Lecture 18: Ensembles, free energies, max/min principles: A Summary

Reading Assignment for Lectures 15--18: PKT Chapter 7
Midterm coming up Friday, Oct 29.
Problem Set 3 due Oct. 22 (accepted up thru Oct. 25) now available at the website.

Summary: (schema)
Ensemble/distribution:
What you know:
Description:
Associated free energy:
Derivatives:
Max/Min principles:

1. Microcanonical ensemble, "equal a priori probability":
Note: From my point of view, this ensemble is the fundamental postulate of equilibrium statistical mechanics and the basis of the derivation of thermodynamics from stat mech.
You know values of extensive variables. e.g., E,V,N.

All states between E and E+ΔE weighted equally, $P_n = \dfrac{1}{W\left(E,V,N,(\Delta E)\right)} = \dfrac{1}{\Omega(E,V,N)\Delta E}$.

$$S(E,V,N) = k_B \ln W, k_B \ln \Omega \quad \text{"entropy"}$$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$

Isolated system maximizes entropy.

2. Canonical ensemble:
Appropriate for system in contact with heat bath at temperature T.

Microstates weighted according to $P_n \sim e^{-\frac{E_n}{k_B T}}$,

i.e., $P_n = \dfrac{1}{Z} e^{-\frac{E_n}{k_B T}}, Z(T,V,N) = \sum\limits_n e^{-\frac{E_n}{k_B T}}$, "partition function"

$$F(T,V,N) = -kT \ln Z = E - TS \quad \text{"Helmholtz free energy"}$$

$$dF = -SdT - PdV + \mu dN$$

System minimizes F at fixed T.

3. Grand (canonical) ensemble:
Appropriate for system in contact with heat bath at T and particle reservoir(s) at chemical potential(s) μ.

Microstates weighted according to $P_n \sim e^{-\frac{1}{k_B T}(E_n - \mu N_n)}$,

i.e., $P_n = \dfrac{1}{\Xi} e^{-\frac{1}{k_B T}(E_n - \mu N_n)}$, $\Xi(T,V,\mu) = \sum\limits_N e^{\frac{\mu N}{k_B T}} Z(T,V,N)$. "Grand partition function"

$$\Psi(T,V,\mu) = -k_B T \ln \Xi = E - TS + \mu N = -PV \quad \text{"Grand free energy"}$$

$$d\Psi = -SdT - PdV - Nd\mu$$

System minimizes Ψ at fixed T and μ.

4. Constant pressure ensemble:
Appropriate for system in contact with heat bath at T and subject to constant pressure P.

Microstates weighted according to $P_n \sim e^{-\frac{1}{k_B T}(E_n + PV_n)}$, i.e.,

$$P_n = \frac{1}{\mathcal{Z}} e^{-\frac{1}{k_B T}(E_n + PV_n)}, \quad \mathcal{Z}(T,P,N) = \int_V dV e^{-\frac{PV}{k_B T}} Z(T,V,N)$$ “constant P partition function”

$$G(T,P,N) = -k_B T \ln \mathcal{Z} = E - TS + PV = \mu N$$ “Gibbs free energy”

$$dG = -SdT + VdP + \mu dN$$

System minimizes G at fixed T and P.

All these are just different fundamental representations of the thermodynamic information.
For systems of a few degrees of freedom, they are inequivalent (use appropriate one!).
For thermodynamically large systems, they are equivalent, provided variables are chosen to correspond.

I want you to be able to use them, as required.
I will not expect you to be able to derive them all from the microcanonical distribution, although I have indicated the steps.

Let me tie up a few loose ends:

The Grand Canonical distribution:
Suppose small system s is in thermal+*particle* contact with the large bath B.
i.e., they are in contact across a “barrier” which particles pass freely but which can, for example, withstand pressure differences.
Q: How are states of s distributed?
Now, both the total energy and the total number of particles of the small system are no longer fixed.

