Relation between Statistical Mechanics and Thermodynamics

- $\langle E \rangle_{NVT} = k_B T^2 \frac{\partial \ln Z}{\partial T}|_{NV} \hat{=} U(N,V,T)$
- $k_B T \frac{\partial \ln Z}{\partial V}|_{N,T} = p$
- $-k_B T \frac{\partial \ln Z}{\partial N}|_{V,T} = \mu$
- $k_B T \frac{\partial \ln Z}{\partial T}|_{NV} + k_B \ln Z = S$

Page 1

Lecture 3

The **partition function** contains all information regarding a given thermodynamic state.

$Z = \sum_i e^{-\beta E_i}$

- Sum over all quantum states (including degeneracy).
- $Z = Z(N,V,T)$ (infinite heat bath)

Page 4

Computing the trace in CM for a continuous system

- Let $H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(r_1, ..., r_N)$.
- $Z_{NVT}^{CM} = \frac{1}{h^{3N}N!} \int dp^{3N} dr^{3N} e^{-\beta H(\{p_i\},\{r_i\})}$.

Normalisation

- **h**: Historically introduced to make dimensions work, but its origin is in QM (Gibbs + Boltzmann couldn't find this).
- **N!**: Gibbs factor, corrects for particles to be indistinguishable. (This is not fully correct since Bose-Einstein/Fermi-Dirac statistics lead to other prefactors in different thermal limits).

Page 5

$Z_{NVT}^{CM} = \frac{1}{N!h^{3N}} \int dp^{3N} \exp[-\beta \sum_i \frac{p_i^2}{2m}] \cdot \int dr^{3N} \exp[-\beta V(r_1, ...r_N)]$

Ideal Gas partition function

- An ideal gas consists of point-like, non-interacting particles confined in a fixed volume.
- $H = \sum_i \frac{p_i^2}{2m_i}$ (assume same m)
- $Z = \frac{1}{N!h^{3N}} \int dp^{3N} \exp[-\beta \sum_i \frac{p_i^2}{2m}] \int_V d^{3N}r = \frac{V^N}{N!h^{3N}} \int dp^{3N} \exp[-\beta \sum_i \frac{p_i^2}{2m}]$
- The momentum integral can be separated: $\int d^{3N}p \exp[-\beta \sum_i \frac{p_i^2}{2m}] = \prod_{i=1}^{N} \int \exp[-\beta \frac{p^2}{2m}] d^3p = \prod_{i=1}^{N} 4\pi \int_0^\infty dp\, p^2 \exp[-\beta p^2/2m]$.
- Using the standard integral: $\int_0^\infty x^2 \exp(-ax^2) dx = \frac{\pi^{1/2}}{4a^{3/2}}$.

Page 3

- $J = -k_B T \ln Z_{\mu VT} = -\rho V$ (Massieu) for the **grand canonical ensemble**.

Evaluating the Partition Function

- $Z = \sum_i e^{-\beta E_i}$
- More correctly, $Z = tr(e^{-\beta \hat{H}})$ (true for both classical and quantum mechanics).

Computing the trace in QM

- $tr(\hat{\theta}) = \sum_i \langle \psi_i | \hat{\theta} | \psi_i \rangle$
- Also, $\hat{H}|\psi_i\rangle = E_i|\psi_i\rangle \Rightarrow e^{-\beta \hat{H}}|\psi_i\rangle = e^{-\beta E_i}|\psi_i\rangle$.
- (Exercise: show that this is true). This allows recovery of $Z = \sum_i e^{-\beta E_i}$.

Page 2

- $-k_B T \ln Z = F(N, V, T)$ (**Helmholtz free energy**)
- Exercise: prove these.
- It holds that $F = U - TS$.
- $dF = -SdT - p\, dV + \mu\, dN$
- Knowing Z as a function of N, V, T defines the thermodynamic state of the system exactly.
- Since $Z = Z(\{E_i(N, V)\}, T)$, knowing all quantum states yields the thermodynamics.

