

Statistical Physics: Workshop Problem 1 Answers

- (1) (a) The first person will belong to some DNA profile anyway. The probability that the second person will belong in the same profile as the first person is $p = 199/(50 \times 10^6 - 1)$. Because the numbers are large, this is almost equal to:

$$\frac{200}{50 \times 10^6} = \frac{1}{250\,000}$$

(b)

$$\frac{1}{200}$$

- (2) The first person will have birthday on some day. The probability the second person does not have the same birthday is $364/365$ and so on. The result is:

$$\frac{364}{365} \times \frac{363}{365} \times \frac{362}{365} \times \frac{361}{365} = 0.973$$

- (3) The distributions are:

Distribution	$(n_0, n_1, n_2, n_3, n_4, n_5, n_6)$	Number of microstates
(1)	(3, 0, 0, 0, 0, 0, 1)	4
(2)	(2, 1, 0, 0, 0, 1, 0)	12
(3)	(2, 0, 1, 0, 1, 0, 0)	12
(4)	(1, 2, 0, 0, 1, 0, 0)	12
(5)	(2, 0, 0, 2, 0, 0, 0)	6
(6)	(1, 1, 1, 1, 0, 0, 0)	24
(7)	(0, 3, 0, 1, 0, 0, 0)	4
(8)	(1, 0, 3, 0, 0, 0, 0)	4
(9)	(0, 2, 2, 0, 0, 0, 0)	6
Average Probabilities	$(1.333, 1, 0.714, 0.476, 0.286, 0.143, 0.048)$ $(0.33, 0.25, 0.18, 0.12, 0.07, 0.04, 0.01)$	$\Omega = 84$ $S = k_B \ln 84 = 4.43 k_B$

Table 1:

$$\begin{aligned} \langle n_0 \rangle &= 112/84 = 1.33, \\ \langle n_1 \rangle &= 84/84 = 1, \\ \langle n_2 \rangle &= 60/84 = 0.714, \\ \langle n_3 \rangle &= 40/84 = 0.476, \\ \langle n_4 \rangle &= 24/84 = 0.286, \\ \langle n_5 \rangle &= 12/84 = 0.143, \\ \langle n_6 \rangle &= 4/84 = 0.048. \end{aligned}$$

- (4) Since the standard deviation $\sigma = 5\Omega$ and the mean $\mu = 100\Omega$, the first part is the probability that the variable takes a value within a standard deviation from the mean. The probability is given by

$$P(\mu - \sigma \leq x \leq \mu + \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \int_{\mu-\sigma}^{\mu+\sigma} dx \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right]$$

With the change of variable $x \rightarrow (x - \mu)/\sigma$, the probability becomes

$$P(\mu - \sigma \leq x \leq \mu + \sigma) = \frac{1}{\sqrt{2\pi}} \int_{-1}^1 dx \exp\left(-\frac{x^2}{2}\right)$$

From the table

$$P(\mu - \sigma \leq x \leq \mu + \sigma) = 0.68269$$

The probability that the resistor has resistance between 80 Ω and 120 Ω is:

$$P(\mu - 4\sigma \leq x \leq \mu + 4\sigma) = 0.99994$$

The probability that the resistance is outside these values is 0.00006.

Hence, the probability that the resistance is less than 80 Ω is half that value (0.00003):

$$P(x < \mu + \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\mu-4\sigma} dx \exp\left[-\frac{(x - \mu)^2}{2\sigma^2}\right]$$
$$\Rightarrow P(x < \mu - 4\sigma) = \frac{1 - P(\mu - 4\sigma \leq x \leq \mu + 4\sigma)}{2} = 0.00003$$

Note that strictly, the lower limit of the integral should be 0 rather than $-\infty$, but because $\mu/\sigma = 20 \gg 1$, and the Gaussian decays extremely rapidly with distance so the integrand in over negative values of x is negligible.

Statistical Physics: Workshop Problems 2

- (1) To obtain the set of probabilities that maximise the entropy under the constraint of normalisation, we must maximise

$$\left[-\sum_{i=1}^6 p_i \ln p_i - \alpha \sum_{i=1}^6 p_i \right]$$

where α is the Lagrange multiplier constraining total probability. Set to zero the derivative of this expression with respect to one of the $\{p_1, p_2, \dots, p_6\}$. For example pick p_3

$$0 = \frac{\partial}{\partial p_3} \left[\right] \Rightarrow 0 = -\ln p_3 - \frac{p_3}{p_3} - \alpha \Rightarrow \ln p_3 = -1 - \alpha \Rightarrow p_3 = e^{-1-\alpha}.$$

However, p_3 is not special and the same result must hold for all the other p_i , With i being any of 1, 2, 3, 4, 5, 6 we have

$$p_i = e^{-1-\alpha}, \quad \text{for } i = 1, 2, \dots, 6.$$

From the constraint of normalisation, we have

$$\sum_{i=1}^6 p_i = 1 \Rightarrow e^{-1-\alpha} \sum_{i=1}^6 1 = 1 \Rightarrow e^{-1-\alpha} \times 6 = 1 \Rightarrow e^{-1-\alpha} = 1/6$$

We conclude that $p_i = 1/6$ for all $i = 1, 2, \dots, 6$.

By assigning equal probability to all events we maximise the entropy under just the constraint of normalisation of the probability and in the lack of any other knowledge. The same idea is used in the principle of equal *a priori* probabilities. In the microcanonical ensemble, all microstates have the same energy and in the lack of any other information we choose equal probabilities which maximise the entropy.

