Gibbs Entropy and more Ensembles

MSE 421 - Ceriotti

Entropy and the ensembles

- How to define entropy when there is no equiprobability between microstates? Let's try this ansatz and see where we get [note that this is compatible with the *microcanonical* entropy we defined before]

$$\boxed{\mathcal{S} = -k_B \sum_\nu P_\nu \ln P_\nu}$$

Gibbs' Entropy Formula

- Consider the canonical ensemble. Given the relation between Q and $\langle E \rangle$,

$$-\frac{\partial \ln Q}{\partial \beta} = \sum_\nu E_\nu \frac{e^{-\beta E_\nu}}{Q} = \langle E \rangle \qquad \rightarrow \qquad \mathrm{d} \ln Q = -\langle E \rangle \, \mathrm{d}\beta$$

① Gibbs entropy formula reads ($P_\nu = e^{-\beta E_\nu}/Q$)

$$\frac{\mathcal{S}}{k_B} = -\sum_\nu \frac{e^{-\beta E_\nu}}{Q} \ln \frac{e^{-\beta E_\nu}}{Q} = \sum_\nu \frac{e^{-\beta E_\nu}}{Q} \left[\beta E_\nu + \ln Q\right] = \ln Q + \beta \langle E \rangle$$

$$\frac{\mathrm{d}\mathcal{S}}{k_B} = \underbrace{\mathrm{d} \ln Q + \langle E \rangle \, \mathrm{d}\beta}_{=0} + \beta \mathrm{d} \langle E \rangle = \beta \mathrm{d} \langle E \rangle$$

② Consistent with the classical thermodynamic definition of entropy for a system: for a reversible constant-(T,V) transformation

$$\mathrm{d}S = \frac{\mathrm{d}\langle E \rangle}{T} = k_B \beta \mathrm{d} \langle E \rangle$$

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Information entropy

- Gibb's entropy has a deep connection with information theory. Given an event A, that occurs with probability $P(A)$, let's define the *information content* $I(A)$ of that event. We require
  1. $I(A) \geq 0$ [the information content is positive]
  2. $I(\Omega) = 0$ [an event that always occurs does not convey information]
  3. If A and B are independent events, $I(A, B) = I(A) + I(B)$
- The only function of $P(A)$ that satisfy these conditions is $I(A) = C \log_b 1/P(A)$
- Given a set of disjoint events A_i, the average information that we can obtain equals the information of all events weighed with their probability

$$\boxed{I = -\sum_i P(A_i) \ln P(A_i)}$$

Shannon's information entropy

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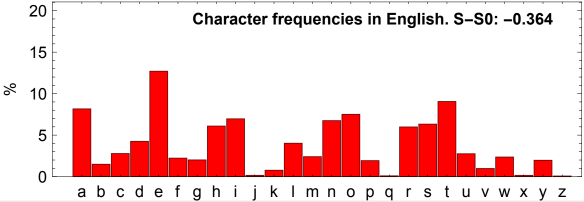

Gibb's Entropy as a principle

- Given the information-theoretical basis, let's take Gibbs formula for granted and see what are the implications
- Consider two non-interacting subsystems A and B

$$\mathcal{S}_A/k_B = -\sum_{\nu_A} P_A(\nu_A)\ln P_A(\nu_A) \qquad \mathcal{S}_B/k_B = -\sum_{\nu_B} P_B(\nu_B)\ln P_B(\nu_B)$$

  - If we consider them as a single system, possible states will include all possible pairs (ν_A, ν_B), occurring with probabilities $P(\nu_A, \nu_B) = P_A(\nu_A)\,P_B(\nu_B)$
  - Consider the overall Gibbs entropy [probabilities are normalized to 1!]

$$-\mathcal{S}/k_B = \sum_{(\nu_A,\nu_B)} P(\nu_A, \nu_B)\ln P(\nu_A, \nu_B) = \sum_{(\nu_A,\nu_B)} P_A(\nu_A)\,P_B(\nu_B)\left[\ln P_A(\nu_A) + \ln P_B(\nu_B)\right]$$

$$= \sum_{(\nu_A,\nu_B)} P_A(\nu_A)\,P_B(\nu_B)\ln P_A(\nu_A) + \sum_{(\nu_A,\nu_B)} P_A(\nu_A)\,P_B(\nu_B)\ln P_B(\nu_B) \underbrace{=}_{\sum_\nu P_\nu=1} -\mathcal{S}_A/k_B - \mathcal{S}_B/k_B$$

