Physics 112
Various Free Energies

Peter Young

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In class we discussed various thermodynamic "free energies". Which one is the most convenient will depend on the problem being considered. Here we summarize them in a table:

Quantity	Depends on $\cdots$	Is equal to $\cdots$	Thermodynamic identity
Energy, U	S, V, N		$dU = TdS - PdV + \mu dN$
Enthalpy, H	S, P, N	$U + PV$	$dH = TdS + VdP + \mu dN$
(Helmholtz) free energy, F	T, V, N	$U - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy, G	T, P, N	$F + PV \; (= \mu N)$	$dG = -SdT + VdP + \mu dN$
Grand potential, Ω	T, V, μ	$F - \mu N \; (= -PV)$	$d\Omega = -SdT - PdV - Nd\mu$

From the thermodynamic identity for each quantity we immediately obtain the first derivatives. For example:

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S\,, \qquad \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = -S\,,$$

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu\,, \qquad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu\,, \qquad \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = -N\,.$$

Note that it is important to understand what quantities are being kept constant in each case.

For us the two most important "free energies" are the Helmholtz free energy and the grand potential. The reason is that they are related to the partition function Z and grand partition function $\mathcal{Z}$ by

$$\boxed{F = -k_B T \ln Z\,, \qquad \Omega = -k_B T \ln \mathcal{Z}\,,} \tag{1}$$

respectively, where

$$\boxed{Z = \sum_l e^{-\beta E_l}\,,} \tag{2}$$

and

$$\boxed{\mathcal{Z} = \sum_N \sum_l e^{\beta(\mu N - E_l)} = \sum_N \lambda^N Z_N\,,} \tag{3}$$

in which

$$\lambda = e^{\beta \mu}$$

is called the "activity" (or "fugacity"). In determining the partition function, Eq. (2), the number of particles N is fixed, and the sum is over all states l with this number of particles. In determining the grand partition function, Eq. (3), N is summed over from 0 to ∞, and, for each value of N, the sum only is over states l with *this* number of particles. We define Z_N to be the partition function with N particles (and so Z in Eq. (2) could equivalently have been written as Z_N).