- (2) (a) When each energy level is doubly degenerate the partition function will be

$$Z = \underbrace{e^{-\beta\epsilon_1}}_{\text{s.p. state 1}} + \underbrace{e^{-\beta\epsilon_1}}_{\text{s.p. state 2}} + \underbrace{e^{-\beta\epsilon_2}}_{\text{s.p. state 3}} + \underbrace{e^{-\beta\epsilon_2}}_{\text{s.p. state 4}} + \dots = \sum_j 2e^{-\beta\epsilon_j}$$

- (b) Obviously, in the general case, this becomes

$$Z = \sum_j g(j) e^{-\beta\epsilon_j}$$

- (3) (a) The single-particle partition function is

$$\begin{aligned} Z_{3D} &= \sum_{n=0}^{\infty} g(\epsilon_n) e^{-\beta(n+3/2)h\nu} \\ &= \sum_{n=0}^{\infty} \frac{1}{2} (n+1)(n+2) e^{-\beta(n+3/2)h\nu}. \end{aligned}$$

This sum over n is complicated by the presence of the coefficient $g(\epsilon_n)$ but still it can be found using properties of sums of geometric series. One can do that, but instead we will use the hint in the question.

The single-particle state n of a 3D SHO is given by specifying the states j, k, l of three 1D SHOs in the directions x, y, z :

$$n = j + k + l, \text{ with } j, k, l = 0, 1, \dots$$

Let's see what happens with the degeneracy

$$\begin{aligned} g(n=0) &= 1, & n=0 &= 0+0+0 \\ g(n=1) &= 3, & n=1 &= 1+0+0 \\ & & &= 0+1+0 \\ & & &= 0+0+1 \\ & & &\dots \end{aligned}$$

So, when we change the sum over n to a sum over j, k, l (three 1D oscillators), the degeneracy $g(n)$ is taken care of by the three separate sums

$$\sum_{n=0}^{\infty} g(n) e^{(\dots)} \rightarrow \sum_{j,k,l=0}^{\infty} 1 e^{(\dots)}.$$

The energy ϵ_n is given by

$$\epsilon_n = \epsilon_j + \epsilon_k + \epsilon_l = (j + 1/2)h\nu + (k + 1/2)h\nu + (l + 1/2)h\nu.$$

The single-particle partition function for the 3D SHO becomes

$$\begin{aligned} Z_{3D} &= \sum_{j,k,l=0}^{\infty} e^{-\beta(j+1/2)h\nu} e^{-\beta(k+1/2)h\nu} e^{-\beta(l+1/2)h\nu} \\ Z_{3D} &= \sum_{j=0}^{\infty} e^{-\beta(j+1/2)h\nu} \sum_{k=0}^{\infty} e^{-\beta(k+1/2)h\nu} \sum_{l=0}^{\infty} e^{-\beta(l+1/2)h\nu} = \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^3 = Z_{1D}^3 \end{aligned}$$

The logarithm of the partition function is

$$\ln Z_{3D} = 3 \ln Z_{1D}.$$

- (b) This means that the thermodynamic functions, i.e., U, F, S , for N 3D SHOs will be the same as the corresponding thermodynamic functions of $3N$ 1D SHOs. Therefore

$$\begin{aligned} U &= -N \frac{\partial \log Z}{\partial \beta} \\ &= \frac{3Nh\nu}{2} + \frac{3Nh\nu}{\exp(\beta h\nu) - 1}, \\ F &= -\frac{N}{\beta} \log Z \\ &= \frac{3Nh\nu}{2} + \frac{3N}{\beta} \ln(1 - \exp(-\beta h\nu)), \\ S &= k_B \beta (U - F) \\ &= 3Nk_B \left[\frac{\beta h\nu}{\exp(\beta h\nu) - 1} - \ln(1 - \exp(-\beta h\nu)) \right]. \end{aligned}$$

(4) Carrying on from the previous problem we have

$$\begin{aligned} C_V &= \left[\frac{\partial U}{\partial T} \right]_V \\ &= \frac{3Nk_B(\beta h\nu)^2 \exp(\beta h\nu)}{(\exp(\beta h\nu) - 1)^2}. \end{aligned}$$

In the above, note that

$$\frac{\partial}{\partial T} = -k_B\beta^2 \frac{\partial}{\partial \beta}.$$

At high temperatures $\beta \rightarrow 0$ and $\exp(\beta h\nu) \rightarrow 1$. We expand the denominator in a Taylor series

$$\frac{1}{(\exp(\beta h\nu) - 1)^2} \simeq \frac{1}{(1 + \beta h\nu - 1)^2} = \frac{1}{(\beta h\nu)^2}$$

so the heat capacity becomes

$$C_V = 3Nk_B.$$

The heat capacity for a mole of a solid at high temperature is (N_A is Avogadro's number)

$$C_V^{mol} = 3N_Ak_B = 3 \times 6.022 \times 10^{23} \times 1.38064852 \times 10^{-23} J/K = 24.9 J/K.$$

Statistical Physics: Workshop Problems 3

- (1) (a) If the microstates of a system occur with probability p_i then the entropy of the system is

$$S = -k_B \sum_i p_i \log p_i.$$

Therefore the entropy of an 8-sided dice is $k_B \log 8$ and for a 12-sided dice it's $k_B \log 12$.

- (b) The phase space density of the microcanonical ensemble is constant in equilibrium.
 (c) The partition functions are dimensionless.
 (d) (N,V,E) in the microcanonical ensemble, (N,V,T) in the canonical ensemble and (μ, V, T) in the grand canonical ensemble (where μ is the chemical potential/Fermi level).
 (2) (a) The partition function is $Z = \sum_{\text{states}} e^{-\beta \epsilon_{\text{states}}}$ where $\beta = 1/k_B T$. Therefore

$$Z = \sum_{i=1}^3 e^{-\beta \hbar \omega_i} = e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}.$$

The probabilities are $p_i = e^{-\beta \epsilon_i} / Z$ hence

$$p_1 = \frac{e^{-\beta \hbar \omega}}{Z}, p_2 = \frac{e^{-\beta \hbar 2\omega}}{Z}, p_3 = \frac{e^{-\beta \hbar 3\omega}}{Z}.$$