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"At least it's additive"

Ensembles from a "maxent" criterion

- The trick is inferring an expression for P_ν by imposing the equilibrium condition $\delta\mathcal{S} = 0$, imposing the conservation conditions characteristic of the ensemble subject to normalization of P_ν, $1 = \sum_\nu P_\nu$:

$$\langle E\rangle = \sum_\nu E_\nu P_\nu, \quad \langle N\rangle = \sum_\nu N_\nu P_\nu.$$

  - Let's start with microcanonical ensemble, where $E_\nu = E$, $N_\nu = N$ and the states are strictly restricted to those fulfilling these conditions.
  - We can use a Lagrange multiplier γ to enforce normalized probability

$$\delta\left(S + \gamma\sum_\nu P_\nu\right) = 0$$

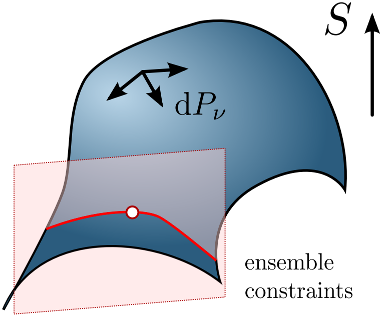
$$0 = \sum_\nu\left[\frac{\partial S}{\partial P_\nu}\mathrm{d}P_\nu + \gamma\mathrm{d}P_\nu\right] = \sum_\nu\left[-k_B\left(1+\ln P_\nu\right)+\gamma\right]\mathrm{d}P_\nu$$

  - The only way the differential form can be zero for any choice of $\mathrm{d}P_\nu$ is if the coefficient is zero, i.e.

$$\ln P_\nu = \frac{\gamma}{k_B} - 1 \quad \rightarrow P_\nu = \text{const.} = \delta\left(E - E_\nu\right)/\Omega\left(E\right)$$

Ensembles from a "maxent" criterion

Note the rationale here: maximizing entropy means choosing the probability distribution of microstates that encodes the least amount of information. However, we must do so consistently with the thermodynamic constraints imposed by the ensemble



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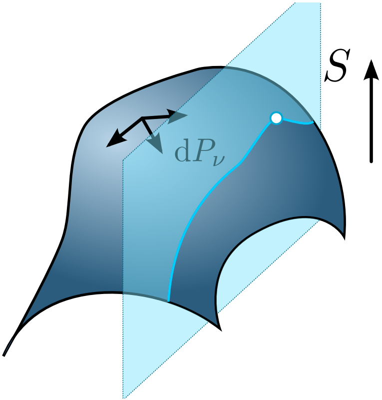

Canonical ensemble, revisited/1

- Now consider the constant-T case. Here we also want to enforce a proper value of the *mean* energy $\langle E\rangle \rightarrow$ another Lagrange multiplier!

$$\delta\left(S+\gamma\sum_\nu P_\nu+\alpha\sum_\nu E_\nu P_\nu\right)=0$$

  - This leads immediately to

$$0=\sum_\nu\left[\frac{\partial S}{\partial P_\nu}\mathrm{d}P_\nu+\gamma\mathrm{d}P_\nu+\alpha E_\nu\mathrm{d}P_\nu\right]=\sum_\nu\left[-k_B\left(1+\ln P_\nu\right)+\gamma+\alpha E_\nu\right]\mathrm{d}P_\nu$$

$$\left[-k_B\left(1+\ln P_\nu\right)+\gamma+\alpha E_\nu\right]=0,\qquad \ln P_\nu=\frac{\gamma+\alpha E_\nu-k_B}{k_B}$$