Claim: Probability of each microstate n of s with $E_n^{(s)}$, $N_n^{(s)}$ is

$$P_n = \frac{e^{-\frac{1}{k_B T^B}\left(E^s - \mu^B N^s\right)}}{\Xi_s\left(T^B, V, \mu^B\right)},$$ “Grand Canonical Ensemble”

where T and μ are the temperature and chemical potential of the bath $\frac{1}{T} = \frac{\partial S_B}{\partial E_B}; -\frac{\mu}{T} = \frac{\partial S_B}{\partial N_B}$ and the normalization factor, $\Xi_s(T,V,\mu) \equiv \sum_n e^{-\frac{1}{k_B T}\left(E_n^{(s)} - \mu N_n^{(s)}\right)} = \sum_{N_s} e^{\frac{\mu N_s}{k_B T}} Z_s(T,V,N_s)$ is called the “grand partition function” of the system and the sum is over all states n of s (*any* number and energy).

Proof: s+B is distributed microcanonically, so, for each particular state s,B, the probability is

$$P_{s+B}(E,N) = \frac{1}{\text{total number of states of } (\mathrm{s}+\mathrm{B})(E \text{ to } E+\Delta E, N)} = \frac{1}{\Omega^{s+B}(E,N)\Delta E}.$$

Consider now the particular state n of s with energy E_s and number N_s.

$$P_n\left(E_n^{(s)},N_n^{(s)}\right)=\frac{\text{total number of states of B}\left(E-E_n^{(s)}\ to\ E-E_n^{(s)}+\Delta E,N-N_n^{(s)}\right)}{\text{total number of states of }(\text{s}+\text{B})(E\ to\ E+\Delta E,N)}$$

$$=\frac{\Omega^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)\Delta E}{\Omega^{s+B}(E,N)\Delta E}\propto\Omega^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)$$

But, $\Omega^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)=e^{\frac{1}{k_B}S^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)}$, so, expanding,

$$S^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)=S_B(E)-\boxed{E_n^{(s)}}\left.\frac{\partial S^B}{\partial E}\right|_{E,N}-\boxed{N_n^{(s)}}\left.\frac{\partial S^B}{\partial N}\right|_{E,N}+\text{small}\ldots$$

Second-derivative terms are small in that they go as the inverse of extensive quantities.

But, $\dfrac{\partial S^B}{\partial E}=\dfrac{1}{T^B}$ and $\dfrac{\partial S^B}{\partial N^B}=-\dfrac{\mu^B}{T^B}$; hence,

$$P_n\propto\Omega^B\left(E-E_n^{(s)},N-N_n^{(s)}\right)\propto e^{-\frac{1}{k_BT_B}\left(E_n^{(s)}-\mu_BN_n^{(s)}\right)}.\quad \text{QED}$$

This probability distribution is called the "grand (canonical) ensemble."

Note the "spread" of energy and number in the system!

Comment: When there are several types of particles in contact, then,

$$P_n\propto e^{-\frac{1}{k_BT_B}\left(E_n^{(s)}-\mu_{1,B}N_{1,n}^{(s)}-\mu_{2,B}N_{2,n}^{(s)}-\ldots\right)}.$$

When the "system" is thermodynamically large, then choice of T and μ fixes very precisely the energy E and number N that you find in the grand canonical ensemble at values $E^*(T,V,\mu),N^*(T,V,\mu)$, so that averages of (almost) all quantities are the same in microcanonical, canonical, and grand canonical ensembles, provided that T,μ,...are chosen to make $E=E^*$, $N=N^*$, etc.,

i.e., μ is just a "dial" for adjusting N just as T was a dial for adjusting E.

Proof: (not required) sketched below:

You can go all the way back to S; but, I'll use the previous change to canonical.

Thus, for example, $\Xi(T,V,\mu)=\sum\limits_{N=0}^{\infty}e^{\frac{\mu N}{k_BT}}Z(T,V,N)=\sum\limits_{N=0}^{\infty}e^{\frac{\mu N}{k_BT}}e^{-\frac{F(T,V,N)}{k_BT}}$.

