7.G. The Grand Canonical Ensemble

A system is open if it can exchange heat and particles with its environment, which serves as a heat & particle reservoir. At equilibrium, the system has the same T & μ as the environment, while $\langle H\rangle$ & $\langle N\rangle$ assume their thermodynamic values U & N. By the 2nd law, S must be a maximum at equilibrium. With the constraints

$$\mathrm{Tr}\,\hat{\rho} = 1 \tag{7.104}$$

$$\mathrm{Tr}\left(\hat{H}\,\hat{\rho}\right) = \langle H\rangle = U \tag{7.105}$$

$$\mathrm{Tr}\left(\hat{N}\,\hat{\rho}\right) = \langle N\rangle = N \tag{7.106}$$

enforced via the Lagrange multipliers α_0, α_E & α_N, respectively, the extremum condition becomes

$$\delta\,\mathrm{Tr}\left(-k_B\,\hat{\rho}\ln\hat{\rho} + \alpha_0\,\hat{\rho} + \alpha_E\,\hat{H}\,\hat{\rho} + \alpha_N\,\hat{N}\,\hat{\rho}\right) = 0$$

$$\rightarrow \quad \mathrm{Tr}\left[\left(-k_B\ln\hat{\rho} - k_B\,\hat{1} + \alpha_0\,\hat{1} + \alpha_E\,\hat{H} + \alpha_N\,\hat{N}\right)\delta\hat{\rho}\right] = 0 \tag{7.107}$$

(7.107) can be satisfied for arbitrary $\delta\hat{\rho}$ if and only if

$$-k_B\ln\hat{\rho} - k_B\,\hat{1} + \alpha_0\,\hat{1} + \alpha_E\,\hat{H} + \alpha_N\,\hat{N} = 0 \tag{7.108}$$

$$\rightarrow \quad \hat{\rho} = \exp\left[\left(\frac{\alpha_0}{k_B} - 1\right)\hat{1} + \frac{\alpha_E}{k_B}\hat{H} + \frac{\alpha_N}{k_B}\hat{N}\right]$$

$$= \exp\left(\frac{\alpha_0}{k_B} - 1\right)\exp\left(\frac{\alpha_E}{k_B}\hat{H} + \frac{\alpha_N}{k_B}\hat{N}\right)$$

$$\equiv \frac{1}{Z}\exp\left(\frac{\alpha_E}{k_B}\hat{H} + \frac{\alpha_N}{k_B}\hat{N}\right) \tag{7.108a}$$

where

$$Z = \exp\left(1 - \frac{\alpha_0}{k_B}\right) \tag{7.109a}$$

$$= \mathrm{Tr}\left(\frac{\alpha_E}{k_B}\hat{H} + \frac{\alpha_N}{k_B}\hat{N}\right) \qquad \text{[(7.104) used.]} \tag{7.109}$$

$\mathrm{Tr}\left[\hat{\rho}\,(7.108)\right]$ gives

$$S - k_B + \alpha_0 + \alpha_E\,U + \alpha_N\,N = 0 \qquad \text{[(7.104-6) used.]}$$

$$\rightarrow \quad S - k_B\ln Z + \alpha_E\,U + \alpha_N\,N = 0 \qquad \text{[(7.109a) used.]} \tag{7.110}$$

The only fundamental equation that involves the variables S, U & N is that for the grand potential [see (2.122) of §2.F.5]

$$\Omega = U - T\,S - \mu'\,N$$

which can be written as

$$S + \frac{1}{T}\Omega - \frac{1}{T}U + \frac{\mu'}{T}N = 0 \tag{7.110a}$$

Comparing (7.110 & a) gives

$$\Omega = -k_B\,T\ln Z \tag{7.111}$$

and

$$\alpha_E = -\frac{1}{T} \qquad \alpha_N = \frac{\mu'}{T} \tag{7.111a}$$

Putting (7.111a) into (7.109) gives the grand partition function

$$Z_\mu(T) = \mathrm{Tr}\left[-\beta\left(\hat{H} - \mu'\,\hat{N}\right)\right] \qquad \left[\ \beta = \frac{1}{k_B\,T}\ \right] \tag{7.112}$$

