Pathria + Beale, Chapter 4

Problem 4.1

The grand partition function can be expressed as a sum over microstates:

$$\mathcal{Z} = \sum_i e^{-\alpha N_i - \beta E_i}$$

where $\alpha = -\mu/T$ and $\beta = 1/T$. The grand potential is

$$\Phi = -\frac{1}{\beta} \log \mathcal{Z}$$

The thermodynamic relation for Φ is

$$d\Phi = -S\,dT - P\,dV - N\,d\mu$$

The entropy can be expressed as a derivative of Φ:

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}$$

It can therefore be expressed as

$$S = \frac{\partial}{\partial T}\left(T \log \mathcal{Z}\right)\Big|_{V,\mu}$$

$$= \left(1 + T\frac{\partial}{\partial T}\right) \log \mathcal{Z}\Big|_{V,\mu}$$

The derivative term is

$$T\frac{\partial}{\partial T}\log Z\Big|_{\mu,V} = \frac{1}{Z}T\frac{\partial}{\partial T}Z\Big|_{\mu,V}$$

$$= \frac{1}{Z}T\frac{\partial}{\partial T}\sum_i e^{-\alpha N_i - \beta E_i}\Big|_{\mu,V}$$

$$= \frac{1}{Z}\sum_i e^{-\alpha N_i - \beta E_i}\, T\frac{\partial}{\partial T}\left(-\alpha N_i - \beta E_i\right)\Big|_{\mu,V}$$

$$= \frac{1}{Z}\sum_i e^{-\alpha N_i - \beta E_i}(-1)\left(-\alpha N_i - \beta E_i\right)$$

$$= \alpha \bar{N} - \beta \bar{E}$$

The thermodynamic entropy is

$$S = \log Z + \alpha \bar{N} + \beta \bar{E}$$

The probability of a microstate with energy E_i and particle number N_i is

$$P_i = \frac{1}{Z}e^{-\alpha N_i - \beta E_i}$$

The information entropy is

$$S = -\sum_i P_i \log P_i$$

$$= -\sum_i\left(\frac{1}{Z}e^{-\alpha N_i - \beta E_i}\right)\left(-\alpha N_i - \beta E_i - \log Z\right)$$

$$= \frac{1}{Z}\sum_i e^{-\alpha N_i - \beta E_i}\left(\log Z + \alpha N_i + \beta E_i\right)$$

$$= \log Z + \alpha \bar{N} + \beta \bar{E}$$

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Problem 4.3

If there is 1 particle in the container of volume V_0, the probability that it is in a specific region of volume V is

$$p = \frac{V}{V_0}$$

If there are N_0 particles in the container, the probability that exactly N of them are in the volume V is

$$P(N,V) = \binom{N_0}{N} p^N (1-p)^{N_0-N}$$

(a) The average value of N is

$$\langle N \rangle = \sum_{N=0}^{N_0} N\, P(N,V)$$

$$= \sum_{N=1}^{N_0} N \binom{N_0}{N} p^N (1-p)^{N_0-N}$$

$$= \sum_{N=1}^{N_0} N \frac{N_0!}{N!\,(N_0-N)!} p^N (1-p)^{N_0-N}$$

$$= \sum_{N=1}^{N_0} \frac{N_0\,(N_0-1)!}{(N-1)!} p \cdot p^{N-1} (1-p)^{N_0-N}$$

$$= N_0\, p \sum_{N=1}^{N_0} \binom{N_0-1}{N-1} p^{N-1} (1-p)^{(N_0-1)-(N-1)}$$

$$= N_0\, p \sum_{N'=0}^{N_0-1} \binom{N_0-1}{N'} p^{N'} (1-p)^{(N_0-1)-N'}$$

$$= N_0 p \left[p + (1-p) \right]^{N_0 - 1}$$

$$= N_0 p \cdot 1 = N_0 p$$

The mean square deviation in N can be expressed as

$$(\Delta N)^2 = \left\langle (N - \langle N \rangle)^2 \right\rangle$$

$$= \langle N^2 \rangle - \langle N \rangle^2$$

The average of N^2 is

$$\langle N^2 \rangle = \sum_{N=0}^{N_0} N^2 P(N,V)$$

$$= \sum_{N=1}^{N_0} N^2 \binom{N_0}{N} p^N (1-p)^{N_0 - N}$$

$$= N_0 p \sum_{N=1}^{N_0} N \frac{(N_0-1)!}{(N-1)!(N_0-N)!} p^{N-1} (1-p)^{N_0-N}$$

