

Solutions to Pathria's Statistical Mechanics

Chapter 4

SM-at-THU

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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,

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

Similarly, we have $\overline{N(N-1)} = N_0(N_0-1)p^2$ so $\overline{N^2} = N_0(N_0-1)p^2 + N_0p$. 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 continuum limit.

(c) Another standard exercise in probability textbook. When $p \ll 1$ and $N \ll N_0$, it is clear that $N_0!/(N_0-N)! \sim N_0^N$, $(1-p)^{\frac{N_0-N}{p}p} \sim e^{-N_0p}$. Now replace $\bar{N} = N_0p$ and we get the desired answer.

Problem 4.4

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

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

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:

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

So the probability that has exactly N particles will be:

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

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

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

Thus Eq.(??) will become:

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

For ideal classical gas, the canonical partition function is:

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

and the grand partition function is

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

Clearly the probability distribution of particle number is

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

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

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

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

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

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

Problem 4.5

We could know from 4.3.20:

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

We can know partial differential:

$$\begin{aligned} \left(\frac{\partial q}{\partial T} \right)_{z,V} - \left(\frac{\partial q}{\partial T} \right)_{\mu,V} &= \left(\frac{\partial q}{\partial z} \right)_{T,V} \left(\frac{\partial z}{\partial T} \right)_{\mu,V} \\ \left(\frac{\partial q}{\partial z} \right)_{T,V} &= \frac{N}{z} \end{aligned}$$

So we can infer that:

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

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

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

While the first part can be written as

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

So the equation equals

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

Problem 4.13

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

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

Now compute \overline{EN} .

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

Therefore,

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

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:

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

so the solution to the differential equation will be:

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

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 4.19

According to the thermodynamic relation:

$$0 = d(G - \mu N) = -Nd\mu + Vdp - SdT$$

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.