$$= e^{-\beta\Omega} \qquad \text{[(7.111) used.]} \tag{7.112a}$$

while (7.108a) becomes

$$\hat{\rho} = \frac{1}{Z_\mu} \exp\left[-\beta\left(\hat{H} - \mu' \hat{N} \right) \right] \qquad (7.113)$$

$$= \exp\left[-\beta\left(\hat{H} - \mu' \hat{N} - \Omega \hat{1} \right) \right] \qquad \text{[(7.112a) used.]} \qquad (7.113a)$$

which is the probability density operator for the grand canonical ensemble of open systems.

Ex.7.6. Black-Body Radiation

Since photons do not interact with each other unless the field intensities are extremely high, equilibrium in a photon gas is established by photon absorption/emission at the container walls, instead of collisions between photons. At equilibrium, the EM field inside a box of opaque walls therefore depends only on the temperature of the walls. Hence the name black-body radiation.

Consider such a black body of volume $V = L^3$ with walls kept at temperature T. The energy of the photons inside are given by $\hbar\,\omega_i = \hbar\,c\;|\,\boldsymbol{k}_i\,|$, where c is the speed of light. ω_i and $\boldsymbol{k}_i$ are the frequency and wave-vector, respectively, of the i^{th} standing mode.

Compute the pressure of this photon gas.

Note: Since photons are quanta of the EM field, their number is not conserved. Hence, there is no chemical potential for photons, i.e. $\mu' \equiv 0$.

Answer

Since there are no interactions between the photons,

$$Z_\mu(T) = \prod_{i=1}^{\infty} Z_{\mu i}(T) \qquad (1a)$$

where $Z_{\mu i}(T)$ is the grand partition function for the i^{th} standing mode. Using $\mu' = 0$, we have

$$Z_{\mu i}(T) = \sum_{n_i=0}^{\infty} \exp\left(-\beta\, n_i\, \hbar\,\omega_i \right) = \frac{1}{1 - e^{-\beta\hbar\omega_i}} \qquad (1b)$$

The grand potential is

$$\Omega = k_B\, T \sum_{i=1}^{\infty} \ln\left(1 - e^{-\beta\hbar\omega_i} \right) \qquad \text{[(7.111) used.]} \qquad (2)$$

$$= -P\,V \qquad (2a)$$

where we have treated the photons as a PVT system and made use of (2.122) of §2.F.5.

Hence,

$$P = -\frac{k_B\, T}{V} \sum_{i=1}^{\infty} \ln\left(1 - e^{-\beta\hbar\omega_i} \right) \qquad (2b)$$

To evaluate the sum over modes, we switch to a sum over the wave vector $\boldsymbol{k}$. For standing modes,

$$\boldsymbol{k} = \frac{\pi}{L}\left(n_x, n_y, n_z \right) \qquad n_j = 1, 2, 3, \ldots \qquad j = x, y, z \qquad (2c)$$

$$\rightarrow \quad \omega(\boldsymbol{k}) = c\,k = c\,\frac{\pi}{L}\sqrt{n_x^2 + n_y^2 + n_z^2} \qquad (3)$$

Since there are two transverse modes for each $\boldsymbol{k}$, (2b) becomes

$$P = -\frac{2\,k_B\, T}{V} \sum_{\boldsymbol{k}} \ln\left(1 - e^{-\beta\hbar\omega(\boldsymbol{k})} \right)$$

$$= -\frac{2\,k_B\, T}{\pi^3} \int_+ d^3k\, \ln\left(1 - e^{-\beta\hbar c k} \right) \qquad (3a)$$

where $\int_+$ means integration over the 1st quadrant where $k_x, k_y, k_z > 0$ [see (2c)] and we have made use of

$$\sum_{k_j=1}^{\infty} = \sum_{k_j} \Delta n_j = \frac{L}{\pi} \sum_{k_j} \Delta k_j \approx \frac{L}{\pi} \int_0^\infty d k_j \qquad [\,\Delta n_j = 1\,] \qquad (3b)$$

