4.5: Grand Canonical Ensemble (GCE)

Grand canonical distribution and partition function

Consider once again the situation depicted in Figure [universe], where a system S is in contact with a world W, their union $U=W\cup S$ being called the 'universe'. We assume that the system's volume V_S is fixed, but otherwise it is allowed to exchange energy and particle number with W. Hence, the system's energy E_S and particle number N_S will fluctuate. We ask what is the probability that S is in a state $|\,n\,\rangle$ with energy E_n and particle number N_n. This is given by the ratio

$$\begin{aligned} P_n &= \lim_{\Delta E\to 0} \frac{D_W(E_U-E_n\,,\,N_U-N_n)\,\Delta E}{D_U(E_U,N_U)\,\Delta E} \\ &= \frac{\text{\# of states accessible to } W \text{ given that } E_S=E_n \text{ and } N_S=N_n}{\text{total \# of states in } U}\ . \end{aligned}$$

Then

$$\begin{aligned} \ln P_n &= \ln D_W(E_U-E_n\,,\,N_U-N_n)-\ln D_U(E_U,N_U) \\ &= \ln D_W(E_U,N_U)-\ln D_U(E_U,N_U) \\ &\qquad\qquad -E_n\,\frac{\partial\ln D_W(E,N)}{\partial E}\bigg|_{\substack{E=E_U\\N=N_U}} -N_n\,\frac{\partial\ln D_W(E,N)}{\partial N}\bigg|_{\substack{E=E_U\\N=N_U}}+\ \ldots \\ &\equiv -\alpha-\beta E_n+\beta\mu N_n\ . \end{aligned}$$

The constants β and μ are given by

$$\begin{aligned} \beta &= \frac{\partial\ln D_W(E,N)}{\partial E}\bigg|_{\substack{E=E_U\\N=N_U}}=\frac{1}{k_BT} \\ \mu &= -k_BT\,\frac{\partial\ln D_W(E,N)}{\partial N}\bigg|_{\substack{E=E_U\\N=N_U}}\ . \end{aligned}$$

The quantity μ has dimensions of energy and is called the *chemical potential*. *Nota bene:* Some texts define the 'grand canonical Hamiltonian' $\hat{K}$ as

$$\hat{K}\equiv\hat{H}-\mu\hat{N}\ . \tag{4.5.1}$$

Thus, $P_n=e^{-\alpha}\,e^{-\beta(E_n-\mu N_n)}$. Once again, the constant α is fixed by the requirement that $\sum_n P_n=1$:

$$P_n=\frac{1}{\Xi}\,e^{-\beta(E_n-\mu N_n)}\quad ,\quad \Xi(\beta,V,\mu)=\sum_n e^{-\beta(E_n-\mu N_n)}=\mathsf{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}=\mathsf{Tr}\ e^{-\beta\hat{K}}\ . \tag{4.5.2}$$

Thus, the quantum mechanical *grand canonical density matrix* is given by

$$\hat{\varrho}=\frac{e^{-\beta\hat{K}}}{\mathsf{Tr}\ e^{-\beta\hat{K}}}\ . \tag{4.5.3}$$

Note that $\big[\hat{\varrho},\hat{K}\big]=0$. The quantity $\Xi(T,V,\mu)$ is called the *grand partition function*. It stands in relation to a corresponding free energy in the usual way:

$$\Xi(T,V,\mu)\equiv e^{-\beta\Omega(T,V,\mu)}\qquad\Longleftrightarrow\qquad \Omega=-k_BT\,\ln\Xi\ , \tag{4.5.4}$$

where $\Omega(T,V,\mu)$ is the *grand potential*, also known as the *Landau free energy*. The dimensionless quantity $z\equiv e^{\beta\mu}$ is called the *fugacity*.

If $\big[\hat{H},\hat{N}\big]=0$, the grand potential may be expressed as a sum over contributions from each N sector, *viz.*

$$\Xi(T,V,\mu)=\sum_N e^{\beta\mu N}\,Z(T,V,N)\,. \tag{4.5.5}$$

When there is more than one species, we have several chemical potentials $\{\mu_a\}$, and accordingly we define

$$\hat{K}=\hat{H}-\sum_a \mu_a\,\hat{N}_a\,, \tag{4.5.6}$$

with $\Xi=\mathsf{Tr}\;e^{-\beta\hat{K}}$ as before.

