Worksheet 8 - Solution

1. Relativistic Particles

a) Each of the N coordinates goes up to L, then the total contrib.

$$\frac{L^N}{N!} \quad (1)$$

b)

The momenta are constrained by

$$\sum_{i=1}^{N} |p_i| = \frac{E}{c} \quad (2)$$

for $p > 0$ (and $p < 0$ similarly), eq 2 represents a hyper-piramid with N dimensions. (Neglecting the difference between surface area and volume for $N \gg 1$)

$$\Omega_p = 2^N \cdot \frac{1}{N!} \left(\frac{E}{c}\right)^N$$

in principle, we are interested on a surface of size ΔE.

$$\Omega'_p = \underbrace{2^N \frac{1}{(N-1)!} \left(\frac{E}{c}\right)^{N-1} \times \frac{\Delta E}{c}}_{\frac{d\text{volume}}{dR} \times \Delta R} \times \underbrace{\sqrt{N}}_{\text{Ratio of the Normal to the base to the side of the piramid}} \quad (3)$$

The Surface area of the pyramid is given by $\frac{\sqrt{d}\, R^{d-1}}{(d-1)!}$

The expressions 2 and 3 gives similar results for $N \gg 1$.

c) The complete available states expression is

$$\Omega(E, L, N) = \frac{1}{h^N} \frac{L^N}{N!} \cdot 2^N \cdot \frac{\sqrt{N}}{(N-1)!} \left(\frac{E}{c}\right)^{N-1} \times \frac{\Delta E}{c}$$

$$\ln(\omega) = \ln\left[\frac{1}{h^N}\frac{L^N}{N!}\cdot 2^N \cdot \frac{\sqrt{N}}{(N-1)!}\left(\frac{E}{c}\right)^{N-1}\cdot\frac{\Delta E}{c}\right]$$

$$= N\ln\left[\frac{2L}{h}\right] + \frac{1}{2}\ln(N) + (N-1)\ln\left(\frac{E}{c}\right) + \ln\left(\frac{\Delta E}{c}\right)$$

$$- N\ln(N) + N - (N-1)\ln(N-1) + N - 1$$

$$= \underbrace{N\ln\left[\frac{2L}{h}\,\frac{E}{c}\,\frac{1}{N}\,e^2\,\frac{1}{(N-1)}\right]}_{\text{order of } N} + \underbrace{\frac{1}{2}\ln(N) - \ln\left(\frac{E}{c}\right) + \ln\left(\frac{\Delta E}{c}\right) + \ln(N-1) - 1}_{O(\ln(N))}$$

$N-1 \approx N$

So, keeping just terms of order N

$$S(E,L,N) = N k_B \ln\left(\frac{2e^2}{hc}\cdot\frac{L}{N}\cdot\frac{E}{N}\right)$$

d) to get the pressure P we have to use

$$dE = T\,dS - P\,dV + \mu\,dN$$

$$\downarrow$$

$$P = T\left.\frac{\partial S}{\partial L}\right|_{E,N} = \frac{N k_B T}{L}$$

e) The temperature and energy are related as

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{L,N} = \frac{N k_B}{E} \rightarrow E = N k_B T$$

$$\downarrow$$

$$C_L = \left.\frac{\partial E}{\partial T}\right|_{L,N} = N k_B$$

The heat capacity at constant pressure needs to include the extra term of the work done against external pressure

$$C_p = \frac{\partial E}{\partial T}\bigg|_{P,N} + P\frac{\partial L}{\partial T}\bigg|_{P,N} = 2N k_B$$

f) if we fix p_1 for the first particle, the rest $N-1$ particles have $E - c|p_1|$. We can compute the ratio as the positions are not important

$$p(p_1) = \frac{\Omega(E - c|p_1|, N-1)}{\Omega(E, N)} = \left[\frac{2^{N-1}}{(N-1)!}\left(\frac{E-c|p_1|}{c}\right)^{N-1}\right] \times \frac{N!}{2^N}\left(\frac{c}{E}\right)^N$$

$$\approx \frac{cN}{2E}\left(1 - \frac{c|p_1|}{E}\right)^N \approx \frac{cN}{2E}\exp\left(-\frac{cN|p_1|}{E}\right)$$

as $E = Nk_BT$

$$p(p_1) = \frac{c}{2k_BT}\exp\left(-\frac{c|p_1|}{k_BT}\right)$$

2. Moleculor Adsortion.

a) The ground state $E = E_{min} = 0$ 2^N states.

