Solutions to Pathria's Statistical Mechanics Chapter 3

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Problem 3.1

In fact the solution to this problem is just a mathematical derivation with only little physics.

(a)

$$\begin{aligned}
\mathcal{LHS} &= \langle (\Delta n_r)^2 \rangle &(1)\\
&= \langle n_r^2 \rangle + \langle n_r \rangle^2 &(2)\\
&= \frac{1}{\Gamma}\left(\omega_r \frac{\partial}{\partial \omega_r}\right)^2 \Gamma\Bigg|_{\omega_r=1,\forall r} - \left(\omega_r \frac{\partial}{\partial \omega_r}(\ln \Gamma)\right)^2\Bigg|_{\omega_r=1,\forall r} &(3)\\
&= \frac{1}{\Gamma}\left(\omega_r \frac{\partial}{\partial \omega_r} + \omega_r^2 \frac{\partial^2}{\partial \omega_r^2}\right)\Gamma\Bigg|_{\omega_r=1,\forall r} - \left(\frac{1}{\Gamma}\omega_r \frac{\partial}{\partial \omega_r}\Gamma\right)^2\Bigg|_{\omega_r=1,\forall r} &(4)\\
\mathcal{RHS} &= \left(\omega_r \frac{\partial}{\partial \omega_r}\right)^2 (\ln \Gamma)\Bigg|_{\omega_r=1,\forall r} &(5)\\
&= \frac{1}{\Gamma}\omega_r \frac{\partial}{\partial \omega_r}\Gamma\Bigg|_{\omega_r=1,\forall r} - \left(\frac{1}{\Gamma}\omega_r \frac{\partial}{\partial \omega_r}\Gamma\right)^2\Bigg|_{\omega_r=1,\forall r} + \frac{1}{\Gamma}\omega_r^2 \frac{\partial^2}{\partial \omega_r^2}\Gamma\Bigg|_{\omega_r=1,\forall r} &(6)\\
&= \mathcal{LHS} &(7)
\end{aligned}$$

(b-1)

$$\begin{aligned}
U &= \frac{\sum_r \omega_r E_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} &(8)\\
\Rightarrow \frac{\partial \beta}{\partial \omega_r} &= \frac{(E_r - U)\exp(-\beta E_r)}{\sum_r \omega_r (E_r - U) E_r \exp(-\beta E_r)} &(9)
\end{aligned}$$

$$\mathcal{LHS} = \frac{\partial \beta}{\partial \omega_r} = \frac{(E_r - U)\exp(-\beta E_r)}{\sum_r \omega_r (E_r - U) E_r \exp(-\beta E_r)} \tag{10}$$

$$= \frac{(E_r - U)\exp(-\beta E_r)/\sum_r \omega_r \exp(-\beta E_r)}{\sum_r \omega_r (E_r - U) E_r \exp(-\beta E_r)/\sum_r \omega_r \exp(-\beta E_r)} \tag{11}$$

$$= \frac{E_r - U}{\langle E_r^2 \rangle - \langle E_r \rangle U} \frac{\langle n_r \rangle}{\mathcal{N}} \tag{12}$$

$$= \frac{E_r - U}{\langle E_r^2 \rangle - U^2} \frac{\langle n_r \rangle}{\mathcal{N}} = \mathcal{RHS} \tag{13}$$

(b-2)

$$\frac{\left\langle (\Delta n_r)^2 \right\rangle}{\mathcal{N}} = \omega_r \frac{\partial}{\partial \omega_r} \left[\frac{\omega_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} \right] \tag{14}$$

$$= \frac{\omega_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} - \frac{\omega_r^2 E_r \exp(-\beta E_r)}{\sum_r \omega_r \exp(-\beta E_r)} \frac{\partial \beta}{\partial \omega_r} \tag{15}$$

$$- \frac{\omega_r^2 \left(\exp(-\beta E_r)\right)^2 - \omega_r^2 \exp(-\beta E_r) \sum_r \omega_r E_r \exp(-\beta E_r)}{\left(\sum_r \omega_r \exp(-\beta E_r)\right)^2} \frac{\partial \beta}{\partial \omega_r} \tag{16}$$

$$= \frac{\langle n_r \rangle}{\mathcal{N}} - \frac{\langle n_r \rangle}{\mathcal{N}} E_r \frac{\partial \beta}{\partial \omega_r} - \left(\frac{\langle n_r \rangle}{\mathcal{N}} \right)^2 + \frac{\langle n_r \rangle}{\mathcal{N}} U \frac{\partial \beta}{\partial \omega_r} \tag{17}$$

$$= \frac{\langle n_r \rangle}{\mathcal{N}} + \frac{\langle n_r \rangle}{\mathcal{N}} (U - E_r) \frac{\partial \beta}{\partial \omega_r} - \left(\frac{\langle n_r \rangle}{\mathcal{N}} \right)^2 \tag{18}$$