Entropy and Gibbs-Duhem relation

In the GCE, the Boltzmann entropy is

$$\begin{aligned} S&=-k_B\sum_n P_n\ln P_n\\ &=-k_B\sum_n P_n\,\big(\beta\Omega-\beta E_n+\beta\mu N_n\big)\\ &=-\frac{\Omega}{T}+\frac{\langle\hat{H}\rangle}{T}-\frac{\mu\,\langle\hat{N}\rangle}{T}\,, \end{aligned}$$

which says

$$\Omega=E-TS-\mu N\,, \tag{4.5.7}$$

where

$$\begin{aligned} E&=\sum_n E_n\,P_n=\mathsf{Tr}\,\big(\hat{\varrho}\,\hat{H}\big)\\ N&=\sum_n N_n\,P_n=\mathsf{Tr}\,\big(\hat{\varrho}\,\hat{N}\big)\,. \end{aligned}$$

Therefore, $\Omega(T,V,\mu)$ is a double Legendre transform of $E(S,V,N)$, with

$$d\Omega=-S\,dT-p\,dV-N\,d\mu\,, \tag{4.5.8}$$

which entails

$$S=-\bigg(\frac{\partial\Omega}{\partial T}\bigg)_{V,\mu}\qquad,\qquad p=-\bigg(\frac{\partial\Omega}{\partial V}\bigg)_{T,\mu}\qquad,\qquad N=-\bigg(\frac{\partial\Omega}{\partial\mu}\bigg)_{T,V}\,. \tag{4.5.9}$$

Since $\Omega(T,V,\mu)$ is an extensive quantity, we must be able to write $\Omega=V\omega(T,\mu)$. We identify the function $\omega(T,\mu)$ as the negative of the pressure:

$$\begin{aligned} \frac{\partial\Omega}{\partial V}&=-\frac{k_BT}{\Xi}\bigg(\frac{\partial\Xi}{\partial V}\bigg)_{T,\mu}=\frac{1}{\Xi}\sum_n\frac{\partial E_n}{\partial V}\,e^{-\beta(E_n-\mu N_n)}\\ &=\bigg(\frac{\partial E}{\partial V}\bigg)_{T,\mu}=-p(T,\mu)\,. \end{aligned}$$

Therefore,

$$\Omega=-pV\qquad,\qquad p=p(T,\mu)\quad(\text{equation of state})\backslash\,. \tag{4.5.10}$$

This is consistent with the result from thermodynamics that $G=E-TS+pV=\mu N$. Taking the differential, we recover the Gibbs-Duhem relation,

$$d\Omega=-S\,dT-p\,dV-N\,d\mu=-p\,dV-V\,dp\quad\Rightarrow\quad S\,dT-V\,dp+N\,d\mu=0\,. \tag{4.5.11}$$

Generalized Susceptibilities in the GCE

We can appropriate the results from §5.8 and apply them, *mutatis mutandis*, to the GCE. Suppose we have a family of observables $\big\{\hat{Q}_k\big\}$ satisfying $\big[\hat{Q}_k\,,\,\hat{Q}_{k'}\big]=0$ and $\big[\hat{H}_0\,,\,\hat{Q}_k\big]=0$ and $\big[\hat{N}_a\,,\,\hat{Q}_k\big]=0$ for all k, k', and a. Then for the grand canonical Hamiltonian

$$\hat{K}(\vec{\lambda}) = \hat{H}_0 - \sum_a \mu_a \, \hat{N}_a - \sum_k \lambda_k \, \hat{Q}_k \ , \tag{4.5.12}$$

we have that

$$Q_k(\vec{\lambda}, T) = \langle \, \hat{Q}_k \, \rangle = -\bigg(\frac{\partial\Omega}{\partial\lambda_k}\bigg)_{T,\mu_a, \, \lambda_{k' \neq k}} \tag{4.5.13}$$

and we may define the matrix of generalized susceptibilities,

$$\chi_{kl} = \frac{1}{V} \, \frac{\partial Q_k}{\partial\lambda_l} = -\frac{1}{V} \, \frac{\partial^2\Omega}{\partial\lambda_k \, \partial\lambda_l} \ . \tag{4.5.14}$$

Fluctuations in the GCE

Both energy and particle number fluctuate in the GCE. Let us compute the fluctuations in particle number. We have

$$N = \langle \, \hat{N} \, \rangle = \frac{\mathrm{Tr} \ \hat{N} \, e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathrm{Tr} \ e^{-\beta(\hat{H} - \mu\hat{N})}} = \frac{1}{\beta} \, \frac{\partial}{\partial\mu} \, \ln\Xi \, . \tag{4.5.15}$$

Therefore,

$$\begin{aligned} \frac{1}{\beta} \, \frac{\partial N}{\partial\mu} &= \frac{\mathrm{Tr} \ \hat{N}^2 \, e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathrm{Tr} \ e^{-\beta(\hat{H} - \mu\hat{N})}} - \bigg(\frac{\mathrm{Tr} \ \hat{N} \, e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathrm{Tr} \ e^{-\beta(\hat{H} - \mu\hat{N})}}\bigg)^2 \\ &= \big\langle \hat{N}^2 \big\rangle - \big\langle \hat{N} \big\rangle^2 \ . \end{aligned}$$

