Classical Statistical Mechanics: Part 2

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Variational approach to equilibrium densities

- Hypothesis: functional form of equilibrium distribution is that which maximizes the statistical entropy.
  - Statistical entropy viewed as a functional of $f(\mathbf{x}^{(N)})$.
  - Form must satisfy basic properties of a probability density: normalized.

Microcanonical Ensemble

- All systems in ensemble have an energy in the energy shell $[E, E+\delta E]$.
- Task is to maximize

$$S = -k \int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \ln\left(h^{3N} N! f(\mathbf{x}^{(N)})\right).$$

  subject to the constraint

$$\int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) \equiv \int' d\mathbf{x}^{(N)} f(\mathbf{x}^{(N)}) = 1.$$

- Procedure:

$$\begin{aligned}
\delta\left(S + \alpha_0 1\right) &= \int' d\mathbf{x}^{(N)}\ \left[-k f(\mathbf{x}^{(N)}) \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) + \alpha_0 f(\mathbf{x}^{(N)})\right] = 0 \\
&= \int' d\mathbf{x}^{(N)}\ \left[-k \ln\left(N! h^{3N} f(\mathbf{x}^{(N)})\right) - k + \alpha_0\right] \delta f(\mathbf{x}^{(N)}) = 0.
\end{aligned}$$

- Since the variation is arbitrary:

  $$-k\ln\left(N!h^{3N}f(\mathbf{x}^{(N)})\right) - k + \alpha_0 = 0$$

  so

  $$\begin{aligned} k\ln\left(N!h^{3N}f(\mathbf{x}^{(N)})\right) &= \alpha_0 - k \\ N!h^{3N}f(\mathbf{x}^{(N)}) &= e^{\alpha_0/k-1} = \tilde{C}. \end{aligned}$$

- Hence, as desired, we get:

  $$f(\mathbf{x}^{(N)}) = \begin{cases} C & \text{for } E < H(\mathbf{x}^{(N)}) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

  where C is a constant.

- From normalization, $C = 1/\Omega$.

- It is cumbersome to work with integrals over restricted energy shells. Can we relax this restriction and obtain ensemble averages that agree with time averages (and each other)?

Canonical Ensemble

- Remove restriction of defining probability only on constant energy hypersurface.

- Allow total energy of systems in ensemble to vary (hopefully) narrowly around a fixed average value.

- Task now is to maximize

  $$S = -k\int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)})\ln\left(h^{3N}N!f(\mathbf{x}^{(N)})\right).$$

  subject to the constraints

  $$\begin{aligned} \int d\mathbf{x}^{(N)}\ f(\mathbf{x}^{(N)}) &= 1 \\ \overline{E} = \int d\mathbf{x}^{(N)} H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)}) & \end{aligned}$$

- Procedure:

  $$\delta \int d\mathbf{x}^{(N)} \ \left[-kf(\mathbf{x}^{(N)}) \ln\left(N!h^{3N} f(\mathbf{x}^{(N)})\right) + \alpha_0 f(\mathbf{x}^{(N)}) + \alpha_E H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)})\right] = 0$$

  So

  $$\begin{aligned} \alpha_0 + \alpha_E H(\mathbf{x}^{(N)}) - k \ln\left(N!h^{3N} f(\mathbf{x}^{(N)})\right) - k &= 0 \\ f(\mathbf{x}^{(N)}) &= \frac{1}{N!h^{3N}} \exp\left\{\frac{\alpha_0}{k} - 1 + \frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \end{aligned}$$

  - What are the Lagrange multipliers?

    1. From normalization:

       $$\begin{aligned} \int d\mathbf{x}^{(N)} \ f(\mathbf{x}^{(N)}) = 1 &= \frac{\exp\{\alpha_0/k - 1\}}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \exp\left\{\frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \\ \exp\{1 - \alpha_0/k\} &= \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \exp\left\{\frac{\alpha_E}{k} H(\mathbf{x}^{(N)})\right\} \end{aligned}$$

    2. From the thermodynamic relation:

       $$\left(\frac{\partial S}{\partial \overline{E}}\right)_{V,\text{norm}} = \frac{1}{T}$$

  - Note from above that since $k \ln(N!h^{3N} f(\mathbf{x}^{(N)})) = \alpha_E H(\mathbf{x}^{(N)}) + \alpha_0 - k$, we have

    $$\begin{aligned} S &= -\int d\mathbf{x}^{(N)} \ f(\mathbf{x}^{(N)}) \left(\alpha_E H(\mathbf{x}^{(N)}) + \alpha_0 - k\right) \\ &= (k - \alpha_0) - \alpha_E \overline{E}. \end{aligned}$$

  - It is now clear that:

    $$\begin{aligned} \left(\frac{\partial S}{\partial \overline{E}}\right)_{V,\text{norm}} &= \frac{1}{T} = -\alpha_E \\ \alpha_E &= -\frac{1}{T}. \end{aligned}$$

  - Thus $TS = T(k - \alpha_0) + \overline{E}$ or $\overline{E} - TS = T(\alpha_0 - k)$.