$$= N_0 p \sum_{N=1}^{N_0} \left[1 + (N-1) \right] \frac{(N_0-1)!}{(N-1)!(N_0-N)!} p^{N-1} (1-p)^{N_0-N}$$

$$= N_0 p \sum_{N=1}^{N_0} \binom{N_0-1}{N-1} p^{N-1} (1-p)^{N_0-N}$$

$$+ N_0 p \sum_{N=2}^{N_0} \frac{(N_0-1)!}{(N-2)!(N_0-N)!} p^{N-1} (1-p)^{N_0-N}$$

$$= N_0 p + N_0 p \sum_{N=2}^{N_0} (N_0-1) \frac{(N_0-2)!}{(N-2)!(N_0-N)!} p \cdot p^{N-2} (1-p)^{N_0-N}$$

$$= N_0 p + N_0 (N_0-1) p^2 \sum_{N=2}^{N_0} \binom{N_0-2}{N-2} p^{N-2} (1-p)^{N_0-N}$$

$$= N_0 p + N_0(N_0-1)p^2 \sum_{N'=0}^{N_0-2} \binom{N_0-2}{N'} p^{N'} (1-p)^{(N_0-2)-N'}$$

$$= N_0 p + N_0(N_0-1)p^2 \left[p + (1-p) \right]^{N_0-2}$$

$$= N_0 p + N_0(N_0-1)p^2$$

The mean square deviation is therefore

$$(\Delta N)^2 = N_0 p + N_0(N_0-1)p^2 - (N_0 p)^2$$

$$= N_0 p - N_0 p^2$$

$$= N_0 p(1-p)$$

(b) The ratio of the probability $P(N,V)$ and its value at $N = \langle N \rangle = N_0 p$ is

$$\frac{P(N,V)}{P(\langle N \rangle, V)} = \frac{N_0!}{N!(N_0-N)!} p^N (1-p)^{N_0-N} \Big/ \frac{N_0!}{\langle N \rangle!(N_0-\langle N \rangle)!} p^{\langle N \rangle}(1-p)^{N_0-\langle N \rangle}$$

$$= \frac{\langle N \rangle!(N_0-\langle N \rangle)!}{N!(N_0-N)!} \left(\frac{p}{1-p}\right)^{N-\langle N \rangle}$$

$$= \frac{(N_0 p)!(N_0(1-p))!}{N!(N_0-N)!} \left(\frac{p}{1-p}\right)^{N-N_0 p}$$

The logarithm of the ratio of probabilities can be expressed as

$$\log\frac{P(N,V)}{P(\langle N\rangle,V)} = \log\left((N_0p)!\right) + \log\left((N_0(1-p))!\right)$$

$$- \log(N!) - \log\left((N_0-N)!\right) + (N-N_0p)\log\frac{p}{1-p}$$

$$\approx N_0p\log\frac{N_0p}{e} + N_0(1-p)\log\frac{N_0(1-p)}{e}$$

$$- N\log\frac{N}{e} - (N_0-N)\log\frac{N_0-N}{e} + (N-N_0p)\log\frac{p}{1-p}$$

$$= N_0\left[p\log(N_0p) + (1-p)\log(N_0(1-p)) - \log(N_0-N) - p\log\frac{p}{1-p}\right].$$

$$- N\left[\log N - \log(N_0-N) - \log\frac{p}{1-p}\right]$$

$$= N_0\log\frac{N_0(1-p)}{N_0-N} - N\log\frac{N/p}{(N_0-N)/(1-p)}$$

Since $\langle N\rangle$ scales as N_0 and ΔN scales as $N_0^{1/2}$, we can expand the logarithm to second order in $N-\langle N\rangle$.

$$\log\frac{P(N,V)}{P(\langle N\rangle,V)} = N_0\log\frac{N_0(1-p)}{N_0-N_0p-(N-\langle N\rangle)} - \left[N_0p+(N-\langle N\rangle)\right]\log\frac{\left[N_0p+(N-\langle N\rangle)\right]/p}{\left[N_0-N_0p-(N-\Delta N)\right]/(1-p)}$$

$$= -N_0\log\left(1-\frac{N-\langle N\rangle}{N_0(1-p)}\right)$$

$$-\left[N_0p+(N-\langle N\rangle)\right]\left[\log\left(1+\frac{N-\langle N\rangle}{N_0p}\right)-\log\left(1-\frac{N-\langle N\rangle}{N_0(1-p)}\right)\right]$$

$$\simeq -N_0\left[\cancel{-\frac{N-\langle N\rangle}{N_0(1-p)}} - \frac{1}{2}\left(\frac{N-\langle N\rangle}{N_0(1-p)}\right)^2\right]$$