Problem 3.2

$$g''(x_0) \simeq \frac{f''(x_0)}{f(x_0)} - \frac{U^2 - U}{x_0^2} \tag{19}$$

$$= \frac{\sum \omega_r E_r (E_r - 1) x_0^{E_r}}{x_0^2 \sum \omega_r x_0^{E_r}} - \frac{U^2 - U}{x_0^2} \tag{20}$$

$$= \frac{\left\langle E_r^2 \right\rangle - \langle E_r \rangle}{x_0^2} - \frac{U^2 - U}{x_0^2} \tag{21}$$

$$= \frac{\left\langle E_r^2 \right\rangle - U^2}{x_0^2} \tag{22}$$

$$= \frac{\left(\langle E_r \rangle - U\right)^2}{x_0^2} \tag{23}$$

Problem 3.3

$$\exp(x) = \sum \frac{1}{n!} x^n \tag{24}$$

$$\frac{1}{n!} = \frac{1}{2\pi\imath} \oint \frac{\exp(z)}{z^{n+1}} dz \tag{25}$$

$$\text{Define: } g(z) \equiv \ln\left(\frac{\exp(z)}{z^{n+1}}\right) \equiv \ln(F(z)) \tag{26}$$

$$g(z) = z - (n+1)\ln z \tag{27}$$

For $F(z)$, the saddle point is defined as $F\prime(x_0) = 0$, which gives $x_0 = n+1$. Notice that $z = x_0$ is also the saddle point for $g(z)$. Expanding $g(z)$ about the point $z = x_0$, along the line $z = x_0 + iy$, we get:

$$g(z) = g(x_0) - \frac{1}{2}g\prime\prime(x_0)y^2 + ... \tag{28}$$

Thus, the integrand, along the line $z = x_0 + iy$, will become:

$$F(z) = \frac{\exp(x_0)}{x_0^{n+1}} \exp\left[-\frac{1}{2}g\prime\prime(x_0)y^2\right] \tag{29}$$

$$\begin{aligned}
\frac{1}{n!} &= \frac{1}{2\pi\imath}\oint \frac{\exp(z)}{z^{n+1}}dz & (30)\\
&\simeq \frac{1}{2\pi\imath}\frac{\exp(x_0)}{x_0^{n+1}}\int_{-\infty}^{+\infty} \exp\left[-\frac{1}{2}g\prime\prime(x_0)y^2\right]\imath dy & (31)\\
&= \frac{\exp(n+1)}{(n+1)^{n+1}}\frac{1}{[2\pi g\prime\prime(x_0)]^{1/2}} & (32)\\
&= \frac{\exp(n+1)}{(n+1)^{n+1}}\left(\frac{n+1}{2\pi}\right)^{1/2} & (33)
\end{aligned}$$

Do a simple calculation and replace $(n+1)$ wit$n$, we get:

$$n! \simeq \sqrt{2\pi n}\left(\frac{n}{e}\right)^n \tag{34}$$

which is just the original form of Stirling formula for $n!$.

Problem 3.4

$$\begin{aligned}
\mathcal{LHS} &= (k/\mathcal{N})\ln\Gamma & (35)\\
&= (k/\mathcal{N})\ln\sum W_{n_r} & (36)\\
&= (k/\mathcal{N})\ln\sum\frac{\mathcal{N}!}{\Pi(n_r!)} & (37)
\end{aligned}$$

When $\mathcal{N}$ is extremely a huge number, only the maximal set n_r^* will make a difference. Thus:

$$\begin{aligned}
\sum\frac{\mathcal{N}!}{\Pi(n_r!)} &= \frac{\mathcal{N}!}{\Pi(n_r!)} & (38)\\
&= \frac{\mathcal{N}!}{\Pi(\langle n_r\rangle!)} & (39)
\end{aligned}$$

$$
\begin{aligned}
\mathcal{LHS} &= (k/\mathcal{N}!)\ln\sum\frac{\mathcal{N}}{\Pi(n_r!)} && (40)\\
&= (k/\mathcal{N})\ln\frac{\mathcal{N}!}{\Pi(\langle n_r\rangle!)} && (41)\\
&= (k/\mathcal{N})\left(\mathcal{N}\ln\mathcal{N} - \sum\langle n_r\rangle\ln\langle n_r\rangle\right) && (42)\\
&= (k/\mathcal{N})\left(\sum\langle n_r\rangle\ln\mathcal{N} - \sum\langle n_r\rangle\ln\langle n_r\rangle\right) && (43)\\
&= (k/\mathcal{N})\sum\left(\langle n_r\rangle\left(\ln\mathcal{N} - \ln\langle n_r\rangle\right)\right) && (44)\\
&= -k\sum\frac{\langle n_r\rangle}{\mathcal{N}}\ln\frac{\langle n_r\rangle}{\mathcal{N}} && (45)\\
&= -k\langle\ln Pr\rangle && (46)\\
&= S = \mathcal{RHS} && (47)
\end{aligned}
$$

Problem 3.5

Since the Helmholtz free energy $A(N,V,T)$ has the property:

$$A(\lambda N,\lambda V,T) = \lambda A(N,V,T)$$

Differentiate with respect to λ and substitute $\lambda = 1$ immediately yields

$$N\left(\frac{\partial A}{\partial N}\right)_{V,T} + V\left(\frac{\partial A}{\partial V}\right)_{N,T} = A$$

Problem 3.6

Problem 3.7

$$
\begin{aligned}
C_p - C_V &= (\frac{\partial H}{\partial T})_p - (\frac{\partial E}{\partial T})_V\\
&= (\frac{\partial(E+pV)}{\partial T})_p - (\frac{\partial E}{\partial T})_V\\
&= p(\frac{\partial V}{\partial T})_p + (\frac{\partial E}{\partial V})_\beta(\frac{\partial V}{\partial T})_p\\
&= (\frac{\partial V}{\partial T})_p(p + (\frac{\partial E}{\partial V})_\beta)\\
&= -\frac{(\frac{\partial p}{\partial T})_V}{(\frac{\partial p}{\partial V})_T}(p - \frac{\partial^2 lnQ}{\partial\beta\partial V})\\
&= -\frac{k(\beta\frac{\partial^2 lnQ}{\partial\beta\partial V} - \frac{\partial lnQ}{\partial V})^2}{(\frac{\partial^2 lnQ}{\partial V^2})_\beta}\\
&= desired\ formula.
\end{aligned}
$$

As for classical ideal gas, $(\frac{\partial E}{\partial V})_\beta = 0$, $pV = NkT$, we soon get that the above result is Nk.

