)/2)} \frac{\Gamma(3N/2)}{\pi^{\frac{3N}{2}}} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3N-3}{2}} \\
&= \left(\frac{1}{2\pi mE}\right)^{\frac{1}{2}} \frac{\Gamma(3N/2)}{\Gamma((3N-1)/2)} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3N-3}{2}}
\end{aligned}$$
- Now let $E = \frac{3}{2}NkT$, $\frac{3N}{2} = \frac{E}{kT}$ then
$$f(p_1; E) = \left(\frac{1}{2\pi mE}\right)^{\frac{1}{2}} \frac{\Gamma(E/kT)}{\Gamma(E/kT - 1/2)} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{E}{k_{\mathrm{B}}T} - \frac{3}{2}}$$
- Using $\lim_{x\to\infty} \frac{\Gamma(x-\alpha)}{\Gamma(x)x^{\alpha}} = 1$ and $\exp(x) = \lim_{n\to\infty}\left(1 + \frac{x}{n}\right)^n$ we find
$$f(p_1; E) = \frac{1}{\sqrt{2\pi m k_{\mathrm{B}} T}} \exp\left(-\frac{p_1}{2mk_{\mathrm{B}}T}\right)$$

Slide 21:

- Ideal gas

$$\begin{aligned}\Omega_\mathrm{A}\Omega_\mathrm{B} &= V_A^{N_A}V_B^{N_B}\,\mu\left(3N_A-1,\sqrt{2mE_A}\right)\mu\left(3N_B-1,\sqrt{2mE_B}\right)\\ &= \frac{V_A^{N_A}V_B^{N_B}\,\pi^{\frac{N}{2}}\sqrt{(2mE_A)^{3N_A-1}(2mE_B)^{3N_B-1}}}{\left(\frac{3N_A-1}{2}\right)!\left(\frac{3N_B-1}{2}\right)!}\end{aligned}$$

Slide 26:

- e.g. observable: $E = \langle H\rangle_f$. Trick:

$$\begin{aligned}E &= -\frac{\partial \ln Z}{\partial\beta}\\ &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta}\\ &= -\frac{1}{N!\;Z}\int \mathrm{d}^{6N}Q\,\frac{\partial}{\partial\beta}\,\exp\left(-\beta H(\vec{Q})\right)\\ &= \frac{1}{N!\;Z}\int d^{6N}Q\;H(\vec{Q})\,\exp\left(-\beta H(\vec{Q})\right)\\ &= \langle H\rangle_f\end{aligned}$$

Slide 27:

- Why is $A = E - TS$? Remember $E = \langle H\rangle_f$
- Use $f(\vec{Q}) = \frac{1}{Z}\exp\left(-\beta H(\vec{Q})\right)$ that minimizes the respective variational expression
- Then:

$$\begin{aligned}S &= -k\frac{1}{Z}\int \mathrm{d}^{6N}Q\,\exp\left(-\beta H(\vec{Q})\right)\left[\ln\exp\left(-\beta H(\vec{Q})\right) - \ln Z\right]\\ &= \frac{\langle H\rangle_f}{T} + k\ln Z\end{aligned}$$

- And hence $TS = E + kT\ln Z$ or $A = E - TS = -kT\ln Z$

Slide 28:

- Partition function (Snuck in a $1/h^{3N}$ there. This comes from quantum statistical mechanics and makes Z dimensionless):

$$\begin{aligned}Z &= \frac{1}{h^{3N}N!}\int d^{6N}Q\,\exp\left(-\beta H(\vec{Q})\right)\\ &= \frac{V^N}{h^{3N}N!}\left(\int \mathrm{d}^{3\mathrm{N}}p\,\exp\left(-\beta\frac{p^2}{2m}\right)\right)^{3N}\\ &= \frac{1}{N!}\left(\frac{V}{h^{3N}}\sqrt{\frac{2m\pi}{\beta}}^{3}\right)^{N}\\ &= \frac{1}{N!}\left(L\sqrt{\frac{2m\pi kT}{h}}\right)^{3N}\end{aligned}$$

$$= \frac{1}{N!}\left(\frac{L}{\lambda}\right)^{3N}$$

- Here, $\lambda = h/2m\pi kT$ is the De Broglie wavelength.

Slide 29:

- Remember: $\sum_{n=0}^{N} x^n = S_N, xS_N = S_N + x^{N+1} - 1, S_N = \frac{1-x^{N+1}}{1-x}, S_\infty = \frac{1}{1-x}$ if $|x| < 1$
- Partition function for $E_n = \epsilon\left(n + \frac{1}{2}\right)$:

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} \exp(-\beta E_n) \\ &= \sum_{n=0}^{\infty} [\exp(-\beta\epsilon)]^n \exp\left(-\frac{1}{2}\beta\epsilon\right) \\ &= \frac{1}{1-\exp(-\beta\epsilon)} \exp\left(-\frac{1}{2}\beta\epsilon\right) \\ &= \frac{1}{\exp\left(\frac{1}{2}\beta\epsilon\right) - \exp\left(-\frac{1}{2}\beta\epsilon\right)} \\ &= 1/2\ \sinh\left(\frac{1}{2}\beta\epsilon\right) \end{aligned}$$

Slide 32:

- Particle number not fixed in grand canonical ensemble
- Average number of particles:

$$\langle N\rangle = kT\frac{\partial}{\partial\mu}\ln\mathcal{Z}$$

- Fluctuation of particle numbers:

$$\Delta N^2 = \langle N^2\rangle - \langle N\rangle^2 = (kT)^2\frac{\partial^2}{\partial\mu^2}\ln\mathcal{Z}$$

Slide 35:

- $W = \int d\delta\, F(\delta)$

Slide 37:

- Free energy:

$$A(\Phi_1;T) = -k_\mathrm{B}T\ln\int \mathrm{d}^{6N}Q\exp\left(-\beta H(\vec{Q})\right)\ \delta(\Phi_1 - \phi_1\ (\vec{Q}))$$

- Dervative of delta function:

$$\int \mathrm{d}x\,\delta'(x)g(x) = -\int \mathrm{d}x\,\delta(x)g'(x)$$

- Force on constraint 1:

$$F_1 = \frac{\partial A}{\partial\Phi_1} = -\frac{k_BT}{Z}\int \mathrm{d}^{6N}Q\exp\left(-\beta H(\vec{Q})\right)\delta'\left(\Phi_1 - \phi_1(\vec{Q})\right)$$

$$= \frac{1}{Z} \int \mathrm{d}^{6N}Q \ \frac{\partial H}{\partial \vec{\Gamma}} \cdot \frac{\partial \vec{Q}}{\partial \phi_1} \exp\left(-\beta H(\vec{Q})\right) \delta\left(\Phi_1 - \phi_1(\vec{Q})\right)$$

$$= \langle \frac{\partial H}{\partial \vec{Q}} \cdot \frac{\partial \vec{Q}}{\partial \phi_1} \rangle_{\phi_1}$$

- For the latter average we invoke ergodicity
- Pair distribution function:

$$g_2(R) = \frac{1}{Z} \int \mathrm{d}^{6N}Q \ \delta(|\vec{r}_1 - \vec{r}_2| - R) \exp\left(-\beta H(\vec{Q})\right)$$