- (b) The limit $T \rightarrow 0$ is $\beta \rightarrow \infty$ so we have

$$(p_1) : \lim_{\beta \rightarrow \infty} \frac{e^{-\beta \hbar \omega}}{e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}} = 1,$$

$$(p_2) : \lim_{\beta \rightarrow \infty} \frac{e^{-2\beta \hbar \omega}}{e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}} = 0,$$

$$(p_3) : \lim_{\beta \rightarrow \infty} \frac{e^{-3\beta \hbar \omega}}{e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}} = 0,$$

and the limit $T \rightarrow \infty$ is $\beta \rightarrow 0$ so we have

$$(p_j) : \lim_{\beta \rightarrow 0} \frac{e^{-j\beta \hbar \omega}}{e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}} = \frac{1}{3}, j = 1, 2, 3$$

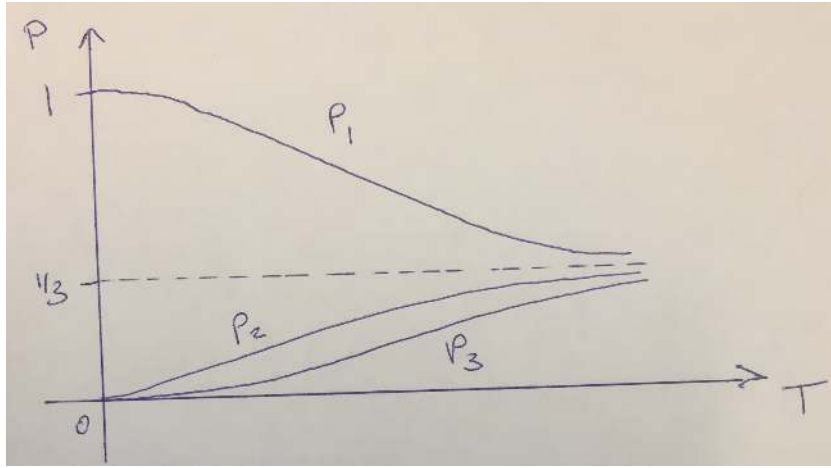
- (c) Internal energy is

$$U = - \left[\frac{\partial \ln Z}{\partial \beta} \right] = \hbar \omega \frac{e^{-\beta \hbar \omega} + 2e^{-2\beta \hbar \omega} + 3e^{-3\beta \hbar \omega}}{e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + e^{-3\beta \hbar \omega}}.$$

Free energy is

$$F = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} \ln (e^{-\beta \hbar \omega} + e^{-\beta \hbar 2\omega} + e^{-\beta \hbar 3\omega}).$$

The difference between internal energy and the free energy is essentially the entropy, $S = -\beta k_B (U - F)$, and so represents the unavailability of energy to do work.



3) (a) Tabulate the possibilities with $N = 3$ and $U = 3\epsilon$

	0ϵ	1ϵ	2ϵ	3ϵ	...	Classical Permutations
D_1	2	0	0	1		$3!/(2! 0! 0! 1!) = 3$
D_2	1	1	1	0		$3!/(1! 1! 1! 0!) = 6$
D_3	0	3	0	0		$3!/(0! 3! 0! 0!) = 1$
						$3+6+1=10$ microstates

For classical particles the distribution D_2 is most likely with a probability of $6/10$.

- (b) For Fermions then only one particle per state is allowed. Distributions D_1 and D_3 are not possible and so only distribution D_2 is allowed. Note also that for indistinguishable particles there is only one microstate in distribution D_2 (no permutations). We find distribution D_2 with 100% probability.
- (c) For Bosons each of the classical distributions are allowed but since the particles are indistinguishable then there is only one microstate per distribution. Hence all 3 distributions are equally likely, probability $1/3$.

(4) The population distribution is given by

$$\frac{n_j}{n_i} = \exp\left(\frac{\epsilon_i - \epsilon_j}{k_B T}\right)$$

therefore

$$T = \frac{\epsilon_i - \epsilon_j}{k_B \log\left(\frac{n_j}{n_i}\right)}.$$

Using the values of n_1 , n_2 and n_3 given in the question, taking each possible pair we obtain the following values of T : 99.0K, 100.2K and 99.6K. Therefore, with the information given the mean value of temperature is 99.6K.

Statistical Physics: Workshop Problems 4

- (1) (a) A particle in a 3D box: density of states in 3D, Schrödinger's equation is

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} - \frac{1}{2} \frac{d^2}{dy^2} - \frac{1}{2} \frac{d^2}{dz^2} + v(x) + v(y) + v(z) \right] \Phi(x, y, z) = E \Phi(x, y, z).$$

This is a separable problem, so $\Phi_{\mathbf{k}}(x, y, z) = \psi_{k_x}(x) \psi_{k_y}(y) \psi_{k_z}(z)$ with

$$k_x = \frac{\pi}{a} n, \quad k_y = \frac{\pi}{a} m, \quad k_z = \frac{\pi}{a} l, \quad n, m, l = 1, 2, \dots$$

The discretisation in 3D k space is $(\pi/a)^3$, so the number $n(k)$ of independent solutions, $\Phi_{\mathbf{q}}$ with $0 \leq q \leq k$ is:

$$n(k) = \frac{\text{Volume in first octant in 3D } \mathbf{q} \text{ space}}{(\pi/a)^3} = \frac{1}{8} \frac{4\pi k^3}{3} \frac{a^3}{\pi^3} = \frac{k^3 V}{6\pi^2}$$

The number of independent solutions between $k \leq q \leq k + \delta k$ is

$$g(k) \delta k = \frac{\delta n(k)}{dk} \delta k = \frac{V k^2}{2\pi^2} \delta k,$$

where, $V = a^3$. The result is valid for $V k^2 \delta k \gg 1$.