Problem 3.8

For classical ideal gas

$$\begin{aligned}
\ln\left(\frac{Q_1}{N}\right)+T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P &= \ln\left\{\frac{V}{h^3N}(2\pi mkT)^{3/2}\right\}+T\frac{\partial}{\partial T}\ln\left\{\frac{N}{h^3P}(2\pi m)^{3/2}(kT)^{3/5}\right\} \\
&= \ln\left\{\frac{V}{N}(\frac{2\pi mkT}{h^2})^{3/2}\right\}+\frac{5}{2} \\
&= \frac{S}{Nk}
\end{aligned}$$

Problem 3.9

For an ideal monaomic gas,its heat capacity C would be 3R/2.While asume the whole progress is quasistatic,it would obey

$$pV = RT$$

$$dU = -pdV + dQ = CdT$$

So we can get

$$\frac{5}{2}pdV + \frac{3}{2}Vdp = dQ$$

For adiabatical process,dQ=0,so the ratio of the final pressure to initial pressure would be

$$\frac{p_f}{p_i} = (1/2)^{5/3}$$

For the process with heat,the equation is difficult to solve,but naively thinking,for a process that the pressure doesn't change,it need heat to be added,so the final pressure would be higher than adiabatical process.

Problem 3.11

Suppose $pV^n = C$, so the work done is

$$\Delta W = \int_{V_1}^{V_2}\frac{C}{V^n}dV = \frac{C}{n-1}(V_2^{1-n} - V_1^{1-n}) \tag{48}$$

The energy difference is given by

$$\Delta U = p_2V_2 - p_1V_1 = C(V_2^{1-n} - V_1^{1-n}) \tag{49}$$

Therefore, the heat absorbed is

$$\Delta Q = C\frac{n-2}{n-1}(V_2^{1-n} - V_1^{1-n}) \tag{50}$$

Problem 3.12

The Hamiltonian of the classical system can be written as:

$$H = \sum_i^N \frac{\mathbf{p}_i^2}{2m} + \sum_i^N U(\mathbf{x}_i) \tag{51}$$

So the partition function of the system is:

$$\begin{aligned} Q(\beta, N, V) &= \frac{1}{N!h^{3N}} \int \prod_{i=1}^{N} d^3x_i d^3p_i e^{-\beta H(x,p)} \\ &= \frac{1}{N!} \left[\left(\frac{2\pi m\beta^{-1}}{h^2} \right)^{3N/2} \int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right] \end{aligned} \tag{52}$$

So the Helmholtz potential is $A = -kT \ln Q$ and the entropy S is the derivative of free energy:

$$\begin{aligned} S &= -\frac{\partial A}{\partial T} \\ &= -\frac{\partial}{\partial T} \left\{ -kT \ln \left[\frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \left(\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right) \right] \right\} \\ &= -\frac{\partial}{\partial T} \left\{ -NkT \ln \left[\frac{1}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] - NkT \right\} \\ &= Nk \ln \left[\frac{1}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] + \frac{3}{2}Nk + \frac{1}{T} \frac{\int \prod_i d^3x_i \sum_i U(\mathbf{x}_i) e^{-\beta U(\mathbf{x}_i)}}{\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)}} + Nk \\ &= \frac{5Nk}{2} + Nk \ln \left[\frac{1}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] + \frac{\overline{U}}{T} \\ &= \frac{5Nk}{2} + Nk \ln \left[\frac{1}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{\frac{\overline{U}}{NkT}} \left(\int \prod_i d^3x_i e^{-\beta U(\mathbf{x}_i)} \right)^{1/N} \right] \\ &= Nk \left\{ \frac{5}{2} + \ln \left[\frac{\overline{V}}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \right\} \end{aligned} \tag{53}$$

Up till now we have shown the entropy of such a system. So if the potential energy is just a constant, the "free volume" is the common volume of classical ideal gas.

Then consider about the hard sphere gas. The potential energy is:

$$U(\mathbf{x}_i) = \begin{cases} 0 & |\mathbf{x}_i - \mathbf{x}_j| > D \\ \infty & |\mathbf{x}_i - \mathbf{x}_j| < D \end{cases}$$

It is obvious that the average of potential energy is $\overline{U} = 0$, so the free volume is

$$\begin{aligned} \overline{V}^N &= \int \prod_i d^3x_i \, e^{-\beta U(\mathbf{x}_i)} \\ &= \int d^3x_N \int d^3x_{N-1} \cdots \int d^3x_1 e^{-\beta U(\mathbf{x}_i)} \\ &= V \left(V - \frac{4\pi}{3} D^3 \right) \left(V - 2 \cdot \frac{4\pi}{3} D^3 \right) \cdots \left(V - \frac{N-1}{3} 4\pi D^3 \right) \end{aligned} \tag{54}$$

Define $v_0 = \pi D^3/6$ is the volume a sphere, so the gas-law will be:

$$\begin{aligned} P &= \frac{NkT}{\overline{V}}\frac{\partial \overline{V}}{\partial V} \\ &= kT\left(\frac{1}{V} + \frac{1}{V-8v_0}\cdots\frac{1}{V+8(N-1)v_0}\right) \\ &\simeq kT\left(\frac{N+N^2\frac{4v_0}{V}}{V}\right) \\ &= kT\frac{N}{V\frac{1}{1+4Nv_0/V}} \\ &\simeq \frac{NkT}{V-4Nv_0} \end{aligned} \tag{55}$$

This result is the same as we have seen in Problem 1.4.

