ENTROPY and COARSE-GRAINING (1)

A. DONEV, COURANT

RECALL ONE OF THE FUNDAMENTAL POSTULATES OF STATISTICAL MECHANICS:

AT THERMODYNAMIC EQUILIBRIUM EVERY MICROSCOPIC STATE $z = \{p_i, q_i\}$ CONSISTENT WITH CONSERVATION (CONSTRAINTS) IS EQUALLY PROBABLE

$$\rho_{eq}(z) = \delta\left[H(z) - E\right]$$

MICROCANONICAL ENSEMBLE (NVE) (ISOLATED SYSTEM)

Now consider a <u>coarse-grained</u> variable $X(z)$. What is the equilibrium distribution of x?

Microstates $\xrightarrow{x}$ meso states
macro states
(coarse-grained).

The prob. of x is the sum over all microstates <u>consistent</u> with x

$$P(\bar{X}) = \int \rho_{eq}(z)\, \delta[X(z) - \bar{X}]\, dz$$

$$= \int \delta[H(z) - E]\, \delta[X(z) - \bar{X}]\, dz$$

$$= \Omega(\bar{X}) =$$ number of microstates consistent with observables $\bar{X}$, E

IF WE HAVE MEASURED / OBSERVED $\bar{X}$,

THEN

$$\boxed{\rho_{\bar{X}}(z) = \frac{\rho_{eq}(z)\, \delta[X(z) - \bar{X}]}{\Omega(\bar{X})}}$$

CONSTRAINED EQUIL. ENSEMBLE

$$P(x) = \Omega(x) = e^{\left(\ln \Omega(x)\right)}$$

$$\boxed{P(x) = Z^{-1} e^{S(x)/k_B}}$$ EINSTEIN DISTRIBUTION

where we define $\boxed{S(x) = k_B \log(\Omega(x))}$ as **ENTROPY**

The normalization constant Z,

$$Z = \int e^{S(x)/k_B} dx$$

was added for normalization to avoid issue of how to count microstates in a continuum setting (quantum)

For an isolated system at equilibrium, the PDF of observing a coarse-grained variable x is the Einstein distribution $\sim e^{S(x)/k_B}$

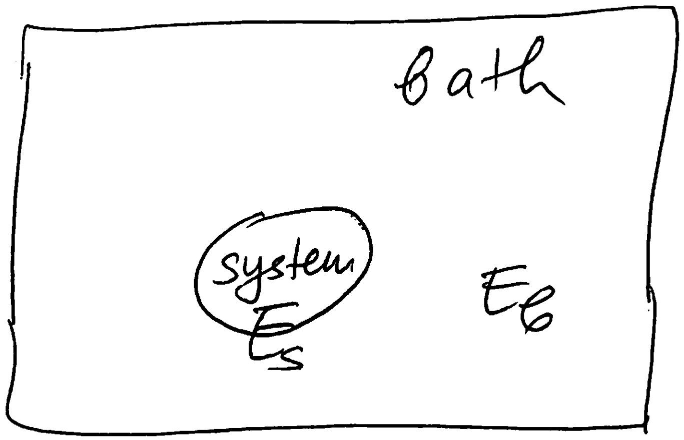
NOTE: Any Langevin equation for a closed system must be time-reversible w.r.t. the Einstein distribution.

We see that:

ENTROPY IS A PROPERTY ASSOCIATED WITH A PARTICULAR LEVEL OF COARSE-GRAINING

IT IS A property of the observer, not intrinsic to the system

In principle the canonical ensemble can be derived from microcanonical:



$$E = E_b + E_s = \text{const}$$

Let $\Omega(E - E_s) = \Omega(E_b)$ be the number of microstates of the bath at energy E_b.

$$P(z_s) \sim \Omega(E - E_s) = \exp\left[\ln \Omega(E - E_s)\right]$$

Since $E_s \ll E$, expand in Taylor series

$$\approx \exp\left[\ln \Omega(E) - E_s \underbrace{\frac{d \ln \Omega(E)}{dE}}_{=\beta} + \text{h.o.t.}\right]$$

Gibbs-Boltzmann $\longrightarrow$ $= \Omega(E) \exp\left[-\beta E_s\right]$, $\boxed{\beta = \frac{1}{k_B T}}$