To find the number of states in energy space we have

$$\epsilon = \frac{\hbar^2 k^2}{2M} \Rightarrow d\epsilon = \frac{\hbar^2 k dk}{M} \Rightarrow k d\epsilon = \frac{\hbar^2 k^2 dk}{M} \Rightarrow \frac{\sqrt{2M^3 \epsilon}}{\hbar^3} d\epsilon = k^2 dk$$

So,

$$g(\epsilon) d\epsilon = g(k) dk = 2\pi V \frac{(2M)^{3/2}}{\hbar^3} \sqrt{\epsilon} d\epsilon$$

The DOS increases with the square root of ϵ .

- (b) A particle in a 2D box follows exactly the same process. A similar analysis as before $\Phi_{\mathbf{k}}(x, y) = \psi_{k_x}(x) \psi_{k_y}(y)$ with

$$k_x = \frac{\pi}{a} n, \quad k_y = \frac{\pi}{a} m, \quad n, m = 1, 2, \dots$$

The discretisation in 2D q space is $(\pi/a)^2$ and so the number $n(k)$ of independent solutions, $\Phi_{\mathbf{q}}$ with $0 \leq q \leq k$ is:

$$n(k) = \frac{\text{Area in first quadrant in 2D } \mathbf{q} \text{ space}}{(\pi/a)^2} = \frac{1}{4} \pi k^2 \frac{a^2}{\pi^2} = \frac{1}{4} \pi k^2 \frac{A}{\pi^2} = \frac{A k^2}{4\pi}$$

where $A = a^2$. So the number of states in k space with $k \leq q \leq k + \delta k$ is

$$g(k) \delta k = \frac{A k}{2\pi} \delta k,$$

and the result is valid for $A k \delta k \gg 1$.

The number of states in energy space is obtained as follows

$$\epsilon = \frac{\hbar^2 k^2}{2M} \Rightarrow d\epsilon = \frac{\hbar^2 k dk}{M} \Rightarrow k dk = \frac{M}{\hbar^2} d\epsilon$$

s,

$$g(\epsilon)d\epsilon = g(k)dk = 2\pi A \frac{M}{\hbar^2} d\epsilon.$$

The DOS in energy is constant and does not increase with ϵ .

- (2) (a) For classical particles the N -particle partition function is

$$Z_N = Z_1^N.$$

- (b) The internal energy is

$$U = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{3}{2} N k_B T.$$

The free energy is:

$$F = -k_B T \ln Z_N = -N k_B T \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta \hbar^2} \right) \right].$$

The entropy is

$$S = \frac{(U - F)}{T} = \frac{3}{2} N k_B + N k_B \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta \hbar^2} \right) \right].$$

- (c) U is linear in N , so it is extensive. The free energy is not extensive since

$$F(2N, 2V) = -2N k_B T \left[\ln(2V) + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta \hbar^2} \right) \right] \neq 2 F(N, V).$$

The entropy is not extensive either, since $S = (U - F)/T$.

- (d) The number of ways of arranging N objects is $N!$. So, one must divide the partition function by $N!$:

$$Z_N = \frac{Z_1^N}{N!}$$

Using the Strling approximation ($\ln N! \approx N \ln N - N$), the free energy becomes

$$F = -k_B T \ln[(Z_1)^N / N!] = -N k_B T \left[\ln \frac{V}{N} + 1 + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta \hbar^2} \right) \right],$$

and the entropy becomes

$$S = \frac{5}{2} N k_B + N k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M}{\beta \hbar^2} \right) \right]$$

- (e) (i) Because the expression for the entropy is extensive, there will be no change in entropy when we calculate the total entropy with and without the partition. This is what we expect, since there is no exchange of heat or work in this reversible process.

- (ii) In the second case, before (subscript b) the removal of the partition, the total entropy is the sum of entropies

$$S_b = S_1 + S_2, \quad \text{with } S_{1,2} = \frac{5}{2} (N/2)k_B + (N/2)k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M_{1,2}}{\beta h^2} \right) \right].$$

The sum is

$$S_b = \frac{5}{2} Nk_B + Nk_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi}{\beta h^2} \right) \right] + \frac{3Nk_B}{4} \ln (M_1 M_2).$$

After (subscript a) the removal of the partition, the two gases do not interact; each gas has $N/2$ particles and occupies volume V instead of $V/2$. The entropy is the sum of entropies, which is

$$S_a = S_1 + S_2, \quad \text{with } S_{1,2} = \frac{5}{2} (N/2)k_B + (N/2)k_B \left[\ln \frac{2V}{N} + \frac{3}{2} \ln \left(\frac{2\pi M_{1,2}}{\beta h^2} \right) \right].$$

The sum is

$$S_a = \frac{5}{2} Nk_B + Nk_B \left[\ln \frac{2V}{N} + \frac{3}{2} \ln \left(\frac{2\pi}{\beta h^2} \right) \right] + \frac{3Nk_B}{4} \ln (M_1 M_2).$$

The difference is the entropy of mixing

$$\Delta S = S_a - S_b = Nk_B \ln 2.$$

The two gases cannot be separated without doing work in the system equal at least to $T\Delta S$.

- (3) (a) The same as in problem (1) but multiplied by 2 for spin.
 (b) The Fermi energy is calculated from the constraint that the number of particles is N . In 3D (with factor of 2) we have

$$n(k) = 2 \times \frac{V k^3}{6\pi^2} \Rightarrow N = n(k_F) = \frac{V k_F^3}{3\pi^2} \Rightarrow k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

$$\epsilon_F = \mu_0 = \frac{\hbar^2 k_F^2}{2M} = \frac{\hbar^2}{2M} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

Similarly in 2D,

$$n(k) = 2 \times \frac{A k^2}{4\pi} \Rightarrow N = n(k_F) = \frac{A k_F^2}{2\pi} \Rightarrow k_F^2 = 2\pi \frac{N}{A}$$

$$\epsilon_F = \mu_0 = \frac{\hbar^2 k_F^2}{2M} = \frac{\hbar^2 \pi}{M} \frac{N}{A} = \frac{h^2}{4\pi M} \frac{N}{A}.$$