Problem 3.13

(a)Use classical method,it is easy to get partition function.

$$Q_N = \frac{1}{N_1!N_2!}[\frac{V}{h^3}(2\pi m_1 kT)^{\frac{3}{2}}]^{N_1}[\frac{V}{h^3}(2\pi m_2 kT)^{\frac{3}{2}}]^{N_2}$$

For the same reason.We get the partition function of another system:

$$Q_N = \frac{1}{(N_1+N_2)!}[\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}]^{N_1+N_2}$$

m is mixed mass.

$$m = \frac{N_1 m_1 + N_2 m_2}{N_1+N_2}$$

Problem 3.15

We have $Q_1(V,T) = \int g(\epsilon)e^{-\beta\epsilon}d\epsilon$. For 3-D extreme relativistic gas, $\epsilon = pc$, hence we have

$$g(p)dp = \frac{V}{h^3}4\pi p^2 dp = \frac{4\pi V}{h^3}\frac{\epsilon^2}{c^2}\frac{d\epsilon}{c} = g(\epsilon)d\epsilon$$

$$\therefore g(\epsilon) = \frac{4\pi V}{(hc)^3}\epsilon^2$$

$$\therefore Q_1(V,T) = \int_0^\infty g(\epsilon)d\epsilon = \frac{4\pi V}{(hc)^3}\int_0^\infty \epsilon^2 e^{-\beta\epsilon}d\epsilon = 8\pi V\left(\frac{kT}{hc}\right)^3$$

$\therefore$for N molecules,

$$Q_N(V,T) = \frac{1}{N!}\left\{8\pi V\left(\frac{kT}{hc}\right)^3\right\}^N$$

From $Q_N(V,T)$, it's easy to calculate:

$$P = \frac{1}{\beta}\frac{\partial Q}{\partial V} = \frac{N}{V}kT$$

$$U = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = 3NkT$$

$$\gamma = \frac{4}{3}$$

As stated in section 3.4, $g(E)$ can be obtained from the inverse Laplace transform, i.e.,

$$g(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E} Q(\beta) d\beta$$

in our case, $Q(\beta) = Q_N(V,T)$, hence

$$\begin{aligned} g(E) &= \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E} Q(\beta) d\beta \\ &= \frac{(8\pi V)^N}{N!(hc)^{3N}} \mathrm{Res}\left[\frac{e^{\beta E}}{\beta^{3N}}\right]_{\beta=0} \\ &= \frac{(8\pi V)^N E^{3N-1}}{N!(3N-1)!(hc)^{3N}} \end{aligned}$$

Problem 3.16

We can get the partition function of the system by utilizing equation (3.5.5):

$$Q_N(V,T) = \frac{1}{N!h^{3N}}\int e^{-\beta H(q,p)} d\omega \tag{56}$$

Since the particles in this system obey the energy-momentum relationship $\epsilon = pc$, and the particles can only move in one dimension, equation.(**??**) becomes:

$$Q_N(L,T) = \frac{1}{(3N)!h^{3N}}\int e^{-\beta|p|c} d^{3N}p d^{3N}x \tag{57}$$

Then we can get the partition function:

$$Q_N(V,T) = \frac{1}{(3N)!}\left[2L\frac{kT}{hc}\right]^{3N} \tag{58}$$

And we can study the thermodynamics of this system:

$$P = \frac{1}{\beta}\frac{\partial \ln Q}{\partial L} = \frac{3N}{V}kT$$

$$U = -\frac{\partial \ln Q}{\partial \beta} = 3NkT$$

$$\gamma = \frac{4}{3}$$

Using the inversion formula (3.4.7), we can derive an expression of the density of states $g(E)$. From equation (3.4.7):

$$\begin{aligned} g(E) &= \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E} Q(\beta) d\beta \\ &= \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{1}{(3N)!}\left[\frac{2L}{hc}\right]^{3N} \frac{e^{\beta E}}{\beta^{3N}} d\beta \end{aligned} \tag{59}$$

Since the integrand have only one singularity, $\beta = 0$, we can calculate this integration by using Residue Theorem:

$$\begin{aligned} g(E) &= \frac{1}{2\pi i}\frac{E^{3N-1}}{(3N)!}\left[\frac{2L}{hc}\right]^{3N}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{e^{\beta E}}{(\beta E)^{3N}} d(\beta E) \\ &= \frac{1}{2\pi i}\frac{E^{3N-1}}{(3N)!}\left[\frac{2L}{hc}\right]^{3N}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{1}{(\beta E)^{3N}}\sum_{j=0}^{\infty}\frac{E^j}{j!} d(\beta E) \\ &= \frac{1}{2\pi i}\frac{E^{3N-1}}{(3N)!(3N-1)!}\left[\frac{2L}{hc}\right]^{3N} \end{aligned} \tag{60}$$

Problem 3.17

$$\int [U - H(p,q)]e^{-\beta H(p,q)} d\omega = 0$$
$$\Rightarrow \int [\frac{\partial U}{\partial \beta} - H(p,q)U + H^2(p,q)]e^{-\beta H(p,q)} d\omega = 0$$
$$\Rightarrow \int [\frac{\partial U}{\partial \beta} - U^2 + H^2(p,q)]e^{-\beta H(p,q)} d\omega = 0$$
$$\Rightarrow \langle H^2 \rangle - U^2 = -\frac{\partial U}{\partial \beta}$$

That is the desired equation.