$$-N_0p\left[\cancel{+\frac{N-\langle N\rangle}{N_0p}} - \frac{1}{2}\left(\frac{N-\langle N\rangle}{N_0p}\right)^2 + \cancel{\frac{N-\langle N\rangle}{N_0(1-p)}} + \frac{1}{2}\left(\frac{N-\Delta N}{N_0(1-p)}\right)^2\right]$$

$$-(N-\langle N\rangle)\left[+\frac{N-\langle N\rangle}{N_0p} + \frac{N-\langle N\rangle}{N_0(1-p)}\right]$$

$$= -\frac{1}{2N_0 p(1-p)}(N-\langle N\rangle)^2$$

Upon exponentiating both sides, we get a Gaussian in N:

$$P(N,V) \simeq P(\langle N\rangle, V)\exp\left(-\frac{(N-\langle N\rangle)^2}{2\langle\ \rangle^2}\right)$$

(c) The logarithm of the probability is

$$\log P(N,V) = \log(N_0!) - \log(N!) - \log((N_0-N)!)$$

$$+ N\log p + (N_0-N)\log(1-p)$$

$$\approx N_0\log\frac{N_0}{e} - N\log\frac{N}{e} - (N_0-N)\log\frac{N_0-N}{e}$$

$$+ N\log p + (N_0-N)\log(1-p)$$

$$= N_0\left[\log\frac{N_0}{N_0-N} + \log(1-p)\right]$$

$$+ N\left[\log\frac{N_0-N}{N} + \log p - \log(1-p)\right]$$

If $p \ll 1$ and $N \ll N_0$, we can expand the logarithm to first order in p and first order in N/N_0:

$$\log P(N,V) = N_0\left[-\log\left(1-\frac{N}{N_0}\right) + \log(1-p)\right]$$

$$+ N\left[\log\frac{N_0}{N} + \log\left(1-\frac{N}{N_0}\right) + \log p - \log(1-p)\right]$$

$$\simeq N_0\left[-\left(-\frac{N}{N_0}\right)+(-p)\right]$$

$$+N\left[\log\frac{N_0}{N}+0+\log p-0\right]$$

$$= N - N_0 p - N\log\frac{N}{N_0 p}$$

Upon exponentiating both sides, we get a Poisson distribution

$$P(N,V) \simeq \exp\left(N - N_0 p - N\log\frac{N}{N_0 p}\right)$$

$$= \exp\left(N - \langle N\rangle\right)\left(\frac{N}{\langle N\rangle}\right)^{-N}$$

$$= e^{-\langle N\rangle}\frac{\langle N\rangle^N}{(N/e)^N}$$

$$\simeq e^{-\langle N\rangle}\frac{\langle N\rangle^N}{N!}$$

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Problem 4.8

The grand partition function for magnetic atoms can be expressed as a sum over the particle number N of an expression that involves the partition function

$$\mathcal{Z}(\beta,\mu,H) = \sum_{N=0}^{\infty} \left(e^{\beta\mu}\right)^N Z_N(\beta,H)$$

The partition function for N atoms can be expressed in terms of the partition function for 1 atom:

$$Z_N(\beta,H) = \frac{1}{N!} Z_1(\beta,H)^N$$

The partition function for 1 atom is

$$Z_1(\beta,H) = \sum_{\pm} \frac{1}{(2\pi\hbar)^3} \int d^3r \int d^3p \, \exp\left(-\beta\frac{\vec{p}^{\,2}}{2m}\right) \exp\left(\pm\beta\mu_B H\right)$$

$$= \frac{1}{(2\pi\hbar)^3} V \left[\int dp_x \exp\left(-\beta\frac{p_x^2}{2m}\right)\right]^3 \sum_{\pm} \exp\left(\pm\beta\mu_B H\right)$$

$$= \frac{1}{(2\pi\hbar)^3} V \left(\frac{2\pi m}{\beta}\right)^{3/2} \cosh\left(\beta\mu_B H\right)$$

The grand partition function is therefore

$$\mathcal{Z}(\beta,\mu,H) = \sum_{N=0}^{\infty} \left(e^{\beta\mu}\right)^N \frac{1}{N!} \left(V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \cosh(\beta\mu_B H)\right)^N$$

$$= \exp\left(e^{\beta\mu} V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \cosh(\beta\mu_B H)\right)$$

The grand potential is

$$\Phi = -\frac{1}{\beta}\log Z$$

$$= -\frac{1}{\beta} e^{\beta\mu} V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \cosh(\beta\mu_B H)$$