Statistical Physics: Workshop Problems 5

- (1) (a) From the hint, or otherwise, note that

$$\int_{-\infty}^{\infty} dx \exp[-b x^2] = \sqrt{\frac{\pi}{b}}$$

$$(\text{derivative wrt } b) \Rightarrow \int_{-\infty}^{\infty} dx x^2 \exp[-b x^2] = \frac{1}{2} \sqrt{\frac{\pi}{b^3}}.$$

Using the Boltzmann distribution and these standard integrals, the average energy for x is

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} dx a x^2 \exp[-\beta a x^2]}{\int_{-\infty}^{\infty} dx \exp[-\beta a x^2]} = a \frac{1}{2} \sqrt{\frac{\pi}{(\beta a)^3}} \sqrt{\frac{\beta a}{\pi}} = \frac{k_B T}{2}$$

where β is the inverse temperature, $\beta = 1/(k_B T)$.

- (b) Since the energy is additive, the internal energy will be

$$U = N\eta \frac{k_B T}{2}.$$

- (2) (a) For the Ne atoms, the energy of each atom is (translational kinetic energy)

$$(1/2)mv_x^2 + (1/2)mv_y^2 + (1/2)mv_z^2$$

so there are three degrees of freedom. The internal energy and heat capacity are therefore

$$U = \frac{3}{2} N k_B T \Rightarrow C_V = \frac{dU}{dT} = \frac{3}{2} N k_B.$$

- (b) For the O₂ molecules, the energy due to translational kinetic energy of the centre of mass is as above. There is additionally rotational motion with energy

$$(1/2)I\omega_1^2 + (1/2)I\omega_2^2$$

where I is the moment of inertia for the two rotations about the centre of the diatomic molecule. The moment of inertia for rotation around axis connecting the two atoms is zero, so we have two degrees of freedom in the energy due to rotations, therefore

$$U = \frac{3+2}{2} N k_B T \Rightarrow C_V = \frac{dU}{dT} = \frac{5}{2} N k_B.$$

- (c) Finally, the O₂ molecule is vibrating along the diatomic bond. The energy of one simple harmonic oscillator has two degrees of freedom defined by the kinetic and potential energies

$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2.$$

The energy U and heat capacity associated with vibrations is therefore

$$U = \frac{2}{2} N k_B T \Rightarrow C_V = \frac{dU}{dT} = N k_B.$$

- (d) For the O₂ molecules, the total energy due to translations, rotations and vibrations is at high temperatures

$$U = \frac{3+2+2}{2}Nk_B T \Rightarrow C_V = \frac{dU}{dT} = \frac{7}{2}Nk_B$$

(3) (a)

$$\begin{aligned} Z_1^{\text{vibr}} &= \sum_{n=0}^{\infty} \exp[-\beta(n+1/2)\hbar\omega] \\ &= \exp\left[\frac{-\beta\hbar\omega}{2}\right] \sum_{n=0}^{\infty} \exp[-\beta\hbar\omega n] \\ &= \frac{\exp\left[\frac{-\beta\hbar\omega}{2}\right]}{1 - \exp[-\beta\hbar\omega]} \\ &= \frac{\exp\left[\frac{\beta\hbar\omega}{2}\right]}{\exp[\beta\hbar\omega] - 1} \end{aligned}$$

(b)

$$\begin{aligned} U^{\text{vibr}} &= -N \frac{\partial \ln Z_1}{\partial \beta} = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega \exp[\beta\hbar\omega]}{\exp[\beta\hbar\omega] - 1} \\ \Rightarrow C_V^{\text{vibr}} &= \frac{\partial U^{\text{vibr}}}{\partial T} = \frac{Nk_B \hbar^2 \omega^2 \beta^2 \exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega) - 1)^2} \end{aligned}$$

The high temperature limits are $U^{\text{vibr}} \simeq Nk_B T$ and $C_V^{\text{vibr}} \simeq Nk_B$. These results are the same as the vibrational contributions to U and C_V in (2) for $\eta = 2$.

- (c) A straightforward substitution gives

$$C_V^{\text{vibr}} = \frac{Nk_B (T^{\text{vibr}}/T)^2 \exp(T^{\text{vibr}}/T)}{(\exp(T^{\text{vibr}}/T) - 1)^2}.$$

- (d) $T^{\text{vibr}} = h\nu/k_B = 2200K \Rightarrow T^{\text{vibr}}/T = 2200/293 = 7.51$. So the heat capacity is

$$C_V^{\text{vibr}} = \frac{Nk_B (T^{\text{vibr}}/T)^2 \exp(T^{\text{vibr}}/T)}{(\exp(T^{\text{vibr}}/T) - 1)^2} = \frac{Nk_B 7.51^2 \exp 7.51}{(\exp 7.51 - 1)^2} = 0.0310 Nk_B.$$

At room temperature $C_V = 5/2 Nk_B$ so the percentage is $0.0310/2.5 = 1.24\%$.

Statistical Physics: Workshop Problems 6

- (1) (a) Maxwell-Boltzmann is for localised, distinguishable particles occupying single particle states, and there is no limit on the number of particles in a state. With α constraining particle number and $\beta = 1/k_B T$ the average number of particles per state with energy ϵ_j and degeneracy g_j is

$$\frac{n_j}{g_j} = \frac{1}{e^\alpha e^{\beta \epsilon_j}}.$$

Fermi-Dirac is for a system made of Fermions which are indistinguishable and, following the Pauli exclusion principle, can only have one particle per state. The average number of particles per energy state is

$$\frac{n_j}{g_j} = \frac{1}{e^\alpha e^{\beta \epsilon_j} + 1}.$$

Bose-Einstein statistics is for a system made of Bosons which are indistinguishable and are not limited in the number of particles that can be in a state. The average number of particles per energy state is

$$\frac{n_j}{g_j} = \frac{1}{e^\alpha e^{\beta \epsilon_j} - 1}.$$

- (b) From the average number of particles per state it can be seen that when $e^\alpha \gg 1$ the difference between the statistics becomes unimportant. In lectures we saw that this can be determined by the thermal de Broglie wavelength

$$\begin{aligned} \lambda_D &= \sqrt{\frac{\beta h^2}{2\pi M}} \\ &= \sqrt{\frac{h^2}{2\pi M k_B T}}. \end{aligned}$$

A small λ_D (relative to volume) indicates we are in the classical regime, so note that as T increases then λ_D decreases, i.e. the three statistics become the same at high T .

