

## 5. Chemical Potential and Gibbs Distribution

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- The **chemical potential** governs the flow of particles between the systems, just as the temperature governs the flow of energy.
- Definition of chemical potential:

$$\mu(\tau, V, N) \equiv \left( \frac{\partial F}{\partial N} \right)_{\tau, V}$$

then

$$\mu_1 = \mu_2$$

expresses the condition of diffusive equilibrium.

- Two systems are in combined thermal and diffusive equilibrium when their temperatures and chemical potentials are equal:  $\tau_1 = \tau_2; \mu_1 = \mu_2$ .
- The chemical potential is equivalent to a true potential energy: the difference in chemical potential between two systems is equal to the potential barrier that will bring the two systems into diffusive equilibrium.
- **Total chemical potential:**

$$\mu = \mu_{ext} + \mu_{int}$$

- Alternative relation:

$$\frac{\mu(U, V, N)}{\tau} = - \left( \frac{\partial \sigma}{\partial N} \right)_{U, V}$$

- **Gibbs factor:**

$$\exp[(N\mu - \epsilon)/\tau]$$

- **Gibbs sum** (grand partition function):

$$\mathcal{Z}(\mu, \tau) = \sum_{ASN} \exp[(N\mu - \epsilon_{s(N)})/\tau]$$

where ASN stands for all states and numbers of particles

- The absolute probability that the system will be found in a state  $N_1, \epsilon_1$  is given by:

$$P(N_1, \epsilon_1) = \frac{\exp[(N_1\mu - \epsilon_1)/\tau]}{\mathcal{Z}}$$

- **Absolute activity:**

$$\lambda \equiv \exp(\mu/\tau)$$