The largest is just one $E = N\epsilon$.

b) let $N_2 = E/\epsilon$

Taking Ω as the number of ways to choose the N_g excited moleculs x Number of possible configurations

$$\Omega(E,N) = \frac{N!}{N_2!\,(N-N_2)!} \times 2^{N-N_2}$$

so

$$S(E,N) = S_{\text{Two-level system}} + k_B (N - N_z)\ln(2)$$

$$= -N k_B \left\{ \frac{E}{N\epsilon} \ln\left(\frac{E}{N\epsilon}\right) + \left(1 - \frac{E}{N\epsilon}\right) \ln\left(1 - \frac{E}{N\epsilon}\right) \right\}$$

$$+ k_B (N - N_z) \ln(2)$$

c) We have that,

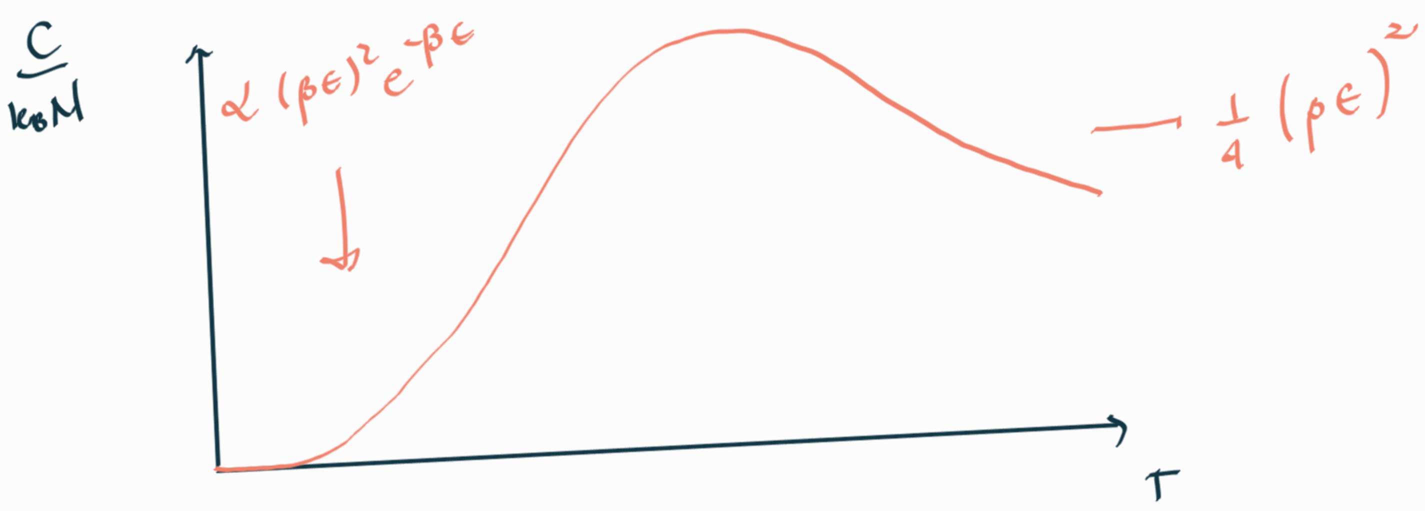
$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N = -\frac{k_B}{\epsilon} \ln\left(\frac{E}{N\epsilon - E}\right) - \frac{k_B}{\epsilon}\ln(2)$$

so

$$E = \frac{N\epsilon}{\exp\left(\frac{\epsilon}{k_B}\left(\frac{1}{T} + \frac{k_B}{\epsilon}\ln 2\right)\right) + 1} = \frac{N\epsilon}{2\exp(\beta\epsilon) + 1}$$

and

$$C = \frac{dE}{dT} = N k_B (\beta\epsilon)^2 \frac{2\exp(\beta\epsilon)}{(1 + 2\exp(\beta\epsilon))^2}$$



d)

$$P(\vec{r}_1 = \hat{z}) = \frac{\Omega(E-\epsilon, N-1)}{\Omega(E,N)}$$

$$= \frac{\cancel{(N-1)!}}{\cancel{(N_z-1)!}\,\cancel{[(N-1)-(N_z-1)]!}} \cancel{2^{(N-1)-(N_z-1)}}$$

$$\times \frac{N_z\cancel{!}\,\cancel{(N-N_z)!}}{N\cancel{!}} \quad \frac{1}{\cancel{2^{N-N_z}}}$$