  - $\overline{E} - TS = A$, the Helmholtz free energy, so

$$T(\alpha_0 - k) = A$$

  and $\exp\{\alpha_0/k - 1\} = \exp\{\beta A\}$ where $\beta = 1/(kT)$.

- We conclude that for the canonical ensemble:

$$f(\mathbf{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\}$$

- We define the *partition function* $Q_N(T, V)$ by

$$Q_N(T,V) = \frac{1}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ \exp\{-\beta H(\mathbf{x}^{(N)})\} = \exp\{-\beta A\}$$

  so

$$f(\mathbf{x}^{(N)}) = \frac{1}{N!h^{3N}} \exp\{\beta(A - H(\mathbf{x}^{(N)}))\} = \frac{1}{N!H^{3N}} \frac{\exp\{-\beta H(\mathbf{x}^{(N)})\}}{Q_N(T,V)}.$$

- Relation $A = -kT \ln Q_N(T,V)$ gives thermodynamic connection: For example

  1. The pressure is:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T.$$

  2. The chemical potential is:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

  3. The energy is:

$$\begin{aligned}
\overline{E} &= \frac{\exp\{\beta A\}}{N!h^{3N}} \int d\mathbf{x}^{(N)} \ H(\mathbf{x}^{(N)}) \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= \frac{\exp\{\beta A\}}{N!h^{3N}} - \frac{\partial}{\partial \beta} \int d\mathbf{x}^{(N)} \ \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= -\frac{1}{Q_N}\frac{\partial Q_N}{\partial \beta} = -\frac{\partial \ln Q_N}{\partial \beta}.
\end{aligned}$$

- We have obtained two different probability densities corresponding to different "ensembles".
  - Microcanonical ensemble: vanishing probability to find a system in ensemble with energy function (Hamiltonian) different from average energy.
  - Canonical ensemble: Hamiltonian can differ among states but states must be weighted so that the ensemble average of Hamiltonian corresponds to the average energy.
- What is the correspondence between averages in the different ensembles?
- We can write the canonical partition function as:

$$\begin{aligned}
Q_N(T,V) &= \frac{1}{N!h^{3N}}\int d\mathbf{x}^{(N)}\ \exp\{-\beta H(\mathbf{x}^{(N)})\} \\
&= \int_0^\infty dE \frac{1}{N!h^{3N}}\int d\mathbf{x}^{(N)}\ \exp\{-\beta H(\mathbf{x}^{(N)})\}\delta(E-H(\mathbf{x}^{(N)})) \\
&= \int_0^\infty dE\ \exp\{-\beta E\}\left(\frac{1}{N!h^{3N}}\int d\mathbf{x}^{(N)}\ \delta E - H(\mathbf{x}^{(N)})\right) \\
Q_N(T,V) &= \int_0^\infty dE\ \exp\{-\beta E\}N(E)
\end{aligned}$$

  where

$$\begin{aligned}
N(E) &\equiv \frac{\tilde{N}(E)}{N!h^{3N}} \\
&= \text{density of \textit{unique} states at energy } E \text{ (microcanonical partition function).}
\end{aligned}$$

  - Partition function $Q_N(\beta, V)$ is the Laplace transform of density of unique states.
  - Q_N is like a generating function for $N(E)$.
- Recall the definition of the statistical entropy:

$$\begin{aligned}
S(E) &= k\ln W = k\ln\left(\frac{\Omega(E,\delta E,N,V)}{N!h^{3N}}\right) \\
&\approx k\ln(N(E)\delta E) = k\ln N(E) + C
\end{aligned}$$

  for small δE where $\Omega \approx \tilde{N}(E)\delta E$.