  - One of the two multipliers is set by the normalization. For the other we need a constraint, e.g. the condition $\beta=\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{V,N}$. Exploiting the fixed normalization that ensures $\sum_\nu \mathrm{d}P_\nu=0$,

$$\frac{1}{k_B}\mathrm{d}S=-\sum_\nu\left(1+\ln P_\nu\right)\mathrm{d}P_\nu=-\frac{1}{k_B}\sum_\nu\left(\gamma+\alpha E_\nu\right)\mathrm{d}P_\nu=-\frac{\alpha}{k_B}\mathrm{d}\left\langle E\right\rangle$$

$$\rightarrow\quad \alpha=-\left(\frac{\partial S}{\partial E}\right)_{V,N}=-k_B\beta\ \rightarrow\ P_\nu=e^{-\beta E_\nu}e^{\gamma/k_B-1}$$

Canonical ensemble, revisited/2

- The connection between the Lagrange multiplier α and the inverse temperature β elucidates the relation between the statistical mechanical formulation and several thermodynamic variables.
  - The (Gibbs') entropy reads $[k_B \ln P_\nu = \gamma + \alpha E_\nu - k_B, \alpha = -k_B\beta = -1/T]$

$$\mathcal{S} = -k_B \sum_i P_\nu \ln P_\nu = \sum_i \left[k_B - \gamma + k_B\beta E_\nu\right] P_\nu = k_B\beta \left\langle E \right\rangle + k_B - \gamma$$

$$\left\langle E \right\rangle - T\mathcal{S} = \gamma T - k_B T = \left\langle A \right\rangle$$

  - Then, the probability distribution reads

$$P_\nu = e^{-\beta E_\nu} e^{\beta(\gamma T - k_B T)} = e^{-\beta(E_\nu - \langle A \rangle)}$$

  - Considering that $Q = \sum_\nu e^{-\beta E_\nu}$, and that $1 = \sum_\nu P_\nu = e^{\beta\langle A\rangle} \sum_\nu e^{-\beta E_\nu}$,

$$e^{\beta\langle A\rangle} = 1/Q, \qquad \langle A \rangle = -k_B T \ln Q$$

Particles in an external potential

- Now consider a system in which the energy of individual particles depends on position. For instance, for a gas in a uniform gravitational field $E(h) = mgh$
- For each particle, there is a uniform density of states along h, and the probability of finding a particle at an altitude h reads

$$P(h) = \frac{1}{Q} e^{-\beta mgh} = \frac{e^{-\beta mgh}}{\beta gm}$$

  - The density as a function of altitude is then proportional to $P(h)$. Concentrations of gases vary with altitude

$$\rho(h) = \rho_0 e^{-\beta mgh} \qquad x_i(h) = \rho_0^i e^{-\beta m_i gh} / \sum_j \rho_0^j e^{-\beta m_j gh}$$

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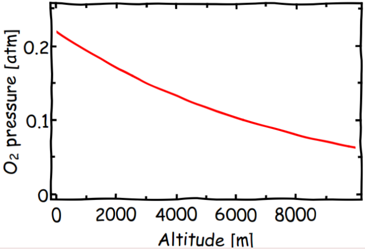

Grand-canonical (constant-μ) ensemble/1

- Now consider a case in which we leave the number of particles N (as well as E) free to fluctuate. We need three Lagrange multipliers

$$\delta\left(\mathcal{S}+\gamma\sum_\nu P_\nu+\alpha\sum_\nu E_\nu P_\nu+\eta\sum_\nu N_\nu P_\nu\right)=0$$

  - Writing the differential form explicitly gives an expression for P_ν

$$\sum_\nu \mathrm{d}P_\nu\left[-k_B\left(1+\ln P_\nu\right)+\gamma+\alpha E_\nu+\eta N_\nu\right]=0\ \rightarrow\ \ln P_\nu=\frac{\gamma-k_B+\alpha E_\nu+\eta N_\nu}{k_B}$$

  - Now we can use this to work out an expression for $\mathrm{d}\mathcal{S}$

$$\mathrm{d}\mathcal{S}=-\sum_\nu k_B\left(1+\ln P_\nu\right)\mathrm{d}P_\nu=-\sum_\nu\left(\alpha E_\nu+\eta N_\nu\right)\mathrm{d}P_\nu=-\alpha\mathrm{d}\left\langle E\right\rangle-\eta\mathrm{d}\left\langle N\right\rangle$$