We can understand this from a physical point of view; when $e^\alpha \gg 1$ the fraction of states filled is very small. This means that the number of microstates available must be very large, much larger than the total number of particles. Therefore the probability of two particles trying to be in the same state is very small so quantum effects such as Pauli exclusion is satisfied “without trying”.

- (c) If there are 10^{18} neutrons per cubic centimeter this means they are separated by, on average, $10^{-6}\text{cm} = 10^{-8}\text{m}$. Set λ_D to this gives a temperature $T \approx 0.03\text{K}$. So temperatures around/below this will require Fermi-Dirac statistics, and for temperatures significantly above this the Fermions can be considered classical.

- (2) (a) The partition function for the atom is

$$Z = e^{-\beta \epsilon} + e^{\beta \epsilon},$$

so the mean energy per atom is

$$\begin{aligned}
 U &= -\frac{\delta \ln Z}{\delta \beta} \\
 &= \epsilon \frac{e^{-\beta\epsilon} - e^{\beta\epsilon}}{e^{-\beta\epsilon} + e^{\beta\epsilon}} \\
 &= \epsilon \tanh\left(\frac{\epsilon}{k_B T}\right).
 \end{aligned}$$

The contribution of one atom to the specific heat is

$$C_V^1 = \left. \frac{\delta U}{\delta T} \right|_V = 4k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{1}{(e^{\epsilon/k_B T} + e^{-\epsilon/k_B T})^2}$$

and so the total specific heat is

$$C_V = 4Nk_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{1}{(e^{\epsilon/k_B T} + e^{-\epsilon/k_B T})^2}.$$

- (b) Using the result above we can immediately step to the contribution of the specific heat from the i^{th} atom,

$$C_V^i = 4k_B \left(\frac{\epsilon_i}{k_B T}\right)^2 \frac{1}{(e^{\epsilon_i/k_B T} + e^{-\epsilon_i/k_B T})^2}.$$

When $k_B T \ll \epsilon_i$ then

$$C_V^i \approx 4k_B \left(\frac{\epsilon_i}{k_B T}\right)^2 e^{-2\epsilon_i/k_B T},$$

therefore summing this for all atoms gives

$$C_V \approx 4k_B \sum_i \left(\frac{\epsilon_i}{k_B T}\right)^2 e^{-2\epsilon_i/k_B T}.$$

Without an explicit statement about the values of ϵ_i this is as far as we can go. However one final step could be to approximate this as an integral

$$C_V \approx 4k_B \int \left(\frac{\epsilon}{k_B T}\right)^2 e^{-2\epsilon/k_B T} g(\epsilon) d\epsilon$$

where $g(\epsilon)$ is the density of states, which is often of the form $g(\epsilon) \approx \sqrt{\epsilon}$.

- (3) (a) The partition function is

$$\begin{aligned}
 Z &= \sum_{j=0}^{\infty} g_j e^{-\epsilon_j/k_B T} \\
 &= \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)h^2/(8\pi^2 m a^2 k_B T)}.
 \end{aligned}$$

Let $x = h^2/(8\pi^2 ma^2 k_B T)$ and for high temperatures $x \ll 1$, and we integrate over j , i.e. at high temperatures high- j values dominate and at that point j can be thought of as a continuous variable, hence

$$\begin{aligned} Z &\approx \int_0^\infty (2j+1)e^{-j(j+1)x} dj \\ &= -\frac{1}{x} e^{-j(j+1)x} \Big|_0^\infty \\ &= \frac{1}{x} \\ &= 8\pi^2 ma^2 k_B T / h^2. \end{aligned}$$

(b) It follows immediately that the internal energy is

$$U = k_B T^2 \frac{\delta}{\delta T} \ln Z = k_B T$$

and the heat capacity is

$$C_V = \frac{\delta U}{\delta T} = k_B.$$

(c) For low temperature we approximate Z by just taking the lowest terms in the expression for Z . Taking the lowest term alone gives $Z = 1$ giving $C_V = 0$ and this is the $T = 0$ behaviour. We are asked for low temperature approximations, so let's take the first two levels which will describe the behaviour just above $T = 0$. Gather some terms to simplify, let $\theta = h^2/(8\pi^2 ma^2 k_B)$ so that

$$\begin{aligned} Z &\approx 1 + 3e^{-2\theta/T}, \\ \Rightarrow U &= \frac{6k_B\theta}{Z} e^{-2\theta/T}, \\ \text{and } C_V &= \frac{12k_B\theta^2}{Z^2 T^2} e^{-2\theta/T}. \end{aligned}$$

(4) (a) The partition function is

$$Z = \sum_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)}.$$

When $T = 0$ this expression is not physically meaningful. However when $T \neq 0$ it also diverges.

(b) The divergence has nothing to do with the choice of zero of energy. If we had chosen $E_n = -E_0/n^2 + E'$ then

$$Z' = e^{-E'/k_B T} \left(\sum_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)} \right)$$

which still contains our divergent sum.