In terms of spherical coordinates, (3a) becomes

$$\begin{aligned} P &= -\frac{2 k_B T}{\pi^3} \int_0^{\pi/2} d\phi \int_0^1 d\cos\theta \int_0^\infty dk\, k^2 \ln\left(1 - e^{-\beta\hbar c k}\right) \\ &= -\frac{k_B T}{\pi^2} \int_0^\infty dk\, k^2 \ln\left(1 - e^{-\beta\hbar c k}\right) \\ &= -\frac{k_B T}{\pi^2 c^3} \int_0^\infty d\omega\, \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right) \qquad (5) \end{aligned}$$

Comparing (5) with (2b), we get

$$\sum_{i=1}^{\infty} = 2 \sum_{\mathbf{k}} = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega\, \omega^2 \qquad (5a)$$

which is valid only if the summand and integrand are independent of angles.

Using

$$d\left[\omega^3 \ln\left(1 - e^{-\beta\hbar\omega}\right)\right] = 3\,\omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right) d\omega + \omega^3 \frac{\beta\hbar e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} d\omega$$

we integrate by part (5) to get

$$P = -\frac{k_B T}{\pi^2 c^3} \frac{1}{3} \left\{ \omega^3 \ln\left(1 - e^{-\beta\hbar\omega}\right) \Big|_0^\infty - \int_0^\infty d\omega\, \omega^3 \frac{\beta\hbar e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right\} \qquad (6a)$$

With

$$\lim_{\omega\to\infty} \omega^3 \ln\left(1 - e^{-\beta\hbar\omega}\right) = \lim_{\omega\to\infty} \omega^3 \left(-e^{-\beta\hbar\omega} - \frac{1}{2} e^{-2\beta\hbar\omega} - \dots\right) = 0$$

$$\lim_{\omega\to 0} \omega^3 \ln\left(1 - e^{-\beta\hbar\omega}\right) = \lim_{\omega\to 0} \omega^3 \left[1 - \left(1 - \beta\hbar\omega + \frac{1}{2} (\beta\hbar\omega)^2 + \dots\right)\right] = 0$$

(6a) becomes

$$\begin{aligned} P &= \frac{\hbar}{3\pi^2 c^3} \int_0^\infty d\omega\, \omega^3 \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{\hbar}{3\pi^2 c^3} \int_0^\infty d\omega\, \omega^3 \frac{1}{e^{\beta\hbar\omega} - 1} \\ &= \frac{(k_B T)^4}{3\pi^2 c^3 \hbar^3} \int_0^\infty dx\, x^3 \frac{1}{e^x - 1} \qquad [\,x = \beta\hbar\omega\,] \qquad (6b) \end{aligned}$$

Using

$$\begin{aligned} I &= \int_0^\infty dx\, x^3 \frac{1}{e^x - 1} \\ &= \int_0^\infty dx\, x^3 \frac{e^{-x}}{1 - e^{-x}} \\ &= \int_0^\infty dx\, x^3 e^{-x} \sum_{n=0}^{\infty} e^{-nx} \\ &= \sum_{n=0}^{\infty} \int_0^\infty dx\, x^3\, e^{-(n+1)x} \\ &= \sum_{n=0}^{\infty} \frac{1}{(n+1)^4} \int_0^\infty dy\, y^3\, e^{-y} \qquad [\,y = (n+1)\,x\,] \end{aligned}$$

$$= \Gamma(4) \sum_{n=0}^{\infty} \frac{1}{(n+1)^4}$$

$$= 3!\ \zeta(4) \ \ = 3! \ \frac{\pi^4}{90} \ = \ \frac{\pi^4}{15}$$

(6b) becomes

$$P = \frac{\pi^2 k_B^4 T^4}{45 c^3 \hbar^3} = \frac{1}{3} \sigma T^4 \qquad (6)$$

where

$$\sigma = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3} = \text{Stefan-Boltzmann constant}.$$

-- End of Ex.7.6. --

The next task is to estimate the fluctuations about the average values $\langle H \rangle = U$ & $\langle N \rangle = N$.