  - Macroscopic thermodynamic relations fix the values of α and η

$$\left(\frac{\partial\mathcal{S}}{\partial E}\right)_N=-\alpha\rightarrow\alpha=-\frac{1}{T}=-k_B\beta,\qquad\left(\frac{\partial\mathcal{S}}{\partial N}\right)_E=-\eta\rightarrow\eta=\frac{\mu}{T}=k_B\beta\mu$$

Recall that $\left(\frac{\partial S}{\partial N}\right)_{E,V}=-\left(\frac{\partial E}{\partial N}\right)_{V,S}/\left(\frac{\partial E}{\partial S}\right)_{V,N}=-\frac{\mu}{T}$

Grand-canonical ensemble/2

- Armed with these expressions we can spell out the probability distribution. The missing multiplier γ could be determined from normalization

$$\ln P_\nu = \gamma/k_B - 1 - \beta E_\nu + \beta\mu N_\nu$$

  - We can however relate γ to macroscopic thermodynamics: first, write out the entropy

$$\mathcal{S} = -k_B \sum_\nu P_\nu \ln P_\nu = k_B - \gamma + \frac{\langle E\rangle}{T} - \frac{\mu}{T}\langle N\rangle$$

  - We can then write out an expression for $(\gamma - k_B)$, based on Gibbs free energy [recall: $\langle G\rangle = \mu\langle N\rangle = \langle E\rangle - TS + pV$]

$$T(\gamma - k_B) = \langle E\rangle - TS - \mu\langle N\rangle = \langle E\rangle - TS - (\langle E\rangle - TS + pV) = -pV$$

  - So the normalized P_ν reads

$$P_\nu = \exp -\beta\left(E_\nu - \mu N_\nu + pV\right)$$

  - And we can introduce the grand-canonical partition function

$$\Xi = \sum_\nu \exp -\beta\left(E_\nu - \mu N_\nu\right) = e^{\beta pV} \quad \rightarrow \quad \langle pV\rangle = \frac{1}{\beta}\ln\Xi$$

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Isothermal-isobaric ensemble

- Let's finish with an ensemble where V and E can fluctuate by coupling to a bath

$$\delta\left(\mathcal{S}+\gamma\sum_\nu P_\nu+\alpha\sum_\nu E_\nu P_\nu+\pi\sum_\nu V_\nu P_\nu\right)=0$$

$$\rightarrow\ \ln P_\nu=\frac{\gamma-k_B+\alpha E_\nu+\pi V_\nu}{k_B}$$

- As usual we write the differential of $\mathcal{S}$

$$\mathrm{d}\mathcal{S}=-\sum_\nu\left(\alpha E_\nu+\pi V_\nu\right)\mathrm{d}P_\nu=-\alpha\mathrm{d}\left\langle E\right\rangle-\pi\mathrm{d}\left\langle V\right\rangle\ \rightarrow\ \alpha=-\frac{1}{T},\ \pi=-\frac{p}{T}$$

so we can write

$$P_\nu=\Delta^{-1}e^{-\beta(E+pV)},\ \ G=-k_BT\ln\Delta$$

Recall that $\left(\frac{\partial S}{\partial V}\right)_E=-\left(\frac{\partial E}{\partial V}\right)_S/\left(\frac{\partial E}{\partial S}\right)_V=\frac{p}{T}$

Particle-number fluctuations

- Let's consider the case of two components, with particle numbers N_ν^A and N_ν^B. [As usual, set $\delta\left(S+\gamma\sum_\nu P_\nu+\alpha\sum_\nu E_\nu P_\nu+\eta^A\sum_\nu N_\nu^A P_\nu+\eta^B\sum_\nu N_\nu^B P_\nu\right)=0$]

$$\to \ln P_\nu = \frac{\gamma - k_B + \alpha E_\nu + \eta^A N_\nu^A + \eta^B N_\nu^B}{k_B}$$

so

$$P_\nu = \Xi^{-1}\exp -\beta\left(E_\nu - \mu^A N_\nu^A - \mu^B N_\nu^B\right)$$