Problem 3.18

$$\begin{aligned}\langle (\Delta E)^3 \rangle &= \langle E^3 - 2E^2\langle E\rangle + 2E\langle E\rangle^2 - \langle E\rangle^3\rangle \\ &= \langle E^3\rangle - 2\langle E^2\rangle\langle E\rangle + \langle E\rangle^3\end{aligned}$$

Considering the relations below

$$\begin{aligned}\langle E \rangle &= \frac{E_r \exp(-\beta E_r)}{\exp(-\beta E_r)} \\ \langle E^2 \rangle &= \frac{E_r^2 \exp(-\beta E_r)}{\exp(-\beta E_r)}\end{aligned}$$

$$C_V = \frac{\langle E^2\rangle - \langle E\rangle^2}{kT^2}$$

$$k^2\left\{T^4\left(\frac{\partial C_V}{\partial T}\right)_V + 2T^3 C_V\right\} = -\frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left\{\beta^2(\langle E^2\rangle - \langle E\rangle^2)\right\} + \frac{2}{\beta}(\langle E^2\rangle - \langle E^2\rangle)$$

We have

$$\langle E^3 \rangle = k^2\left\{T^4\left(\frac{\partial C_V}{\partial T}\right)_V + 2T^3 C_V\right\}$$

Problem 3.19

$$< \frac{dG}{dt} >=< \sum p_i \frac{dq_i}{dt} > + < \sum q_i \frac{dp_i}{dt} >= 0$$

Above equation has used equation (3.7.5) and equation (3.7.6). The equation (3.7.5) and equation(3.7.6) both come from (3.7.2),so validity of one equation implies another's.

Problem 3.21

(a) Classically, the harmonic equation of motion leads to $x = A \sin \omega t$. As a result, the kinetic energy and potential energy will be $m\omega^2 A^2 \cos^2 \omega t/2$ and $m\omega^2 A^2 \sin^2 \omega t/2$ respectively. Average them it's easy to see that $\bar{K} = \bar{U} = m\omega^2 A^2/4$. Quantum-mechanically, $\psi = \sum_n c_n \psi_n$ where ψ_n is the n-th Hermitian polynomial. Using the recursive relations, we have

$$\bar{K} = -\frac{\hbar^2}{2m}\sum_n |c_n|^2 \int \psi^* \frac{d^2}{dx^2}\psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{61}$$

$$\bar{U} = \frac{m\omega^2}{2}\sum_n |c_n|^2 \int \psi^* x^2 \psi dx = \sum_n |c_n|^2 \frac{\hbar\omega(2n+1)}{4} = \frac{1}{2}\sum_n |c_n|^2 E_n \tag{62}$$

(b) In Bohr-sommerfeld model, a quantized orbits are hypothesized, namely $m_e v r = n\hbar$. In the n-th orbit, the total energy is $E_n = -Z^2k^2e^4m_e/2\hbar^2n^2$. The radius of which is $r_n = n^2\hbar^2/Zke^2m_e$. By a naive calculation $\bar{U} = -Z^2k^2e^4m_e/\hbar^2n^2$ and $\bar{T} = Z^2k^2e^4m_e/2\hbar^2n^2$.
In the Schroedinger hydrogen atom, $\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi)$. The kinetic energy is given by

$$\begin{aligned}\bar{T} &= \frac{\hbar^2}{2m}\int \psi^*_{nlm}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right)\psi_{nlm} r^2 \sin\theta dr d\theta d\phi \\ &= \frac{\hbar^2}{2m}\int R_{nl}(r)\left(\frac{1}{n^2a^2}\right)R_{nl}(r)r^2 dr \\ &= \frac{e^2}{2an^2} \end{aligned} \tag{63}$$

so $\bar{U} = -e^2/an^2$. a is the Bohr radius.
(c) This is also a central force case. The results are quite identical to (b).

Problem 3.22

Anharmonic Oscillator.

This anharmonic oscillator has the Hamiltonian:

$$H = \frac{p^2}{2m} + \frac{1}{4}kx^4$$

So the canonical partition function of the system is:

$$Q = \frac{1}{h}\int dp dx\, e^{-\beta\left(\frac{p^2}{2m} + \frac{1}{4}kx^4\right)} \tag{64}$$

Use the "equipartition theorem", we can get the following result:

$$\left\langle x\frac{\partial H}{\partial x}\right\rangle = kT \tag{65}$$

Thus because $\partial H/\partial x = kx^3$, we can get

$$x\frac{\partial H}{\partial x} = kx^4 = 4V$$

So the expectation value of the potential is $\langle V\rangle = kT/4$. For the same reason, we can get the mean value of the kinetic energy:

$$\langle K\rangle = \frac{1}{2}\left\langle p\frac{\partial H}{\partial p}\right\rangle = \frac{kT}{2} \tag{66}$$

So clearly we can get $\langle K\rangle = 2\langle V\rangle$.

Problem 3.23

According to the equation 3.7.15

$$\frac{PV}{NkT} = 1 - \frac{1}{NdkT} * \overline{\sum_{i<j}\frac{\partial u(r_{ij})}{\partial r_{ij}}r_{ij}}$$

For the ideal gas.There is not interaction term.

$$PV = NkT$$

The Hamiltonian of the system happens to be a quadratic function of its coordinates.The virial theorem states that

$$\boldsymbol{\nu_0} = -3NkT$$

So we can infer that

$$\boldsymbol{\nu_0} = -3PV$$

Let's consider the interaction between the particles and walls of container.

$$\boldsymbol{\nu_0} = -P\int(\nabla\cdot\boldsymbol{r})dV = -3PV$$

They show walls of container are the main factor interaction with particles.