$2^{N-N_z \cancel{-1} \cancel{+1}}$

$$= \frac{N_z}{N} = \frac{E}{N\epsilon} = \frac{1}{2\exp(\beta\epsilon)+1}$$

e) as $\frac{dE}{dT} > 0$ and $T > 0 \longrightarrow T \to \infty$ gives

$$E_{max} = \frac{N\epsilon}{3}$$

3) Curie Susceptibility

The gibbs partition function

$$Z = \sum_{\{m_i\}} \exp(\beta \vec{B}\cdot\vec{M}) = \sum_{\{m_i\}} \exp\left(\beta\mu B \sum_i^N m_i\right)$$

$$= \left[\sum_{m_i=-s}^{s} \exp(\beta\mu B \cdot m_i)\right]^N$$

so

$$Z = \left[e^{-\beta\mu B s} + e^{-\beta\mu B(s-1)} + \cdots\cdots + e^{+\beta\mu B(s-1)} + e^{\beta\mu B s} \right]^N$$

and it has the form of a geometrical series.

$$S = x^{-s} + x^{-(s-1)} + \cdots + x^{s-1} + x^{s}$$

so

$$xS = x^{-s+1} \cdots + x^{s} + x^{s+1}$$

and

$$S - xS = x^{-s} - x^{s+1} \to S = \frac{x^{-s} - x^{s+1}}{1-x}$$

so;

$$z = \left(\frac{e^{-\beta E\mu s} - e^{\beta E\mu(s+1)}}{1 - \exp(\beta B\mu)} \right)^N$$

$$= \left[\frac{\sinh(\beta\mu B(s+1/2))}{\sinh(\beta\mu B/2)} \right]^N$$

b) we have that

$$G = E - BM = -k_B T \ln(z)$$

$$G = -N k_B T \ln\left[\sinh(\beta\mu B(s+1/2))\right] + N k_B T \ln\left[\sinh(\beta\mu B/2)\right]$$

for small B, we can use the approximation

$$\sinh(\theta) = \frac{e^{\theta} - e^{-\theta}}{2} \approx \frac{1}{2}\left(2\theta + 2\frac{\theta^3}{2}\right) + \mathcal{O}(\theta^5)$$

Taking $\alpha = B\mu B$

$$G \approx -Nk_BT \left\{ \ln\left[\alpha\left(s+\tfrac{1}{2}\right)\left(1 + \frac{\alpha^2}{6}\left(s+\tfrac{1}{2}\right)^2\right)\right] - \ln\left[\frac{\alpha}{2}\left(1+\frac{\alpha^2}{24}\right)\right] + \mathcal{O}(\alpha^4) \right\}$$

Using the expansion

$$\ln(x+1) = x - \frac{x^2}{2} + \frac{x^3}{3} \cdots$$

$$\Rightarrow G \approx -N k_B T \left[\ln(2s+1) + \frac{1}{6}\left(\alpha(s+1/2)\right)^2 - \frac{1}{6}(\alpha/2)^2 + \mathcal{O}(\alpha^4) \right]$$

$$\approx -N k_B T \ln(2s+1) - N k_B T \alpha^2 \frac{(s^2+s)}{6}$$

$$= G_0 - \frac{N \mu^2 B^2 s(s+1)}{6 k_B T} + \mathcal{O}(B^4).$$

c) The magnetic susceptibility $\chi = \partial \langle M_z \rangle / \partial B$, so

$$\langle M_z \rangle = k_B T \frac{\partial \ln(z)}{\partial B} = \frac{-\partial G}{\partial B}$$

$$\chi = \frac{\partial \langle M_z \rangle}{\partial B} = -\frac{\partial}{\partial B}\frac{\partial G}{\partial B} = \frac{N \mu^2 s(s+1)}{3 k_B T}$$

so

$$\chi = \frac{c}{T} \quad \text{with} \quad c = \frac{N \mu^2 s(s+1)}{3 k_B}$$

d)

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$$C_V = \left.\frac{dQ}{dT}\right|_V = \left.\frac{dE - dW}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \left.\frac{dE}{dT}\right|_V$$

$$C_P = \left.\frac{dQ}{dT}\right|_P = \left.\frac{dE - dW}{dT}\right|_P = \frac{dE + PdV}{dT} = \left.\frac{dE}{dT}\right|_P + P\left.\frac{dV}{dT}\right|_P$$