- The fluctuations in number of particles and compositions vanish in the thermodynamic limit

$$\left\langle N^A\right\rangle = \sum_\nu N_\nu^A P_\nu = \frac{\partial \ln \Xi}{\partial\left(\beta\mu^A\right)}$$

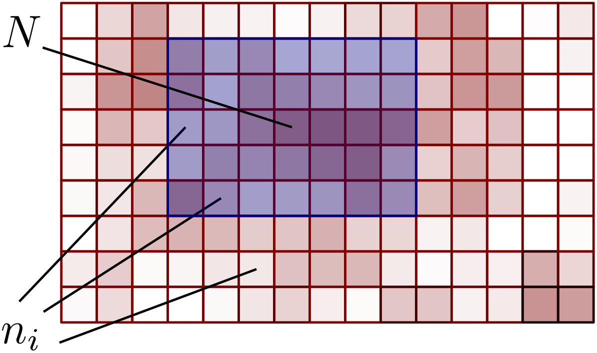
$$\frac{\partial^2 \ln \Xi}{\partial\left(\beta\mu^A\right)^2} = \frac{\partial\left\langle N^A\right\rangle}{\partial\left(\beta\mu^A\right)} = \sum_\nu N_\nu^A \frac{\partial P_\nu}{\partial\beta\mu^A} = \sum_\nu \left[N_\nu^A\right]^2 P_\nu - N_\nu^A P_\nu \frac{1}{\Xi}\frac{\partial \Xi}{\partial\left(\beta\mu^A\right)} = \operatorname{var} N^A$$

$$\frac{\partial\left\langle N^A\right\rangle}{\partial\beta\mu^B} = \sum_\nu N_\nu^A N_\nu^B P_\nu - N_\nu^A P_\nu \frac{1}{\Xi}\frac{\partial \Xi}{\partial\left(\beta\mu^B\right)} = \left\langle N^A, N^B\right\rangle$$

Uncorrelated fluctuations/1

- Let's consider a large reservoir, filled with a gas of mean density $\bar{\rho}$. Partition it in disjoint cells of volume v, and consider the number of particles that is observed within a region containing M of such cells.

$$N = \sum_i n_i, \quad \langle N \rangle = \sum_i \langle n_i \rangle = M \langle n \rangle = Mv\bar{\rho}$$



Uncorrelated fluctuations/2

- Now consider the variance of N, $\operatorname{var} N = \left\langle (N - \langle N \rangle)^2 \right\rangle$

$$\operatorname{var} N = \left\langle \left[\sum_i (n_i - \langle n_i \rangle) \right]^2 \right\rangle = \sum_{ij} \langle n_i n_j \rangle - M^2 \langle n \rangle^2$$

  - Central assumptions: uncorrelated fluctuations - $\langle n_i n_j \rangle \underset{i \neq j}{=} \langle n_i \rangle \langle n_j \rangle$

$$\sum_{ij} \langle n_i n_j \rangle = \sum_i \left\langle n_i^2 \right\rangle + \sum_{i \neq j} \langle n_i n_j \rangle = M \left\langle n^2 \right\rangle + M (M - 1) \langle n \rangle^2$$

$\rightarrow$ relative fluctuations are *scale-independent*

$$\operatorname{var} N = M \left[\left\langle n^2 \right\rangle - \langle n \rangle^2 \right] \quad \rightarrow \quad \frac{\operatorname{var} N}{\langle N \rangle} = \frac{\operatorname{var} n}{\langle n \rangle}$$

Uncorrelated fluctuations/3

- Now, we assume that the volume v of the cells is small enough that the probability of having more than one particle is negligible [alternatively, you can say that different particles are independent, consider the probability of having k particles as $(\bar{\rho}v)^k$, and consider the limit for $v \to 0$]

$$\langle n \rangle = 1 \cdot \bar{\rho}v + \mathcal{O}\left(v^2\right), \quad \left\langle n^2 \right\rangle = 1^2 \bar{\rho}v + \mathcal{O}\left(v^2\right) \;\to \frac{\mathrm{var}\, n}{\langle n \rangle} \underset{v \to 0}{=} 1$$

- These considerations will hold as long as fluctuations are uncorrelated on the scale on which we can consider the probability of having more than one particle per cell to be negligible → *dilute limit*!