The thermodynamic relation for Φ is

$$d\Phi = -S\,dT - P\,dV - N\,d\mu - M\,dH$$

The average particle number is

$$\bar{N} = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V,H}$$

$$= -\left(-\frac{1}{\beta}\right)\left(e^{\beta\mu}\beta\right) V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \cosh(\beta\mu_B H)$$

$$= e^{\beta\mu} V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \cosh(\beta\mu_B H)$$

The magnetization is

$$M = -\left(\frac{\partial\Phi}{\partial H}\right)_{T,V,\mu}$$

$$= \frac{1}{\beta} e^{\beta\mu} V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \sinh(\beta\mu_B H)\,\beta\mu_B$$

$$= \bar{N}\mu_B \tanh(\beta\mu_B H)$$

The entropy is

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu,H}$$

$$= +\beta^2\left(\frac{\partial \Phi}{\partial \beta}\right)_{V,\mu,H}$$

$$= \beta^2\left[-V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right]\frac{\partial}{\partial\beta}\left[e^{\beta\mu}\,\beta^{-5/2}\cosh(\beta\mu_B H)\right]$$

$$= -\beta^2 V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}\left[\left(\mu\beta^{-5/2} - \frac{5}{2}\beta^{-7/2}\right)\cosh(\beta\mu_B H) + \beta^{-5/2}\sinh(\beta\mu_B H)\mu_B H\right]$$

$$= e^{\beta\mu} V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\left[\left(-\beta\mu + \frac{5}{2}\right)\cosh(\beta\mu_B H) - \beta\mu_B H\sinh(\beta\mu_B H)\right]$$

$$= \bar{N}\left[\left(\frac{5}{2} - \beta\mu\right) - \beta\mu_B H\tanh(\beta\mu_B H)\right]$$

The heat given off by changing the magnetic field from H to 0 at constant volume V, temperature T, and particle number $\bar{N}$ is

$$Q = \int T\,dS = T\int dS$$

$$= T\Delta S = T\left[S(H=0) - S(H)\right]$$

$$= T\,\bar{N}\,\beta\mu_B H\tanh(\beta\mu_B H)$$

$$= \bar{N}\mu_B H\tanh(\beta\mu_B H)$$

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Problem 4.10

The surface has N_0 adsorption centers. If the partition function for 1 adsorbed molecule is $a(T)$, the partition function for N adsorbed molecules is

$$Z_N = \binom{N_0}{N} a(T)^N$$

The grand partition function with chemical potential μ is

$$\mathcal{Z} = \sum_{N=0}^{N_0} \left(e^{\beta\mu}\right)^N \binom{N_0}{N} a(T)^N$$

$$= \sum_{N=0}^{N_0} \binom{N_0}{N} \left(e^{\beta\mu} a(T)\right)^N$$

$$= \left[1 + e^{\beta\mu} a(T)\right]^{N_0}$$

The grand potential is

$$\Phi = -\frac{1}{\beta} \log \mathcal{Z}$$

$$= -\frac{N_0}{\beta} \log\left(1 + e^{\beta\mu} a(T)\right)$$

The thermodynamic relation for Φ is

$$d\Phi = -S\,dT - N\,d\mu$$

The average number of particles is

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_T$$

$$= \frac{N_0}{\beta}\left(\frac{\partial}{\partial \mu} \log\left(1 + e^{\beta\mu} a(T)\right)\right)_\beta$$

$$= \frac{N_0}{\beta} \frac{1}{1 + e^{\beta\mu} a(T)} e^{\beta\mu} \beta a(T)$$

$$= N_0 \frac{e^{\beta\mu} a(T)}{1 + e^{\beta\mu} a(T)}$$

We can solve the equation for $e^{\beta\mu}$

$$e^{\beta\mu} = \frac{N}{(N_0 - N) a(T)}$$

The chemical potential is therefore

$$\mu = kT \log \frac{N}{(N_0 - N) a(T)}$$

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Problem 4.14

The Clausius-Clapeyron equation for the slope of the coexistence line in the pressure-volume plane is

$$\frac{d}{dT} P_\sigma(T) = \frac{L}{T(v_{vapor} - v_{liquid})}$$

where L is the latent heat per particle, and v_X is the volume per particle in phase X. If v_{liquid} is negligible compared to v_{liquid}, we can use the ideal gas law $P v_{vapor} = kT$ to express the equation as

$$\frac{d}{dT} P_\sigma(T) = \frac{L \, P_\sigma(T)}{k T^2}$$

If L is independent of T, the equation can be integrated

$$\frac{dP_\sigma(T)}{P_\sigma(T)} = \frac{L}{k} \frac{dT}{T^2}$$

$$d \log P_\sigma(T) = \frac{L}{k} \, d\left(\frac{1}{T}\right)$$

$$\log \frac{P_\sigma(T)}{P_\sigma(T_0)} = -\frac{L}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$P_\sigma(T) = P_\sigma(T_0) \exp\left(-\frac{L}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

