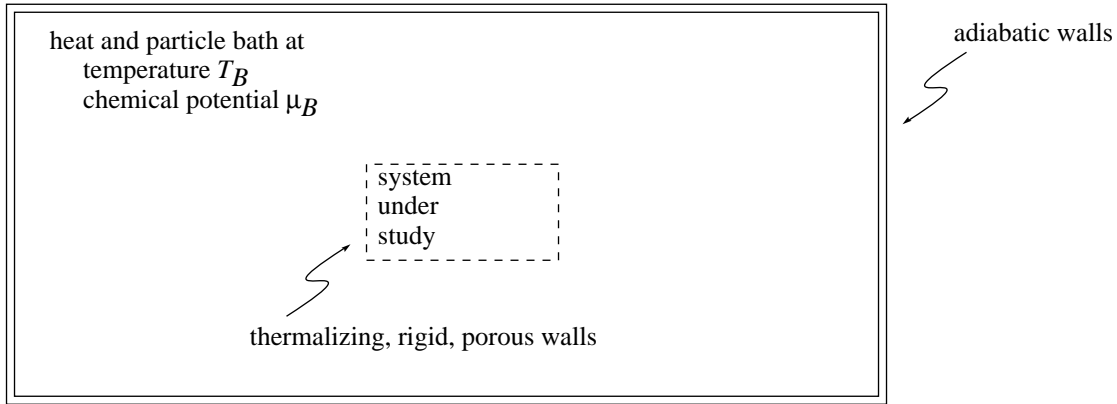


Derivation of Grand Canonical Ensemble

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Microstate x of system under study means, for example, positions and momenta of all atoms plus number of atoms, or direction of all spins, plus number of spins.

Macrostate of system under study specified by variables (T, V, μ) .

What is the probability $\mathcal{P}(x)$ that system under study is in microstate x ?

Total energy is bath energy plus system energy; total number is bath number plus system number

$$E_T = E_B + H(x); \quad N_T = N_B + N(x).$$

As with the canonical ensemble

$$\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} = e^{[S_B(x_2) - S_B(x_1)]/k_B}.$$

As system under study changes from state x_1 to x_2 , bath changes through

$$\begin{aligned} dS_B &= \frac{1}{T_B} (dE_B + p_B dV_B - \mu_B dN_B) \\ \Delta S_B &= \frac{1}{T_B} (\Delta E_B - \mu_B \Delta N_B) = -\frac{1}{T_B} (\Delta E - \mu_B \Delta N) \end{aligned}$$

so

$$\frac{\mathcal{P}(x_2)}{\mathcal{P}(x_1)} = e^{-\{H(x_2) - \mu_B N(x_2)\} - \{H(x_1) - \mu_B N(x_1)\} / k_B T_B}.$$

But $T_B = T$ of system under study, and $\mu_B = \mu$ of system under study. All references to the bath have vanished. Using separation of variables

$$\frac{\mathcal{P}(x_1)}{e^{-\{H(x_1) - \mu N(x_1)\} / k_B T}} = \frac{\mathcal{P}(x_2)}{e^{-\{H(x_2) - \mu N(x_2)\} / k_B T}} \equiv \frac{1}{\Xi(T, V, \mu)}$$

and

$$\mathcal{P}(x) = \frac{e^{-\{H(x) - \mu N(x)\} / k_B T}}{\Xi(T, V, \mu)}.$$

The grand canonical partition function is the normalization factor

$$\Xi(T, V, \mu) = \sum_x e^{-\beta\{H(x) - \mu N(x)\}},$$

where now the sum over microstates includes a sum over microstates with different $N(x)$. Exactly what is meant by a “sum over all states” depends on the system under study. For classical atoms modeled as point particles

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N! h_0^{3N}} \int d\Gamma e^{-\{H(\Gamma) - \mu N\} / k_B T}$$

where the integral extends over all phase space.

What is the connection to thermodynamics?

Interpret the thermodynamic number N as $\langle N(\mathbf{x}) \rangle$:

$$N = \langle N(\mathbf{x}) \rangle = \frac{\sum_{\mathbf{x}} N(\mathbf{x}) e^{-\beta\{H(\mathbf{x}) - \mu N(\mathbf{x})\}}}{\sum_{\mathbf{x}} e^{-\beta\{H(\mathbf{x}) - \mu N(\mathbf{x})\}}} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \left\{ \sum_{\mathbf{x}} e^{-\beta\{H(\mathbf{x}) - \mu N(\mathbf{x})\}} \right\} \Bigg|_{T,V}$$

Comparison of this equation to the corresponding thermodynamic equation,

$$N = k_B T \left. \frac{\partial \ln \Xi}{\partial \mu} \right)_{T,V} \quad \text{to} \quad N = - \left. \frac{\partial \Pi}{\partial \mu} \right)_{T,V},$$

leads to the identification

$$\Pi(T, V, \mu) = -k_B T \ln \Xi(T, V, \mu).$$

Additional reasoning results in (1) the interpretation of chemical potential as control parameter for number and (2) a dispersion-susceptibility relation

$$\Delta N \sim \sqrt{\left. \frac{\partial N}{\partial \mu} \right)_{T,V}} \sim \sqrt{\kappa_T}.$$

This equation shows that in the thermodynamic limit the spread of particle number grows small in the sense that

$$\frac{\Delta N}{\langle N(\mathbf{x}) \rangle} \rightarrow 0.$$