Note: Thermodynamic Potentials

- $F = -k_B T \ln Z_{NVT}$ (Helmholtz) for the **canonical ensemble**.
- $G = -k_B T \ln Z_{NPT}$ (Gibbs) for the **isothermal-isobaric ensemble**.
- $S = +k_B T \ln Z_{NVE}$ (entropy) for the **microcanonical ensemble**.

Page 6

- $\Rightarrow Z = \frac{V^N}{N!}(\frac{1}{\lambda_T})^{3N}$
- Where $\lambda_T = \frac{h}{[2\pi m k_B T]^{1/2}}$ is the **thermal de Broglie wavelength**.

Motivating Monte Carlo Statistical Sampling 🎲

- How to compute $Z = tr(e^{-\beta \hat{H}})$?
- It is often not feasible to determine all eigenstates of $\hat{H}$ or to integrate analytically over all of phase space.
- Not all of phase space is relevant. Many regions are exponentially suppressed and thus don't contribute to Z.

Page 7

The probability of a state is given by $\frac{\exp(-\beta H)}{Z}$.

Importance Sampling

- The expectation value of an observable θ is $\langle\theta\rangle = \int \theta(r,p)P(r,p)dr^{3N}dp^{3N} \approx \frac{1}{M}\sum_{i=1}^{M}\theta(r_i,p_i)$.
- This approximation holds if the M configurations (r_i,p_i) are drawn from the distribution $P(r,p)$.
- $\langle\theta\rangle = \lim_{M\to\infty}\frac{1}{M}\sum_{i=1}^{M}\theta(r_i,p_i)$
- Recall $P(r,p) = \frac{\exp[-\beta H(r,p)]}{Z}$, where $Z = \int \exp(-\beta H)drdp$.
- Note that (a) $\exp(-\beta H(r,p))$ is relatively easy to compute, but (b) Z is difficult to compute.

Page 8

Key point in Metropolis Monte Carlo: It allows us to draw samples from a probability distribution $P(\underline{x})$ when we only know the distribution up to a constant, i.e., $h(\underline{x}) = cP(\underline{x})$.

- It relies on the fact that the ratio of probabilities can be computed without knowing the constant: $\frac{h(\underline{x}_1)}{h(\underline{x}_2)} = \frac{p(\underline{x}_1)}{p(\underline{x}_2)}$.
- **Downside**: The generated samples are no longer independent.

Figure 3.1: Measuring the depth of the Nile: a comparison of conventional quadrature (left), with the Metropolis scheme (right).

- The left image shows a map of Africa and the Middle East with a uniform grid of sample points laid over it.
- The right image is a cartoon depicting a more targeted sampling method, with a person sampling in the Nile river itself, near pyramids.

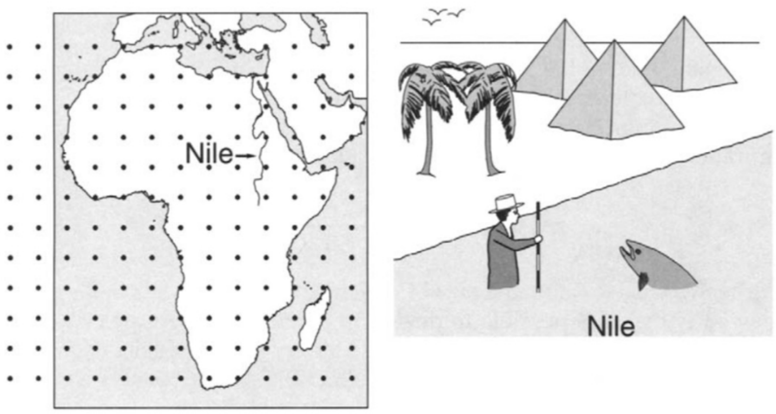

Figure 3.1: Measuring the depth of the Nile: a comparison of conventional quadrature (left), with the Metropolis scheme (right).