The latent heat for water is given as 2260 kJ/kg. Since the molecular mass of water is 18.02 g/mol, the latent heat per molecule divided by Boltzmann's constant is

$$\frac{L}{k} = \left(2260\ kJ/kg\right)\left(18.02\ g/mole\right)\frac{1\ mole}{6.02\times10^{23}}\frac{1}{1.38\times10^{-23}\ J/K}$$

$$= 4900\,K$$

The equilibrium vapor pressure at $T_0 = 373K$ is $P_\sigma(T_0) = 1$ atm. Using the as initial condition, we can predict the vapor pressure at othe temperatures. The Table below gives the predicted and observed vapor pressure at the triple point temperature 273 K and at the critical point temperature

T	P_σ predicted	P_σ observed
273	0.0081 atm	0.0060 atm
373	(input)	1 atm
647	261 atm	218 atm

Given that the observed vapor pressure changes by more than 5 orders of magnitude, the accuracy of the prediction is surprisingly good.

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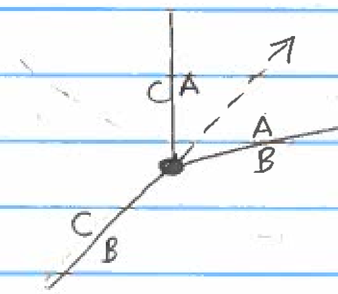
Problem 4.17

The Clausius-Clapeyron equation implies that the coexistence curve $P_{AB}(T)$ separating two phases A and B satisfies.

$$P'_{AB}(T) \equiv \frac{d}{dT} P_{AB}(T) = \frac{s_B(T) - s_A(T)}{v_B(T) - v_A(T)}$$

where s_X is the entropy per particle in phase X and v_X is the volume per particle in phase X.



At a triple point with phase A, B, C, there are three such curves that meet. Their slopes are

$$P'_{AB}(T_t) = \frac{s_B - s_A}{v_B - v_A}$$

$$P'_{BC}(T_t) = \frac{s_C - s_B}{v_C - v_B}$$

$$P'_{CA}(T_t) = \frac{s_A - s_C}{v_A - v_C}$$

Their numerators and denominator satisfy

$$(s_B - s_A) + (s_C - s_B) + (s_A - s_C) = 0$$

$$(v_B - v_A) + (v_C - v_B) + (v_A - v_C) = 0$$

If we multiply the expressions for $P'_{XY}(T_t)$ by $v_X - v_Y$, we get

$$(v_A - v_B)\, P'_{AB}(T_t) = s_A - s_B$$

$$(v_B - v_C)\, P'_{BC}(T_t) = s_B - s_C$$

$$(v_C - v_A)\, P'_{CA}(T_t) = s_C - s_A$$

Adding the 3 equations, we get

$$(v_A - v_B)\, P'_{AB}(T_t) + (v_B - v_C)\, P'_{BC}(T_t) + (v_C - v_A)\, P'_{CA}(T_t)$$

$$= (s_A - s_B) + (s_B - s_C) + (s_C - s_A)$$

$$= 0$$

Without loss of generality, we can choose

$$0 < v_A < v_B < v_C$$

We can solve our equation for $P'_{CA}(T_t)$, expressing it in terms of positive volume differences:

$$P'_{CA}(T_t) = \frac{v_B - v_A}{v_C - v_A} P'_{AB}(T_t) + \frac{v_C - v_B}{v_C - v_A} P'_{BC}(T_t)$$

The two coefficients are positive, between 0 and 1, and they add up to 1. This implies that the CA coexistence line point into the B phase.

The solution for $P_{AB}'(T_t)$ can be expressed as

$$P_{AB}'(T_t) = \frac{v_C - v_A}{v_B - v_A} P_{CA}'(T_t) - \frac{v_C - v_B}{v_B - v_A} P_{BC}'(T_t)$$

The interpretation of the equation in terms of the direction of the AB coexistence line is less obvious.

The solution for $P_{BC}'(T_t)$ can be expressed as

$$P_{BC}'(T_t) = \frac{v_C - v_A}{v_C - v_B} P_{CA}'(T_t) - \frac{v_B - v_A}{v_C - v_B} P_{AB}'(T_t)$$

Again the interpretation is not so obvious.