- Thus

  $$N(E) \sim \exp\{S(E)/k\} \qquad Q_N(T,V) \sim \int_0^\infty dE \; \exp\{-\beta(E-TS)\}$$

  - Typically, $N(E)$ is a rapidly increasing function of E

    $$N(E) \sim f\,(E/N, V/N)\, \exp\{Ng(E/n, V/N)\} \qquad S(E) \sim Nk\, g(E/N, V/N).$$

Thermodynamic Stability

- Define $P(E)dE$ to be the probability of finding a system with energy E in the canonical ensemble.

  $$P(E) = \langle \delta(E - H(\mathbf{x}^{(N)}))\rangle = \int d\mathbf{x}^{(N)} \; \delta(E - H(\mathbf{x}^{(N)}))f(\mathbf{x}^{(N)}) = \exp\{\beta A\}\; \exp\{-\beta E\}\, N(E)$$

- From normalization, it follows that

  $$\exp\{-\beta A\} = \int_0^\infty dE \; \exp\{-\beta E\} N(E).$$

- At low temperatures, how much more likely are we to find a system with $E = E_1$ than $E = E_2$?

  $$\begin{aligned} \frac{P(E_1)}{P(E_2)} &= \frac{e^{\beta A}\, e^{-\beta E_1}\, N(E_1)}{e^{\beta A}\, e^{-\beta E_2}\, N(E_2)} \\ &= e^{-\beta \Delta E} \frac{N(E_1)}{N(E_2)} \qquad \Delta E \equiv E_1 - E_2 \end{aligned}$$

  - Since $S(E) \sim k \ln(N(E))$,

    $$\frac{P(E_1)}{P(E_2)} = e^{-\beta(\Delta E - T\Delta S)} \qquad \Delta S \equiv S(E_1) - S(E_2)$$

  - The density of states is important (entropic factor).
  - Probabilities determined by balance between ΔE and ΔS.

- Consider a bio-molecule (like a polymer chain): Each phase point corresponds to a particular configuration (and set of momenta) of the molecule.

- Suppose there are two different *types* of configuration Γ_1 and Γ_2: represented by *basins* in configurational space.
- Define conditional probabilities partioning configurational space:

$$P(E) = \sum_i P(E|\Gamma_i)$$

$$\begin{aligned}
P(E|\Gamma_1) &= \int_{\Gamma_1} d\mathbf{x}^{(N)}\ \delta(E - H(\mathbf{x}^{(N)}))f(\mathbf{x}^{(N)}) = \frac{e^{\beta A}e^{-\beta E}}{N!h^{3N}} \int_{\Gamma_1} d\mathbf{x}^{(N)}\ \delta(E - H(\mathbf{x}^{(N)})) \\
&= e^{\beta A}e^{-\beta E} N(E|\Gamma_1) \\
N(E|\Gamma_1) &= \int_{\Gamma_1} d\mathbf{x}^{(N)}\ \frac{\delta(E - H(\mathbf{x}^{(N)}))}{N!h^{3N}} = \#\text{ of unique states in basin } \Gamma_1.
\end{aligned}$$

- Thus

$$\frac{P(E_1|\Gamma_1)}{P(E_2|\Gamma_2)} = e^{-\beta\Delta E}\frac{N(E_1|\Gamma_1)}{N(E|E_2)}$$

gives the relative stability of the conformations at the given energies.

Relationship between ensemble averages

- How likely are we to observe a system in the canonical ensemble with an energy very different from the average energy $\overline{E} = \langle H(\mathbf{x}^{(N)})\rangle$?

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{\sigma_E^2}{\lambda^2\overline{E}^2}$$

- Now the variance in the energy is:

$$\sigma_E^2 = \left\langle H(\mathbf{x}^{(N)})^2\right\rangle - \langle H(\mathbf{x}^{(N)})\rangle^2 = \frac{\partial^2 \ln Q_N}{\partial\beta^2} = -\frac{\partial\overline{E}}{\partial\beta} = kT^2C_v$$

and hence

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{kT^2C_v}{\lambda^2\overline{E}^2}$$

- We will show that for an ideal gas system, $\overline{E} = 3/2NkT$ and hence $C_v = 3/2Nk$.
- Typically, $\overline{E} \sim N$ and $C_v \sim N$.

$$Pr\left(\left|H(\mathbf{x}^{(N)}) - \overline{E}\right| \geq \lambda\overline{E}\right) \leq \frac{kT^2C_v}{\lambda^2\overline{E}^2} \sim \frac{1}{N\lambda^2}$$

  - As N increases, it becomes less and less likely to observe a system with energy very different from $\overline{E}$,

$$\langle B(\mathbf{x}^{(N)})\rangle_{\text{canon}} = \int dE\ P(E)\langle B(\mathbf{x}^{(N)})\rangle_{\text{micro at }E} \approx \langle B(\mathbf{x}^{(N)})\rangle_{\text{micro at }\overline{E}}\left(1 + O(1/N)\right).$$

- $P(E)$ is sharply-peaked around $E = \overline{E}$: Can show (homework?)

$$P(E) \;\approx\; P(\overline{E})\left(\frac{1}{2\pi\sigma_E^2}\right)^{1/2}\exp\left\{-\frac{(E-\overline{E})^2}{2kT^2C_v}\right\}$$

- Relative spread of energy $\sigma_E/\overline{E} \sim N^{-1/2}$.