Calculation for $\text{var}(H)$ is the same as that for the canonical ensemble with the replacement $A \to \Omega$. Hence, (7.50) of §7.D.1 holds for the grand canonical ensemble so that fluctuations about $\langle H \rangle = U$ can be ignored in the thermodynamic limit.

Calculation for $\text{var}(N)$ is as follows.

Putting (7.113a) into the normalization condition (7.104), we get

$$\text{Tr}\left\{ \exp\left[-\beta\left(\hat{H} - \mu' \hat{N} - \Omega \hat{I} \right) \right] \right\} = 1 \qquad (7.114)$$

$\frac{\partial}{\partial \mu'}$(7.114) gives

$$\text{Tr}\left\{ \beta\left(\hat{N} + \frac{\partial \Omega}{\partial \mu'} \right) \exp\left[-\beta\left(\hat{H} - \mu' \hat{N} - \Omega \hat{I} \right) \right] \right\} = 0 \qquad (7.114a)$$

$$= \beta \,\text{Tr}\left\{ \left(\hat{N} + \frac{\partial \Omega}{\partial \mu'} \right) \hat{\rho} \right\}$$

$$\to \quad \frac{\partial \Omega}{\partial \mu'} = -\langle N \rangle = -N \qquad (7.114b)$$

$$= \left(\frac{\partial \Omega}{\partial \mu'} \right)_{T,X} \qquad \text{for} \quad \Omega = \Omega(T, X, \mu')$$

which is simply the thermodynamic relation (2.126) of §2.F.5.

$\frac{\partial}{\partial \mu'}$(7.114 a) gives

$$\text{Tr}\left\{ \left[\beta \frac{\partial^2 \Omega}{\partial \mu'^2} \right) + \beta^2 \left(\hat{N} + \frac{\partial \Omega}{\partial \mu'} \right)^2 \right] \exp\left[-\beta\left(\hat{H} - \mu' \hat{N} - \Omega \hat{I} \right) \right] \right\} = 0$$

$$= \beta \,\text{Tr}\left\{ \left[\frac{\partial^2 \Omega}{\partial \mu'^2} + \beta \left(\hat{N} + \frac{\partial \Omega}{\partial \mu'} \right)^2 \right] \hat{\rho} \right\}$$

$$\to \quad \frac{\partial^2 \Omega}{\partial \mu'^2} + \beta\left[\langle N^2 \rangle + 2 \frac{\partial \Omega}{\partial \mu'} \langle N \rangle + \left(\frac{\partial \Omega}{\partial \mu'} \right)^2 \right] = 0$$

$$\frac{\partial^2 \Omega}{\partial \mu'^2} + \beta\left[\langle N^2 \rangle - \langle N \rangle^2 \right] = 0 \qquad [\text{ (7.114b) used. }]$$

$$\therefore \quad \text{var}(N) = \langle N^2 \rangle - \langle N \rangle^2 = -k_B T \left(\frac{\partial^2 \Omega}{\partial \mu'^2} \right)_{T,X}$$

$$= k_B T \left(\frac{\partial N}{\partial \mu'} \right)_{T,X} \qquad [\text{ (7.114b) used. }] \qquad (7.115)$$

$$\propto N$$

Therefore,

$$\frac{\sqrt{\langle N^2\rangle - \langle N\rangle^2}}{\langle N\rangle} \propto \frac{\sqrt{N}}{\langle N\rangle} = N^{-1/2} \xrightarrow[N\to\infty]{} 0 \qquad (7.116)$$

Thus, the grand canonical ensemble is effectively the same as the canonical ensemble in the thermodynamic limit.