Problem 3.25

Consider a particle inside a box with $\dot{q}_i$ and p_i, the volumn of the box is V. If the particle hits an area ΔS on a wall during time Δt, it has to be in volumn $\dot{q}_i\Delta S\Delta t$. Also, the momentum p_i it has must be oriented to the wall, which gives a 1/2 coefficient to the probability. Hence the pressure on the wall satisfies

$$\left\langle\sum_N \frac{1}{2}\frac{\dot{q}_i\Delta S\Delta t}{V}\cdot 2p_i\right\rangle = P\Delta S\Delta t$$

$$i.e., \left\langle\sum_i p_i\dot{q}_i\right\rangle = 3PV, i = 1, ..., 3N$$

From the equipartition theorem, $\langle\sum_i p_i\dot{q}_i\rangle = 3NkT$, hence

$$PV = NkT$$

for noninteracting systems.

Problem 3.26

To calculate the multiplicity of an s-dimensional oscillator, we can write the energy eigenvalues in this form:

$$\epsilon_j = (j + s/2)\hbar\omega = (\sum_{i=1}^{s} n_i + s/2)\hbar\omega \tag{67}$$

Where n_i is the "eigenvalues" of each dimension. And n_i can be a integer between 0 to j, just have to obey $\sum_{i=1}^{s} n_i = j$. So this problem is equivalent to putting $s-1$ "clapboards" between N particles. Hence we can get the multiplicity:

$$m_j = \frac{(j+s-1)!}{j!(s-1)!} \tag{68}$$

Then we can get the partition function of a single oscillator:

$$\begin{aligned} Q_1 &= \sum_j m_j \exp\left(-\beta\epsilon_j\right) \\ &= \frac{(j+s-1)!}{j!(s-1)!}\exp\left[-\beta(j+s/2)\hbar\omega\right] \\ &= \left[\frac{\exp(-\beta\hbar\omega/2)}{1-\exp(-\beta\hbar\omega)}\right]^s \end{aligned} \tag{69}$$

The partition function of a system of N oscillators is:

$$Q_N = Q_1^N = \left[\frac{\exp(-\beta\hbar\omega/2)}{1-\exp(-\beta\hbar\omega)}\right]^{sN} \tag{70}$$

We can study the thermodynamics of this system from equation.(**??**): And we can study the thermodynamics of this system:

$$U = -\frac{\partial \ln Q_N}{\partial \beta} = sN\left[\frac{1}{2} + \frac{1}{1-\exp(-\beta\hbar\omega)}\right]\hbar\omega$$
$$\mu_s = -\frac{1}{\beta}\frac{\partial \ln Q_N}{\partial N} = s\left[\frac{\hbar\omega}{2} + \frac{\ln[1-\exp(-\beta\hbar\omega)]}{\beta}\right]$$

For a system of sN one-dimensional oscillators:

$$Q_{sN} = Q_1^s N = \left[\frac{\exp(-\beta\hbar\omega/2)}{1-\exp(-\beta\hbar\omega)}\right]^{sN}$$

$$U = -\frac{\partial \ln Q_N}{\partial \beta} = sN\left[\frac{1}{2} + \frac{1}{1-\exp(-\beta\hbar\omega)}\right]\hbar\omega$$
$$\mu_1 = -\frac{1}{\beta}\frac{\partial \ln Q_N}{\partial sN} = \left[\frac{\hbar\omega}{2} + \frac{\ln[1-\exp(-\beta\hbar\omega)]}{\beta}\right]$$

And we have:

$$\mu_s = s\mu_1$$

Problem 3.27

$$\begin{aligned} g(E) &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{(\beta+i\gamma)(E-(N/2)\hbar\omega)}(1-e^{-\hbar\omega(\beta+i\gamma)})^{-N}d\gamma \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{(\beta+i\gamma)(E-(N/2)\hbar\omega)}(1+C_N^1 e^{-\hbar\omega(\beta+i\gamma)} + C_{N+1}^2 e^{-2\hbar\omega(\beta+i\gamma)} + C_{N+2}^3 e^{-3\hbar\omega(\beta+i\gamma)} + ...)d\gamma \\ &= \sum_{k=0}^{\infty}\delta(E-(N/2)\hbar\omega - k\hbar\omega)C_{N+k-1}^k \end{aligned}$$

The above result is the same as that derived from direct state counting for N distinguishable quantum SHOs. Assume $E = (m+N/2)\hbar\omega$, then we have:

$$S = k\ln(g(E)dE) = k\ln(C_{N+m-1}^m)$$

while $m \gg 1$, $N \gg 1$, using the Stiring formula we can find:

$$S \approx k(m\ln\frac{N+m-1}{m} + (N-1)\ln\frac{N+m-1}{N-1}) \approx Nk(\frac{m+N}{N}\ln\frac{m+N}{N} - \frac{m}{N}\ln\frac{m}{N})$$

which is the desired formula.

Problem 3.28

a)

Define

$$R = \left(E - \frac{1}{2}N\hbar\omega\right)\Big/\hbar\omega$$

Number of states avaliable for the whole system is

$$m_0 = \frac{(R+N-1)!}{R!(N-1)!}$$

Number of states avaliable for a particular oscillator in state n

$$m = \frac{(R+N-1-n-1)!}{(R-n)!(N-1)!}$$

Probability

$$p_n = \frac{m}{m_0} = \frac{R(R-1)\cdots(R-n+1)(N-1)}{(R+N-1)\cdots(R+N-1-n-1)}$$

for $N \gg 1$ and $R \gg n$

$$p_n \approx \frac{(\bar{n})^n}{(\bar{n}+1)^{n+1}}$$

where $\bar{n} = R/N$

b)

The number of states avaliable for total energy E and N particles are

$$g(E,N) = \frac{1}{N!}(\frac{V}{h^3})^N \frac{(2\pi m)^{3N/2}}{(3N/2-1)!} E^{3N/2-1}$$

Probability

$$p = \frac{g(E-\epsilon, N-1)}{g(E,N)}$$

For $N \ll 1$ and $E \ll \epsilon$

$$p \propto \left(\frac{E-\epsilon}{E}\right)^{3N/2} \approx \exp(-\beta\epsilon)$$

where $\beta = 3N/2E$.

