Solutions to Pathria's Statistical Mechanics
Chapter 4

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Problem 4.1

Problem 4.3

The probability $P(N,V) = \binom{N_0}{N} p^N (1-p)^{N_0-N}$. Here for convenience I set $N_0 = N^{(0)}$. This is a binomial distribution.
(a) One can directly use the results from any standard probability textbook. For example,

$$\bar{N} = \sum_{N=0}^{N_0} NP(N,V) = N_0 p \sum_{N=1}^{N_0} \frac{(N_0-1)!}{(N-1)!(N_0-N)!} p^{N-1}(1-p)^{N_0-N} = N_0 p \tag{1}$$

Similarly, we have $\overline{N(N-1)} = N_0(N_0-1)p^2$ so $\overline{N^2} = N_0(N_0-1)p^2 + N_0 p$. Therefore $\overline{(\Delta N)^2} = \overline{N^2} - \bar{N}^2 = \sqrt{N_0 p(1-p)}$.
(b) For large enough number, the discrete binomial distribution can be seen as gaussian distribution simply by taking a continum limit.
(c) Another standard exercise in probability textbook. When $p \ll 1$ and $N \ll N_0$, it is clear that $N_0!/(N_0-N)! \sim N_0^N$, $(1-p)^{\frac{N_0-N}{p}p} \sim e^{-N_0 p}$. Now replace $\bar{N} = N_0 p$ and we get the desired answer.

Problem 4.4

The probability of a state with energy E_r and particle number N is

$$p_{r,N} = \frac{e^{-\beta E_{r,N} + \beta\mu N}}{\mathcal{Q}(\mu, V, \beta)} \tag{2}$$

in which $\mathcal{Q} = \sum_{r,N} e^{-\beta E_{r,N} + \beta\mu N}$ is the grand canonical partition function. Since we have define that $z = e^{\beta\mu}$, the probability can be written as:

$$p_{r,N} = \frac{z^N e^{-\beta E_{r,N}}}{\mathcal{Q}(z, V, \beta)} \tag{3}$$

So the probability that has exactly N particles will be:

$$p_N = \sum_r p_{r,N} = \frac{z^N \sum_r e^{-\beta E_{r,N}}}{\mathcal{Q}(z, V, \beta)} \tag{4}$$

easily we can find the summation in the numerator is the canonical partition function of system with V, N and β:

$$Q_N(V,\beta) = \sum_r e^{-\beta E_{r,N}} \tag{5}$$

Thus Eq.(4) will become:

$$p_N = \frac{z^N Q_N(V,\beta)}{\mathcal{Q}(z,V,\beta)} \tag{6}$$

For ideal classical gas, the canonical partition function is:

$$Q_N(V,T) = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \tag{7}$$

and the grand partition function is

$$\mathcal{Q}(z,V,\beta) = \sum_{N=0}^{\infty} z^N Q_N(V,T) = \exp\left[zV\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \tag{8}$$

Clearly the probability distribution of particle number is

$$p_N = \frac{1}{N!}\frac{(zV\lambda_T^{-3})^N}{e^{zV\lambda_T^{-3}}} \tag{9}$$

It is obvious that this distribution is a Poison distribution. From the knowledge of Poison distribution, we know the root-mean-square value of (ΔN) is

$$\Delta N = \sqrt{zV\lambda_T^{-3}} = \sqrt{e^{\beta\mu}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \tag{10}$$

We can also get this result from the formula of grand canonical ensemble:

$$\begin{aligned} \Delta N &= kT\sqrt{\left(\frac{\partial^2 \ln \mathcal{Q}}{\partial \mu^2}\right)_{T,V}} \\ &= \sqrt{e^{\beta\mu}V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \end{aligned} \tag{11}$$

And this result is consistent with the one we get by Poison distribution.

Problem 4.5

We could know from 4.3.20:

$$S = kT(\frac{\partial q}{\partial T})_{z,V} - Nkln(z) + kq$$

We can know partial differential:

$$(\frac{\partial q}{\partial T})_{z,V} - (\frac{\partial q}{\partial T})_{\mu,V} = (\frac{\partial q}{\partial z})_{T,V}(\frac{\partial z}{\partial T})_{\mu,V}$$

$$(\frac{\partial q}{\partial z})_{T,V} = \frac{N}{z}$$

So we can infer that:

$$S = k[\frac{\partial (Tq)}{\partial T}]_{V,\mu}$$

Problem 4.6

$\ln Y_N(P,T) = \ln Q_N(V,T) + \beta pV = -\beta A + \beta pV$
$G = A + pV = -kT \ln Y_N$
Thus the Gibbs free energy is proportional to $\ln Y_N(P,T)$, with a factor of $-kT$.
As for classical ideal gas, the canonical partition function writes as $Q_N = \frac{1}{h^{3N}N!}V^N(2\pi mkT)^{N/2}$
$Y_N = \frac{1}{h^{3N}N!}(2\pi mkT)^{3N/2}\int_0^\infty V^N e^{-\beta pV}dV = \frac{1}{h^{3N}}(2\pi mkT)^{3N/2}(\frac{kT}{p})^N$
Use the fact $V = (\frac{\partial G}{\partial p})_{T,N}$, we can easily obtain the relation $pV = NkT$.

Problem 4.9

This problem is totally identical with Mr.Ni's material for class, I regard it meaningless to move those calculations here.