To evaluate $\left(\frac{\partial N}{\partial \mu'}\right)_{T,X}$ for a PVT system, we set $T = \text{const}$ and use (2.6) of §2.B to write

$$\left(\frac{\partial N}{\partial \mu'}\right)_{T,V}\left(\frac{\partial \mu'}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial N}\right)_{T,\mu'} = -1$$

$$\to \quad \left(\frac{\partial N}{\partial \mu'}\right)_{T,V} = -\left(\frac{\partial V}{\partial \mu'}\right)_{T,N}\left(\frac{\partial N}{\partial V}\right)_{T,\mu'} \qquad \text{(a)}$$

Now,

$$\left(\frac{\partial \mu'}{\partial V}\right)_{T,N} = -\left(\frac{\partial P}{\partial N}\right)_{T,V} \qquad \text{[(2.102) of §2.F.3 used.]} \qquad \text{(b)}$$

Using (2.6) again, we have

$$\left(\frac{\partial P}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial V}\right)_{T,P}\left(\frac{\partial V}{\partial P}\right)_{T,N} = -1$$

$$\to \quad \left(\frac{\partial \mu'}{\partial V}\right)_{T,N}\left(\frac{\partial N}{\partial V}\right)_{T,P}\left(\frac{\partial V}{\partial P}\right)_{T,N} = 1 \qquad \text{[(b) used.]}$$

$$\therefore \quad \left(\frac{\partial V}{\partial \mu'}\right)_{T,N} = \left(\frac{\partial N}{\partial V}\right)_{T,P}\left(\frac{\partial V}{\partial P}\right)_{T,N} \qquad \text{(c)}$$

Putting (c) into (a) gives

$$\left(\frac{\partial N}{\partial \mu'}\right)_{T,V} = -\left(\frac{\partial N}{\partial V}\right)_{T,P}\left(\frac{\partial V}{\partial P}\right)_{T,N}\left(\frac{\partial N}{\partial V}\right)_{T,\mu'} \qquad \text{(d)}$$

Since $\mu' = \mu'(T, P)$, keeping (T, P) constant will keep (T, μ') constant, and vice versa. Hence,

$$\left(\frac{\partial N}{\partial V}\right)_{T,P} = \left(\frac{\partial N}{\partial V}\right)_{T,\mu'} \qquad \text{(e)}$$

Furthermore, in a PVT system, keeping (T, P) constant means $N \propto V$ so that

$$\left(\frac{\partial N}{\partial V}\right)_{T,P} = \frac{N}{V} \qquad \text{(f)}$$

For example, the van der Waals equation (2.12) of §2.C.3

$$\left(P + a\,\frac{n^2}{V^2}\right)(V - n\,b) = n\,R\,T$$

can be written as

$$\left(P + \frac{a}{N_A^2}\,\frac{N^2}{V^2}\right)\left(\frac{V}{N} - \frac{b}{N_A}\right) = k_B\,T \qquad \text{[} N_A = \text{Avogadro number.]}$$

which can be solved to give

$$\frac{N}{V} = \text{const} \qquad \text{for} \qquad (T, P) = \text{constant}$$

Putting (d), (e) & (f) into (7.115) gives

$$\text{var}(N) = -k_B\,T\left(\frac{N}{V}\right)^2\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

$$= k_B\, T\, \frac{N^2}{V}\, \kappa_T \tag{7.117}$$

where

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \text{isothermal compressibility}$$

Using

$$\rho = \frac{N}{V} = \text{number density}$$

(7.117) becomes

$$\text{var}(N) = k_B\, T\, \rho\, N\, \kappa_T$$
$$\propto N$$

in agreement with (7.116).

Near a critical point,

$$\kappa_T \to \infty \qquad \Rightarrow \qquad \text{var}(N) \to \infty$$

which is typical for phase transitions in PVT systems.