Problem 3.29

I can't solve this problem.The intergral of the unharnomic terms in the partition fuction is infinite.

Problem 3.31

"Partition function" for single particle is

$$Q_1 = 1 + e^{-\varepsilon/kT}. \tag{71}$$

So a list of quatities can be obtained:

$$Q_N = (1 + e^{-\varepsilon/kT})^N \tag{72}$$
$$A = -NkT\ln(1 + e^{-\varepsilon/kT}) \tag{73}$$
$$\mu = -kT\ln(1 + e^{-\varepsilon/kT}) \tag{74}$$
$$p = 0 \tag{75}$$
$$S = Nk\ln(1 + e^{-\varepsilon/kT}) + \frac{N\varepsilon}{T}\frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \tag{76}$$
$$U = N\varepsilon\frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} \tag{77}$$
$$C_p = C_V = \frac{N\varepsilon^2 e^{-\varepsilon/kT}}{kT^2(1 + e^{-\varepsilon/kT})^2} \tag{78}$$

This specific heat is sometimes referred to *Schottky anomaly.*

Problem 3.32

(a) Since the distribution is given by canonical distribution, the probabilities are:

$$p_i = Q^{-1}g_i e^{-\beta\epsilon_i}$$

and the entropy should be:

$$\begin{aligned}
S &= -k\left[p_1\ln(p_1/g_1) + p_2\ln(p_2/g_2)\right] \\
&= -k\left[\frac{g_1 e^{-\beta\epsilon_1}}{Q}\ln\frac{e^{-\beta\epsilon_1}}{Q} + \frac{g_2 e^{-\beta\epsilon_2}}{Q}\ln\frac{e^{-\beta\epsilon_2}}{Q}\right] \\
&= k\ln Q + \frac{1}{T}\frac{g_1\epsilon_1 e^{-\beta\epsilon_1} + g_2\epsilon_2 e^{-\beta\epsilon_2}}{Q} \\
&= k\ln g_1 + k\ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{1}{T}\frac{g_2(\epsilon_2 - \epsilon_1)e^{-\beta\epsilon_2}}{Q} \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{g_2 e^{-\beta\epsilon_2}x}{Q}\right] \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1 + \frac{g_1}{g_2}e^{x}}\right]
\end{aligned} \tag{79}$$

When $g_1 = g_2 = 1$, the situation is the same as Fermi oscillator with energy 0 and $\epsilon_2 - \epsilon_1$.

(b) The entropy is the derivative of the free energy, so we can get the entropy by the following process:

$$\begin{aligned}
S &= -\frac{\partial A}{\partial T} \\
&= \frac{\partial}{\partial T}\{kT\ln Q\} \\
&= k\ln Q + \frac{1}{T}\frac{g_1\epsilon_1 e^{-\beta\epsilon_1} + g_2\epsilon_2 e^{-\beta\epsilon_2}}{Q} \\
&= k\left[\ln g_1 + \ln\left(1 + \frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1 + \frac{g_1}{g_2}e^{x}}\right]
\end{aligned} \tag{80}$$

which is the same as we get in (a).

(c) Clearly from equation (**??**), when temperature is $T = 0$, the entropy will be:

$$S = \lim_{x\to+\infty} k\left[\ln g_1 + \ln\left(1+\frac{g_2}{g_1}e^{-x}\right) + \frac{x}{1+\frac{g_1}{g_2}e^{x}}\right] = k\ln g_1 \tag{81}$$

From the distribution of canonical ensemble, we know that when the temperature is $T = 0$, the system will stay on the ground state. Since the ground is g-fold degenerate, there are g_1 possible states. So the entropy is $S = k\ln g_1$.

Problem 3.33

Let's consider parameter $\frac{\mu H}{kT}$.
If you plot the Langevin's function:

$$L(x) = coth(x) - \frac{1}{x}$$

You will find when $\frac{\mu H}{kT} = 5.12$ magnetic moment is saturated.

Problem 3.35

For $\epsilon = \frac{p^2}{2m} + \left\{\frac{p_\theta^2}{2I} + \frac{p_\phi}{2I\sin^2\theta}\right\} - \mu E\cos\theta$, just calculate

$$\begin{aligned}
Q &= \frac{1}{h^3}\int e^{-\beta\epsilon}d^3pd^3q \\
&= \int_0^\infty \exp\left(-\frac{\beta p^2}{2m}\right)dp\int_0^\infty \exp\left(-\frac{\beta p_\theta^2}{2I}\right)dp_\theta\int_0^\infty \exp\left(-\frac{\beta p_\phi^2}{2I\sin^2\theta}\right)dp_\phi\int \exp(-\mu E\cos\theta)drd\theta d\phi \\
&= \frac{2\pi I}{\beta}\sqrt{\frac{2\pi m}{\beta}}\int_0^R dr\int_0^\pi \sin\theta\exp(-\mu E\cos\theta)d\theta\int_0^{2\pi}d\phi \\
&= \frac{4\pi^2 IR}{\beta}\sqrt{\frac{2\pi m}{\beta}}\frac{e^{\mu E}-e^{-\mu E}}{\mu E}
\end{aligned}$$

$$\therefore Q_N = \frac{1}{N!}Q^N$$

Once Q_N is obtained, all thermodynamics of the system can be obtained. I forget the definition of electric polarization, etc. I hope you can obtain them from Q_N by yourself.