Problem 4.12

$$\overline{NE} = \frac{\sum NEe^{-\alpha N-\beta E}}{\sum e^{-\alpha N-\beta E}} = \frac{\frac{\partial}{\partial\alpha}(\frac{\partial}{\partial\beta}\Xi)}{\Xi} = \frac{\frac{\partial}{\partial\alpha}(\Xi\frac{\partial}{\partial\beta}\ln\Xi)}{\Xi} = \frac{1}{\Xi}\frac{\partial\Xi}{\partial\alpha}\frac{\partial}{\partial\beta}\ln\Xi + \frac{\partial}{\partial\alpha}(\frac{\partial}{\partial\beta}\ln\Xi) \tag{12}$$

While the first part can be written as

$$\frac{1}{\Xi}\frac{\partial\Xi}{\partial\alpha}\frac{\partial}{\partial\beta}\ln\Xi = \frac{\partial\ln\Xi}{\partial\alpha}\frac{\partial}{\partial\beta}\ln\Xi = \overline{N} * \overline{E} \tag{13}$$

So the equation equals

$$\overline{NE} - \overline{N} * \overline{E} = \frac{\partial}{\partial\alpha}(\frac{\partial}{\partial\beta}\ln\Xi) = -\frac{\partial}{\partial\alpha}U = -\frac{\partial U}{\partial N}\frac{\partial N}{\partial\alpha} = (\frac{\partial U}{\partial N})\overline{(\Delta N)^2} \tag{14}$$

Problem 4.13

Use the linearity of expectation. From $J = E - N\mu$,

$$\begin{aligned}\overline{(\Delta J)^2} &= \overline{E^2} - 2\mu\overline{EN} + \mu^2\overline{N^2} - \bar{E}^2 - \mu^2\bar{N}^2\\ &= \overline{(\Delta E)^2} + \mu^2\overline{(\Delta N)^2} - 2\mu\overline{EN}\\ &= kT^2C_V + \left[(\frac{\partial U}{\partial N})^2 + \mu^2\right]\overline{(\Delta N)^2} - 2\mu\overline{EN}\end{aligned} \tag{15}$$

Now compute $\overline{EN}$.

$$\overline{EN} = -\frac{\partial U}{\partial\alpha} = -\frac{\partial U}{\partial N}\frac{\partial N}{\partial\alpha} = \frac{\partial U}{\partial N}\overline{(\Delta N)^2}. \tag{16}$$

Therefore,

$$\overline{(\Delta J)^2} = kT^2C_V + \left[(\frac{\partial U}{\partial N})^2 - 2\mu\frac{\partial U}{\partial N} + \mu^2\right]\overline{(\Delta N)^2} = kT^2C_V + \left[\frac{\partial U}{\partial N} - \mu\right]^2\overline{(\Delta N)^2} \tag{17}$$

Problem 4.14

The ClausiusClapeyron equation is

$$\frac{dP_\sigma}{dT} = \frac{L}{T\Delta v}$$

Since the volume of liquid is negligible compared to that of gas, we can alternate Δv by $v_g = kT/P_\sigma$. Put all of these into the ClausiusClapeyron equation, we can get a differential equation:

$$\frac{dP_\sigma}{P_\sigma} = \frac{L}{R}\frac{dT}{T^2} \tag{18}$$

so the solution to the differential equation will be:

$$P_\sigma(T) = P_0 \exp\left[\frac{L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{19}$$

From the problem we know that $L = 2260\text{kJ/kg} = 40680\text{J/mol}$, $T_0 = 373\text{K}$ and $P_0 = 101\text{kPa}$. Then we put all these numbers into Eq.(19) and we get the equilibrium vapor pressure is

$$P_\sigma(473\text{K}) = 1619\text{kPa}$$

Experiment result is $P_\sigma \sim 1500\text{kPa}$, and our calculation is approximately correct.

Problem 4.15

According to Clausius-Clapeyron equation.And ignore the volume of solid phase.

$$\frac{dP_\sigma}{dT} = \frac{L}{TV}$$

Use the gas equation.

$$ln(p) = -\frac{L}{kT} + A$$

Use the triple point parameter.

$$ln(p) = -\frac{L}{kT} + 6.6 \times 10^{26}$$

Problem 4.16

Utilizing Clausius-Clapeyron equation near water triple point.

$$\frac{dp}{dT} = \frac{L}{T\Delta v} \tag{20}$$

$$= \frac{80cal/g * 1g}{273.16K(\frac{1g}{0.92g/cm^3} - \frac{1g}{1g/cm^2})} \tag{21}$$

$$= 1.409 * 10^7 Pa/K \tag{22}$$

$$\frac{dT}{dp} = 0.007096K/atm \tag{23}$$

The melting temperature of water would be near $273.16K - 0.7096K = 272.4504K$ under the pressure of $100atm$.

Problem 4.17

According to Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{L}{T\Delta v} \tag{24}$$

Therefore the tagent vector of the coexistence line of phase A and B is

$$\boldsymbol{t}_{AB} = (\Delta v_{AB}, \Delta s_{AB}) \tag{25}$$

At the triple point,

$$\begin{aligned}
&\Delta v_{AB} + \Delta v_{BC} + \Delta v_{CA} = 0 \\
&\Delta s_{AB} + \Delta s_{BC} + \Delta s_{CA} = 0 \\
&\text{i.e.,} \\
&\boldsymbol{t}_{AB} + \boldsymbol{t}_{BC} + \boldsymbol{t}_{CA} = \mathbf{0}
\end{aligned}$$

Therefore, the slope of the coexistance line points into the third phase.

Problem 4.19

According to the thermodynamic relation:

$$0 = d(G - \mu N) = -N d\mu + V dp - S dT$$

We have:

$$\begin{aligned}
d\mu_1 &= \frac{V_1}{N_1} dp - \frac{S_1}{N_1} dT \\
d\mu_2 &= \frac{V_2}{N_2} dp - \frac{S_2}{N_2} dT
\end{aligned}$$

On the coexisting curve, $d\mu_1 = d\mu_2$. So,

$$\frac{dp_\sigma}{dT} = \frac{s_B - s_A}{v_B - v_A}$$

Proved.