Ideal gas law

- Now let's combine this result with the grand canonical relation and $\mathrm{var}\, N/\left\langle N\right\rangle = \mathrm{var}\, n/\langle n\rangle = 1$

$$\left[\partial\left\langle N\right\rangle/\partial\left(\beta\mu\right)\right]_{\beta,V} = \mathrm{var}\, N \quad \rightarrow \qquad \mathrm{var}\, N = \left\langle N\right\rangle$$

  - We get the relation for the chemical potential in a dilute system

$$\left[\frac{\partial\left(\beta\mu\right)}{\partial\left\langle N\right\rangle}\right]_{\beta,V} = \frac{1}{\left\langle N\right\rangle} \rightarrow \beta\mu = \ln\left\langle N\right\rangle + \text{const.}$$

    which one can also write, dividing $\left\langle N\right\rangle$ by V as

$$\left[\frac{\partial\left(\beta\mu\right)}{\partial\rho}\right]_{\beta} = \frac{1}{\rho} \rightarrow \beta\mu = \ln\rho + \text{const.}$$

  - Now, consider

$$\frac{\partial\left(\beta p\right)}{\partial\rho} = \frac{\partial\left\langle N\right\rangle}{\partial\rho}\frac{\partial\beta p}{\partial\left\langle N\right\rangle} = -V\frac{\partial\beta\mu}{\partial V} = -V\frac{\partial\beta\mu}{\partial\rho}\frac{\partial\rho}{\partial V} = \rho\frac{\partial\beta\mu}{\partial\rho} = 1$$

    so (considering that pressure should vanish at zero density)

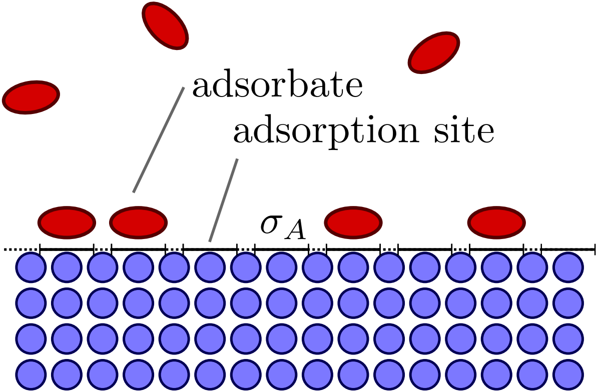
$$\boxed{\beta p = \rho \quad pV = k_B T\left\langle N\right\rangle} \quad \text{ideal gas law}$$

NB: Maxwell relation $\left(\frac{\partial(p\beta)}{\partial N}\right)_{\beta} = -\left(\frac{\partial\beta\mu}{\partial V}\right)_{\beta}$, obtained from $\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{p}{T}$

Langmuir adsorption isotherm/1

- Number of ways of arranging M molecules on N surface sites. Energy for M adsorbed molecules is ϵM

$$\Omega = \frac{N!}{M!\,(N-M)!}$$



Langmuir adsorption isotherm/2

- Grand-canonical partition function (*including density of states!*)

$$P\left(M\right)=\Xi^{-1}\frac{N!\,e^{-\beta((\epsilon-\mu)M)}}{M!\left(N-M\right)!}\approx\Xi^{-1}e^{-\beta((\epsilon-\mu)M)+N\ln N-M\ln M-(N-M)\ln(N-M)}$$

- The chemical potential is set to equal that in the gas phase (ideal gas limit)

$$e^{\beta\mu}=\frac{\rho}{\rho^{\ominus}}=\frac{p}{p^{\ominus}}$$

- We look for the maximum in $\ln P$ [$\theta=M/N$ is the *coverage*!]

$$0=\frac{\partial\ln P}{\partial M}=-\beta\epsilon+\ln\frac{p}{p^{\ominus}}-\ln M+\ln\left(N-M\right)$$

$$\frac{1}{\theta}=\frac{p^{\ominus}}{p}e^{\beta\epsilon}+1\qquad\rightarrow\qquad\theta=\frac{p}{p+p^{\ominus}e^{\beta\epsilon}}$$