Compare: $\boxed{Z(T,V,N)=\int_{E_0}^{\infty}dE\,\Omega(E,V,N)e^{-\frac{E}{k_BT}}=\int_{E_0}^{\infty}dE\,e^{\frac{S(E,V,N)}{k_BT}}e^{-\frac{E}{k_BT}}.}$

The summand is a product of an increasing function of N and a decreasing function of N.

There is a maximum at $0=\mu-\left.\dfrac{\partial F}{\partial N}\right|_{T,V}$, which fixes $N^*(T,V,\mu)$

Can show that this is a maximum and that it is sharp by looking at second and higher derivatives.

Upshot:

Sum is dominated by term with (near) $N = N^*$.

This dominance is strong enough so that $\Xi(T,V,\mu) = e^{\frac{\mu N^* - F(T,V,N^*)}{kT}} \cdot \sqrt{O(N)}(1+\text{small});$

hence, $\Psi(T,V,\mu) \equiv -k_BT\ln\Xi = F(T,V,N^*(T,V,\mu)) - \mu N^*(T,V,\mu) + \text{small}$

i.e., $\boxed{\Psi = -kT\ln\Xi = F - \mu N = E - TS - \mu N = -PV\ (\text{Euler})}$

"Grand (canonical) free energy" (see Lect. 14.1)

with, $dF(T,V,N) = -SdT - PdV + \mu dN$, so

$$d\Psi(T,V,\mu) = dF - d(\mu N) = (-SdT - PdV + \mu dN) - (\mu dN + Nd\mu) = \boxed{-SdT - PdV - Nd\mu = d\Psi}$$

Example: Classical Ideal Gas in Grand Ensemble

Recall: $Z(T,V,N) = \frac{1}{N!}\left[\frac{V}{\lambda_{th}^d}\right]^N$, where $\frac{1}{\lambda_{th}} = \int_{-\infty}^{\infty}\frac{dp}{2\pi\hbar}e^{-\frac{p^2}{2mk_BT}} = \sqrt{\frac{mk_BT}{2\pi\hbar^2}}$.

Calculate Grand partition function: $\Xi = \sum_{N=0}^{\infty} e^{\frac{\mu N}{k_BT}} Z(T,V,N) = \sum_{N=0}^{\infty}\frac{e^{\frac{\mu N}{k_BT}}}{N!}\left[\frac{V}{\lambda_{th}^d}\right]^N = \exp\left(\frac{V e^{\frac{\mu}{k_BT}}}{\lambda_{th}^d}\right)$.

Evaluate Grand free energy: $\Psi(T,V,\mu) = -k_BT\ln\Xi = -\frac{kTVe^{\frac{\mu}{k_BT}}}{\lambda_{th}^d}$.

Calculate derivatives $P = -\frac{\partial\Psi}{\partial V} = \frac{k_BT\,e^{\frac{\mu}{k_BT}}}{\lambda_{th}^d}$; $N = -\frac{\partial\Psi}{\partial\mu} = \frac{Ve^{\frac{\mu}{k_BT}}}{\lambda_{th}^d}$.

Eliminating the chemical potential gives the ideal-gas equation of state, as usual.

For future reference:

A. Note that $n = \frac{N}{V} = \frac{e^{\frac{\mu}{k_BT}}}{\lambda_{th}^d}$, which is equivalent to $\mu = k_BT\left[\ln\left(\frac{N}{V}\right) + d\ln\lambda_{th}\right]$ as above.

B. With several different types of (non-interacting classical) particles α, $n_\alpha \equiv \frac{N_\alpha}{V} = \frac{e^{\frac{\mu_\alpha}{k_BT}}}{\lambda_\alpha^d}$.

C. If particle has additional internal energy, then $\varepsilon_\alpha(\vec{p}) = \frac{\vec{p}^2}{2m_\alpha} \to \frac{\vec{p}^2}{2m_\alpha} + \varepsilon_\alpha^0$ and

$$n_\alpha \equiv \frac{N_\alpha}{V} = \frac{e^{\frac{\mu_\alpha}{k_BT}}}{\lambda_\alpha^d}e^{-\frac{\varepsilon_\alpha^0}{kT}}.$$