(c) The average energy is

$$\begin{aligned}\langle E \rangle &= \frac{\sum_{n=1}^{\infty} \left(-\frac{E_0}{n^2}\right) 2n^2 e^{E_0/(n^2 k_B T)}}{\sum_{n=1}^{\infty} 2n^2 e^{E_0/(n^2 k_B T)}} \\ &= 0.\end{aligned}$$

Note on the above, one has to be careful in dealing with divergent series. In the above, for a given finite length of sum on both the denominator and numerator (set the sums to N rather than ∞), then sum the in the denominator is much larger than the numerator so the fraction tends to zero as sums head off to infinity.

(d) The divergence has the origin in the very large degeneracy of the excited states of hydrogen and that the wavefunctions for hydrogen are extended. If we can limit this degeneracy and infinite extent of the wavefunction (for example with external interactions, putting the atom in a large box) these highly excited, highly degenerate states no longer exist and there is no divergence. This illustrates problems that may arise unexpectedly by “model” systems.

Statistical Physics: Workshop Problems 7

- (1) (a) Simply substitute for $k = \epsilon/c\hbar$ and $dk = d\epsilon/c\hbar$ to get

$$g(\epsilon)d\epsilon = \frac{V}{2\pi^2 c^3 \hbar^3} \epsilon^2 d\epsilon.$$

- (b) The partition function for a system with density of states $g(\epsilon)d\epsilon$ is

$$Z = \int_0^\infty g(\epsilon) e^{-\beta\epsilon} d\epsilon,$$

therefore we have

$$\begin{aligned} Z &= \int_0^\infty \frac{V}{2\pi^2 c^3 \hbar^3} \epsilon^2 e^{-\epsilon/(k_B T)} d\epsilon \\ &= \frac{V}{\hbar^3 c^3 \pi^2} (k_B T)^3. \end{aligned}$$

The non-relativistic case is calculated similarly with $\epsilon = \hbar^2 k^2/2m$. Its temperature dependence goes as $T^{3/2}$ rather than T^3 . Of course with the partition function as a function of T (or β) it's straightforward to calculate thermodynamic quantities such as internal energy, free energy, specific heat, etc.

- (2) (a) Given the density of states $g(\epsilon)$ in the question, $f_{FD}(\epsilon) = 1$ for $\epsilon < E_F$ (zero otherwise) at $T = 0$ and the definition of Fermi energy, we get

$$\begin{aligned} N &= \frac{2\pi V}{h^3} (2M)^{3/2} \int_0^{E_F} \sqrt{\epsilon} d\epsilon \\ \Rightarrow E_F &= \frac{\hbar^2}{2M} \left(\frac{3\pi^2 N}{V} \right)^{2/3}. \end{aligned}$$

(Note change from h to \hbar absorbing factors of 2π).

- (b) We have the relativistic density of states from (1) and the same simple expression for $f_{FD}(\epsilon)$ at $T = 0$, therefore

$$\begin{aligned} N &= \int_0^{E_F} \frac{V}{2\pi^2 c^3 \hbar^3} \epsilon^2 d\epsilon \\ \Rightarrow E_F &= hc \left(\frac{3N}{8\pi V} \right)^{1/3}. \end{aligned}$$

- (c) We have the density of states for relativistic Fermions $g(\epsilon)d\epsilon = A\epsilon^2 d\epsilon$ from question (1) (constants collected together into A) and $f_{FD}(\epsilon)$ at $T = 0$. Therefore the average energy per particle is

$$\begin{aligned} \langle \epsilon \rangle &= \frac{\int_0^{E_F} \epsilon g(\epsilon) f_{FD}(\epsilon) d\epsilon}{\int_0^{E_F} g(\epsilon) f_{FD}(\epsilon) d\epsilon} \\ &= \frac{A \int_0^{E_F} \epsilon^3 d\epsilon}{A \int_0^{E_F} \epsilon^2 d\epsilon} \\ &= 3E_F/4, \end{aligned}$$

therefore the total energy for N particles is $3NE_F/4$. In the non-relativistic case (collecting constants into B) $g(\epsilon)d\epsilon = B\sqrt{\epsilon}$ giving

$$\begin{aligned}\langle \epsilon \rangle &= \frac{B \int_0^{E_F} \epsilon \sqrt{\epsilon} d\epsilon}{B \int_0^{E_F} \sqrt{\epsilon} d\epsilon} \\ &= 3E_F/5\end{aligned}$$

so the energy for N particles is $3NE_F/5$.

- (d) Calculator time. The point of this question is that you think about the order of magnitude of the values of these quantities in a wide range of different systems. The Fermi energies and temperatures ($T_F = E_F/k_B$) are

(i) 0.425 meV and 4.9 K.

(ii) 11.5 eV and 134,000 K.

(iii) 33 MeV and 3.8×10^{11} K.

- (3) (a) For non-relativistic electrons we have

$$\begin{aligned}U_{\text{elec}} &= \frac{3}{5}NE_F \\ &= \frac{3}{5}N \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}.\end{aligned}$$

Now we have to obtain N and V from the information given in the question. There are $m_p + m_p$ protons and neutrons in the star which make up (near enough) all of the mass, so the number of electrons will be $N = M/2m_p$. The star has radius R and so $V = 4\pi R^3/3$. Substitute this into the above equation for energy gives

$$U_{\text{elec}} = \frac{3}{5} \frac{M}{2m_p} \frac{\hbar^2}{8\pi^2 m_e} \left(3\pi^2 \frac{M}{2m_p} \frac{3}{4\pi R^3} \right)^{2/3}.$$

Collecting all of the numbers and π 's together into a single value we can simplify to

$$U_{\text{elec}} = 0.0088 \frac{\hbar^2 M^{5/3}}{m_e m_p^{5/3} R^2}.$$

- (b) The total energy is of the form

$$U_{\text{total}} = -\frac{A}{R} + \frac{B}{R^2},$$

where A and B are the constants gathered together in the expressions for U_{grav} and U_{elec} . The energy will be minimised when $dU_{\text{total}}/dR = 0$ at $R = 2B/A$. Therefore we obtain

$$\begin{aligned}R &= 2 \times 0.0088 \frac{\hbar^2 M^{5/3}}{m_e m_p^{5/3} R^2} \frac{5}{3GM^2} \\ &= \frac{0.028 \hbar^2}{m_e m_p^{5/3} G} M^{-1/3}.\end{aligned}$$