Now consider doing the same for the canonical ensemble

[NOTE THAT THE VERY CONCEPT OF CANONICAL INVOLVES COARSE-GRAINING SO it involves maximizing entropy]

$$\rho_{eq}(z) = Z^{-1} e^{-\mathcal{H}(z)/k_B T}$$

Hamiltonian

$$P(\underline{X}) \sim \int e^{-\mathcal{H}(z)/k_B T} \, \delta[x(z) - \underline{X}] \, dz$$

$$\equiv e^{-F(\underline{X})/k_B T}$$

where

$F(z)$ is the coarse-grained free energy function (al)

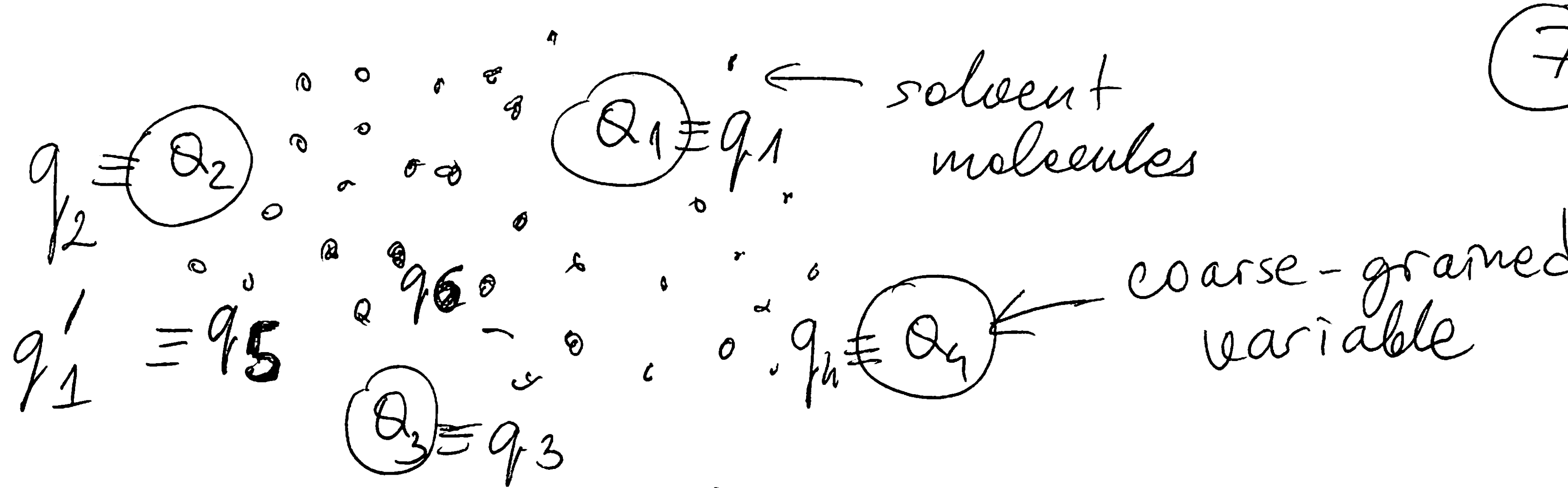
$$\boxed{P(z) = Z^{-1} e^{-F(z)/k_B T}}$$

Generalized Gibbs-Boltzmann distribution.

As an application / illustration, consider a colloidal suspension

$$\mathcal{H}(z) = \sum_i \frac{p_i^2}{2m_i} + U(q)$$

not relevant (trivial)



$$\mathcal{U}(q) = \underline{\mathcal{U}}(\vec{Q}) + \tilde{\mathcal{U}}(\vec{q})$$

$$e^{-F(Q)/k_BT} = \int e^{-\underline{\mathcal{U}}(Q)/k_BT}\, e^{-\tilde{\mathcal{U}}(q)/k_BT}\, dq'$$

$$= e^{-\underline{\mathcal{U}}(Q)/k_BT} \int e^{-\tilde{\mathcal{U}}(q)/k_BT}\, dq'$$

$$\equiv e^{-[\underline{\mathcal{U}}(Q) - TS(Q)]/k_BT}$$

where

$$e^{S(Q)/k_B} \equiv \int e^{-\tilde{U}(q)/k_B T} \, dq'$$

"entropy" of coarse-grained variables

$$F(Q) = \underline{U(Q)} - T\,S(Q)$$

"energetical" contribution

"entropic" contribution

BUT NOTE THAT THIS DIVISION IS SOMEWHAT ARBITRARY

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If the solvent molecules are very small, then it is a good approximation that

$$e^{S(Q)/k_B} = \int e^{-\tilde{u}(Q,q')/k_BT}\, dq' = \text{const. } \underline{\underline{\text{indep.}}} \text{ of } Q$$

So then there is no entropic contribution and

$$P(Q) = Z^{-1} e^{-U(Q)/k_BT}$$

which is the usual Gibbs-Boltzmann distribution (the solvent particles have become a "heat bath" or reservoir)

But if there was a polymer added to the suspension

induces generally attractive "depletion" forces between the colloids which are "entropic" in origin

This is also the physics of the entropic "springs" for polymer chain we discussed in first lecture.