Note now that

$$\frac{\big\langle \hat{N}^2 \big\rangle - \big\langle \hat{N} \big\rangle^2}{\big\langle \hat{N} \big\rangle^2} = \frac{k_B T}{N^2} \, \bigg(\frac{\partial N}{\partial\mu}\bigg)_{T,V} = \frac{k_B T}{V} \, \kappa_T \ , \tag{4.5.16}$$

where κ_T is the isothermal compressibility. Note:

$$\begin{aligned} \bigg(\frac{\partial N}{\partial\mu}\bigg)_{T,V} &= \frac{\partial(N, T, V)}{\partial(\mu, T, V)} = -\frac{\partial(N, T, V)}{\partial(V, T, \mu)} \\ &= -\frac{\partial(N, T, V)}{\partial(N, T, p)} \cdot \frac{\partial(N, T, p)}{\partial(V, T, p)} \cdot \overbrace{\frac{\partial(V, T, p)}{\partial(N, T, \mu)}}^{1} \cdot \frac{\partial(N, T, \mu)}{\partial(V, T, \mu)} \\ &= -\frac{N^2}{V^2} \, \bigg(\frac{\partial V}{\partial p}\bigg)_{T,N} = \frac{N^2}{V} \, \kappa_T \ . \end{aligned}$$

Thus,

$$\frac{(\Delta N)_{RMS}}{N} = \sqrt{\frac{k_B T \, \kappa_T}{V}} \ , \tag{4.5.17}$$

which again scales as $V^{-1/2}$.

Gibbs ensemble

Let the system's particle number N be fixed, but let it exchange energy and volume with the world W. *Mutatis mutandis*, we have

$$P_n = \lim_{\Delta E \to 0} \ \lim_{\Delta V \to 0} \ \frac{D_W(E_U - E_n \, , \, V_U - V_n) \, \Delta E \, \Delta V}{D_U(E_U, V_U) \, \Delta E \, \Delta V} . \tag{4.5.18}$$

Then

$$\begin{aligned}\ln P_n &= \ln D_W(E_U - E_n\,,\,V_U - V_n) - \ln D_U(E_U, V_U)\\ &= \ln D_W(E_U, V_U) - \ln D_U(E_U, V_U)\\ &\qquad - E_n\,\frac{\partial \ln D_W(E,V)}{\partial E}\bigg|_{\substack{E=E_U\\ V=V_U}} - V_n\,\frac{\partial \ln D_W(E,V)}{\partial V}\bigg|_{\substack{E=E_U\\ V=V_U}} + \ldots\\ &\equiv -\alpha - \beta E_n - \beta p\, V_n\ .\end{aligned}$$

The constants β and p are given by

$$\begin{aligned}\beta &= \frac{\partial \ln D_W(E,V)}{\partial E}\bigg|_{\substack{E=E_U\\ V=V_U}} = \frac{1}{k_B T}\\ p &= k_B T\,\frac{\partial \ln D_W(E,V)}{\partial V}\bigg|_{\substack{E=E_U\\ V=V_U}}\ .\end{aligned}$$

The corresponding partition function is

$$Y(T,p,N) = \mathsf{Tr}\ e^{-\beta(\hat{H}+pV)} = \frac{1}{V_0}\int\limits_0^\infty \! dV\, e^{-\beta pV}\ Z(T,V,N) \equiv e^{-\beta G(T,p,N)}\ , \tag{4.5.19}$$

where V_0 is a constant which has dimensions of volume. The factor V_0^{-1} in front of the integral renders Y dimensionless. Note that $G(V_0') = G(V_0) + k_B T \ln(V_0'/V_0)$, so the difference is not extensive and can be neglected in the thermodynamic limit. In other words, it doesn't matter what constant we choose for V_0 since it contributes subextensively to G. Moreover, in computing averages, the constant V_0 divides out in the ratio of numerator and denominator. Like the Helmholtz free energy, the Gibbs free energy $G(T,p,N)$ is also a double Legendre transform of the energy $E(S,V,N)$, *viz.*

$$\begin{aligned}G &= E - TS + pV\\ dG &= -S\,dT + V\,dp + \mu\,dN\ ,\end{aligned}$$

which entails

$$S = -\bigg(\frac{\partial G}{\partial T}\bigg)_{p,N} \quad , \quad V = +\bigg(\frac{\partial G}{\partial p}\bigg)_{T,N} \quad , \quad \mu = +\bigg(\frac{\partial G}{\partial N}\bigg)_{T,p}\ . \tag{4.5.20}$$