Problem 3.37

Prof.Ni's ppt has given a detailed and complete solution to this problem. If someone regards it worthwhile I will renew this text later.

Problem 3.38

As defined in the problem, we examine the patition function

$$\begin{aligned}
Q_1(\beta) &= \int_{-J}^{J}\exp(\beta g\mu_B mH) \\
&= \frac{1}{\beta g\mu_B H}(\exp(\beta g\mu_B JH) - \exp(\beta g\mu_B JH))
\end{aligned}$$

Choose $x = \beta g\mu_B JH$
Thermal dynamic properties

$$\begin{aligned}\bar{\mu}_z &= \frac{1}{\beta}\frac{\partial}{\partial H}\ln Q_1(\beta) \\ &= J^2 g\mu_B(\coth(x) - \frac{1}{x})\end{aligned}$$

Problem 3.39

By using equation (3.9.18) we could get

$$Q = \sum_{m=-1/2}^{1/2} \exp(\beta g\mu_b mH) = \exp(-\beta g\mu_b H/2)(1 + \exp(\beta g\mu_b H))$$

The mean magnetic moment is

$$M = \frac{N}{\beta}\frac{\partial}{\partial H}\ln Q = \frac{1}{2}N\mu_b g\frac{1-\exp(-\beta g\mu_b H)}{1+\exp(-\beta g\mu_b H)}$$

While the number of parallel atoms N_+ and antiparallel N_- satisfied that

$$\begin{cases} \dot{N}_+ + N_- = N \\ (N_+ - N_-)g\mu_b J = M \\ J = 1/2 \end{cases} \tag{82}$$

So we could get the answer

$$\begin{cases} \dot{N}_+/N = \dfrac{1}{1+\exp(-\beta g\mu_b H)} \\ N_-/N = \dfrac{\exp(-\beta g\mu_b H)}{1+\exp(-\beta g\mu_b H)} \end{cases} \tag{83}$$

Acoording to the given situation,flux density 0.1 $weber/m^2$ and temperature of 1000K,the respective fractions are

$$\begin{cases} \dot{N}_+/N = 50.00168\% \\ N_-/N = 49.99832\% \end{cases} \tag{84}$$

Problem 3.41

The equilibrium temperature will be positive, since the energy of the whole system is not bounded from above. This case is a bit like the spin and lattice case. For the subsystem of spins, its energy is bounded from above, so it is possible to attain a negative temperature. While the subsystem of lattice, i.e. ideal gas in this problem, only has positive temperature. The whole system doesn't have a energy limit, so the temperature will only be positive. And energy may flow from the spin subsystem to the ideal gas.

Problem 3.42

Paramagnetic system.

For a given energy E, we can know that:

$$E = \mu_B H(N_\uparrow - N_\downarrow) \tag{85}$$
$$N = N_\uparrow + N_\downarrow \tag{86}$$

So the occupying number of up(down)-spin is

$$N_{\uparrow} = \frac{1}{2}\left(N + \frac{E}{\mu_B H}\right) \quad N_{\downarrow} = \frac{1}{2}\left(N - \frac{E}{\mu_B H}\right)$$

And the number of the possible states will be:

$$\Omega(N, E) = \mathrm{C}_N^{N_{\uparrow}} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} \tag{87}$$

So the entropy in micro canonical ensemble representation is:

$$\begin{aligned} S &= k \ln \Omega(E, N) \\ &= Nk \ln N - N_{\uparrow} k \ln N_{\uparrow} - N_{\downarrow} k \ln N_{\downarrow} \\ &= Nk \ln N - k\frac{N\mu_B H + E}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - k\frac{N\mu_B H - E}{2\mu_B H} \ln \frac{N\mu_B H - E}{2\mu_B H} \end{aligned} \tag{88}$$

This result is the same as (3.10.9) in Pathria's Book. Then the temperature:

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ &= -\frac{k}{2\mu_B H} \ln \frac{N\mu_B H + E}{2\mu_B H} - \frac{k}{2\mu_B H} + \frac{k}{2\mu_B H} \ln \frac{N\mu_B H - E}{2mu_B H} + \frac{k}{2\mu_B H} \\ &= \frac{k}{2\mu_B H} \ln \left(\frac{N\mu_B H - E}{N\mu_B H + E}\right) \end{aligned} \tag{89}$$

And this result is also the same as equation (3.10.8).

Problem 3.43

The hamiltonian of the system is :

$$\boldsymbol{H} = e\phi(\boldsymbol{q}) + \frac{1}{2m_e}\sum_{i=1}^{N}(\boldsymbol{P_i} - \frac{e}{c}\boldsymbol{A_i})^2$$

$$\dot{q_i} = -\frac{\partial H}{\partial p_i} \propto p_i$$

On the other hand

$$\vec{\mu} = \frac{e}{2c}\vec{r} \times \vec{v} = \sum_{i=1}^{N} \vec{a_i} \cdot \dot{q_i}$$

a_i are vector coefficients depending on the position coordinates.

$$\overline{\mu} = \frac{\displaystyle\int \mu * d\omega}{\displaystyle\int d\omega} \propto \int_{-\infty}^{+\infty} p * dp = 0$$

The integrand is an odd function of p, so it vanishes.