An alternative, perhaps more fundamental view/definition of entropy is an <u>information-theoretic</u> view:

$$\tilde{S} = \max_{\substack{\int \rho(z)\,dz = 1 \\ \text{and any constraints}}} \left[-k_B \int \rho(z) \log\left(\rho(z)/\rho_{eq}(z)\right) dz \right]$$

Gibbs-Jaynes entropy

In the discrete setting

$$S = \max_{\text{s.t. constraints}} \left[-k_B \sum_i p_i \ln p_i \right]$$

If there are no constraints, the maximum is achieved for $p_i = \text{const}$

this gives the microcanonical ensemble and the Boltzmann entropy

$$p_i = \frac{1}{\Omega} \Rightarrow$$

$$\tilde{S} = k_B \sum_1^{\Omega} \frac{\ln \Omega}{\Omega} = k_B \ln \Omega = S$$

Similarly, the canonical ensemble can be obtained by observing or constraining the average energy

$$\langle E \rangle = \int \rho(z) \mathcal{H} \, dz$$

and temperature would be the Lagrange multiplier for the constraint.

Consider the case when we know the PDF for a coarse-grained variable $X(z)$: (13)

$$\lambda(\bar{X}) \left\{ \int \rho(z)\, \delta\left[X(z) - \bar{X}\right] dz = P(\bar{X}) \right.$$

for all $\bar{X}$

Lagrange multiplier

$$\mathcal{L}\text{agrangian} = \mathcal{L} = \tilde{S}\boxed{\rho(z)} - \iint \lambda(\bar{X})\, \rho(z)\, \delta\left[X(z) - \bar{X}\right] dz\, d\bar{X}$$

$$\frac{\delta \mathcal{L}}{\delta \rho} = -\left(1 + \ln \frac{\rho}{\rho_{eq}}\right) - \int \lambda(\bar{X})\, \delta\left[X(z) - \bar{X}\right] d\bar{X}$$

$$= -1 - \ln \frac{\rho}{\rho_{eq}} - \lambda(X(z)) = 0$$

$$\Rightarrow \rho(z) \sim e^{-\lambda(x(z))}$$

This is a generalitation of the microcanonical distribution called the "mesocanonical" distribution (Pep Español).

Going back to constraint

$$\frac{\delta \mathcal{L}}{\delta \lambda} = 0 \Rightarrow \int \rho(z)\, \delta[x(z) - \underline{\bar{x}}]\, dz = P(\underline{x})$$

$$Z^{-1} \int e^{-\lambda(x(z))} \delta[x(z) - \underline{\bar{x}}]\, dz =$$

$$= Z^{-1} e^{-\lambda(\underline{\bar{x}})} \int \delta[x(z) - \underline{\bar{x}}]\, dz =$$

$$= Z^{-1} e^{-\lambda(\underline{\bar{x}})}\, \Omega(\underline{\bar{x}}) = P(\underline{\bar{x}})$$

This means

$$\boxed{\varrho(z) = \varrho_0 \, \frac{P\left[X(z)\right]}{\Omega\left[X(z)\right]}}$$

meso-canonical distribution

If we plug this into the Gibbs-Jaynes entropy

$$\tilde{S} = -k_B \int \varrho(z) \ln \frac{\varrho}{\varrho_{eq}} = \cdot$$

some manipulations

$$\boxed{\tilde{S} = -k_B \int P(X) \ln \left[\frac{P(X)}{\Omega(X)}\right] dX}$$

mesocanonical Gibbs-Jaynes entropy

this is a generalization of the previous formula $-k_B \int \rho \ln \rho \, dz$, which corresponds to no coarse-graining [$\Omega = 1$].

In the case

$$P(X) = \delta(X - \bar{X})$$

up to "irrelevant constants"

$$\tilde{S}(X) = k_B \ln [\Omega(X)] = S(X)$$

which is the same as our previous definition of coarse-grained entropy. In general, however, the two are different (next lecture).