Equivalently, The heat capacity difference goes as

$$C_P - C_V = P \frac{\partial V}{\partial T}\bigg|_P$$

$$\underbrace{\left(\text{we used that } \frac{dE}{dT}\bigg|_V = \frac{dE}{dT}\bigg|_P = \frac{dE}{dT} \right)}_{\text{assuming dependence only on temperature}}$$

$$C_B - C_M = B \frac{\partial M}{\partial T}\bigg|_B$$

$$\Rightarrow \quad \chi = \frac{C}{T} = \frac{\partial \langle M \rangle}{\partial B} \rightarrow \langle M \rangle = \frac{C}{T} \cdot B + \text{constant.}$$

$$C_B - C_M = B \times C\, B \frac{\partial}{\partial T}\left[\frac{1}{T}\right] = C \times \frac{B^2}{T^2}$$

4) 2d - Solid

We have that the partition function.

$$Z = \frac{1}{N_a!} \sum_{i=1}^{N_s} e^{-\beta E_i} = \frac{N_s!}{N_a!\,(N_s - N_a)!} e^{\beta N_a \varepsilon}$$

as we have that $N_a \ll N_s$

$$Z = \frac{N_s^{N_a} e^{\beta N_a \varepsilon}}{N_a!}$$

and as $F = -k_B T \ln(z)$ $\quad -\beta F = \ln(z) \Rightarrow z = e^{-\beta F}$

and $\mu = \frac{\partial F}{\partial N} \longrightarrow \mu N_a = F \longrightarrow z = e^{-\beta N_a \mu}$

$$\frac{N_s^{N_a} e^{\beta N_a \varepsilon}}{N_a!} = e^{-\beta N_a \mu}$$

$$\ln\left[\frac{N_s^{N_a}}{N_a!}\right] + \ln\left(e^{\beta N_a \varepsilon}\right) = \ln\left(e^{-\beta N_a \mu}\right)$$

$$N_a \ln[N_s] - \ln[N_a!] + \beta N_a \varepsilon = -\beta N_a \mu.$$

$$\mu = -\varepsilon - \frac{1}{\beta} \ln[N_s] + \frac{1}{N_a \beta} \ln[N_a!]$$

$$\mu = -\varepsilon - \frac{1}{\beta} \ln[N_s] + \frac{1}{N_a \beta}\left[N_a \ln[N_a] - N_a\right]$$

$$\mu = -\varepsilon - \frac{1}{\beta}\ln[N_s] + \frac{1}{\beta}\ln[N_a] - \frac{1}{\beta}$$

$$= -\varepsilon - \frac{1}{\beta}\ln\left[\frac{N_s}{N_a}\right] - \frac{1}{\beta} \approx -\varepsilon - k_B T \ln\left[\frac{N_s}{N_a}\right]$$

b)

For an ideal gas

$$\mu^{ig} = k_B T \ln\left(\frac{P\lambda_T^3}{k_B T}\right)$$

equating the chemical potentials.

$$-\frac{\varepsilon}{k_B T} - \ln\frac{N_s}{N_a} = \ln\left(\frac{P\lambda_T^3}{k_B T}\right)$$

$$e^{-\beta\varepsilon}\frac{N_a}{N_s} = \frac{P\lambda_T^3}{k_B T}$$

$$\frac{N_a}{N_s} = e^{\beta\epsilon}\frac{P\lambda_T^3}{k_B T}$$

5 Mixture of gases.

For each component

$$Z_N = \left(\sum_{\vec{k}} e^{-\beta p^2/2m} \right)^N = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N$$

So, from the helmholtz Free energy

$$F_N = -k_B T N \ln\left(\frac{eV}{N}\right) \underbrace{\left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2}}_{=} = N f(T) - N k_B T \ln\left(\frac{eV}{N}\right)$$

where $f(T)$

So

$Z = Z_N^3$ and

$$F = 3N f(T) - 3N k_B T \ln\left(\frac{eV}{N}\right)$$

and

$$S = 3N k_B \ln\left(\frac{eV}{N}\right) - 3N f'(T)$$

$$= 3N k_B \ln\left(\frac{eV}{N}\right) - 3N \left[\frac{3}{2} \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{1/2} \frac{m k_B}{2\pi \hbar^2} \right]$$

b) for a single color

$$S_1 = 3N k_B \ln\left(\frac{eV}{3N}\right) - 3N f'(T)$$

$$S - S_1 = 3N \ln(3)$$