Lecture 5 - Fluctuations, and Free Energy

- **Fluctuations:**

  The variance of the energy is:

$$\Delta E^2 = \sum_i \frac{E_i^2 e^{-E_i \beta}}{Z} - \frac{1}{Z^2}\left(\sum_i E_i e^{-E_i\beta}\right)^2 = \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{(1)}$$

  Also:

$$\left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{=} - \left(\frac{\partial \langle E\rangle}{\partial \beta}\right)_{=} T^2 \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{=} T^2 c_V \tag{2}$$

  Where $c_V = C_V/N$ is the **heat capacity per particle**, which above is per particle.

  Note that if we looked at fluctuations of the total energy:

$$\langle \Delta U^2\rangle = \left(\frac{\partial^2 \ln Z_N}{\partial \beta^2}\right)_{=} N \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{=} T^2 N c_V = T^2 C_V \tag{3}$$

  The standard deviation of energy per particle:

$$\sigma_E = \frac{1}{N}\sqrt{\langle \Delta U^2\rangle} = \frac{T\sqrt{c_V}}{\sqrt{N}} \tag{4}$$

  So the fluctuations of **energy per particle** fall off as $1/\sqrt{N}$. Just like in the central limit theorem.

- **Minimal free energy principal:**

  The entropy of the combined system+bath:

$$S_{total} = S - U/T = -\beta F(U; T, V, N) \tag{5}$$

  Maximum entropy $\delta S = 0$ translates to:

$$\frac{\delta F(U; T, V, N)}{\delta U} = 0 \tag{6}$$

  This is the *minimum free energy principal*.

- **Definition of the free energy:**

$$F = U(T, V, N) - TS(T, N, V) \tag{7}$$

  Which corresponds to $F(\overline{U}_{eq}; T, V, N)$.

- **Connection between free energy and the partition function:**

$$F = -T \ln Z \tag{8}$$

- **Differential and partial derivatives of the free energy:**

$$dF = dU - T\left(\frac{\partial S}{\partial U}\right)_{VN} dU - T\left(\frac{\partial S}{\partial V}\right)_{NU} dV - T\left(\frac{\partial S}{\partial N}\right)_{UV} - SdT = -pdV - SdT + \mu dN \tag{9}$$

  From which we obtain:

$$\left(\tfrac{\partial F}{\partial T}\right)_{NV} = -S,\ \left(\tfrac{\partial F}{\partial V}\right)_{NT} = -p,\ \left(\tfrac{\partial F}{\partial N}\right)_{TV} = \mu. \tag{10}$$