- (c) Looking up the constants and putting them into the equation for the radius of a white dwarf gives $R \approx 6000$ km.
- (d) For one solar mass and the radius in (c), the Fermi energy is ~ 0.5 MeV. This is about the rest mass energy of an electron hence a relativistic treatment is required.
- (e) The above set of calculations can be performed using the relativistic expressions, however it's easier just to note that the expression for the Fermi energy (and hence average electron energy) of a relativistic Fermion gas scales as $(N/V)^{1/3} \sim R^{-1}$.
- (f) The white dwarf is now unstable to gravitational collapse as, for large enough M , there is no minimum in energy. This is called the Chandrasekhar limit.

Statistical Physics: Workshop Problems 8

- (1) (a) The density of states in k space is

$$g(k)dk = 2 \frac{V}{2\pi^2} k^2 dk$$

remembering a factor of 2 for spin and with $\epsilon = \hbar^2 k^2 / 2m$ we have

$$g(\epsilon)d\epsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} d\epsilon.$$

At $T = 0$ the N electrons fill up the energy levels with $f_{FD}(\epsilon) = 1$ to the Fermi level so

$$\begin{aligned} N &= \int_0^{E_F} g(\epsilon) f_{FD}(\epsilon) d\epsilon \\ &= \frac{2}{3} g(E_F) E_F \end{aligned}$$

where

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}.$$

The specific heat is

$$\begin{aligned} C_V &\sim k_B^2 T g(E_F) \\ &\sim \frac{N}{E_F} k_B^2 T. \end{aligned}$$

There are many ways to do this, covered in lectures and workshops. Other methods are valid.

- (b) We need to obtain $g(E_F)$ which can be done in several ways, such as in (a). Using that result we get immediately that

$$\begin{aligned} \chi &= \mu_B^2 g(E_F) \\ &\sim \frac{N}{E_F} \mu_B^2. \end{aligned}$$

- (c) As the electrons are non-interacting then there is no potential and so the internal energy of the system is the kinetic energy. Therefore

$$\begin{aligned} \langle E_k \rangle &= \int_0^{E_F} \epsilon g(\epsilon) d\epsilon \\ &= \dots \text{Done many times...} = \frac{3}{5} N E_F. \end{aligned}$$

- (d)

$$\begin{aligned} P &= \frac{d \langle E_k \rangle}{dV} \\ &= \frac{3}{5} \frac{N E_F}{V}. \end{aligned}$$

- (2) Similar to above there are several ways to approach this, and we can simply take the results of (1) and put in the numbers. To demonstrate another method, let's do it in momentum space rather than energy space. We have the number of neutrons (or protons) on momentum range p to $p + dp$ as

$$dN = \frac{4V}{h^3} 4\pi p^2 dp$$

so the total number of neutrons is

$$N = \int dN = \frac{16\pi V}{h^3} \int_0^{p_F} p^2 dp = \frac{16\pi V}{3h^3} p_F^3$$

where p_F is the Fermi momentum. The total kinetic energy of the neutrons is

$$E_k = \int \frac{p^2}{2m} dN = \frac{16\pi V}{10h^3 m} p_F^5.$$

Therefore

$$\frac{E_k}{A} = \frac{3}{5} \frac{p_F^2}{2m},$$

noting this is the equivalent expression to (1)(c). The volume can be expressed by the usual formula for a sphere and also via the above expression for A , so

$$V = \frac{4}{3}\pi R_0^3 A = \frac{3(2\pi)^3}{16\pi} p_F^3 A$$

giving

$$p_F = R_0^{-1} \left(\frac{9\pi}{8} \right)^{1/3}$$

and

$$\frac{E_k}{A} = \frac{3}{10} \left(\frac{9\pi}{8} \right)^{1/3} \frac{1}{m R_0^2} \sim 16 \text{ MeV}.$$

- (3) We have calculated in several ways in lectures and workshops (for example, (1)(a) in this workshop) $N = \int_0^{E_F} g(\epsilon) f_{FD}(\epsilon) d\epsilon$ to get the relation between particle number and Fermi energy. This gives

$$\frac{N}{V} = \frac{8\pi}{3} \left(\frac{2mE_F}{h^2} \right)^{3/2}.$$

The condition for the reaction is $E_F \geq 0.8 \text{ MeV}$ so this is satisfied with a minimum value of N/V of $3.24 \times 10^{36} \text{ m}^{-3}$. Multiply number density by neutron mass to get the minimum density of a neutron star to be $5.4 \times 10^9 \text{ kg m}^{-3}$. A relativistic calculation gives $\sim 10^{16} \text{ kg m}^{-3}$.

- (4) (a) This can be done in energy or momentum space. Let's do the momentum space calculation. Taking the usual density of states in k space we have

$$E = \frac{8\pi V}{h^3} \int_0^{p_F} \epsilon p^2 dp$$

where p_F is the Fermi momentum which is

$$p_F = \left(\frac{3Nh^3}{8\pi V} \right)^{1/3}.$$

In the extreme relativistic case we have $\epsilon = cp$ so the energy is

$$E = \frac{2\pi cV}{h^3} p_F^4$$

and the pressure $p = -(\partial E / \partial V)_{T=0}$ gives $p = E/(3V)$ and hence the equation of state is $pV = E/3$.

- (b) From relativity, the extreme relativistic limit is when the rest mass is not a significant part of the total energy, i.e.

$$\epsilon = \sqrt{(mc^2)^2 + (pc)^2} \sim pc \left[1 + \frac{1}{2} \left(\frac{mc}{p} \right)^2 \right].$$

Using the result in (a) we get

$$E \sim 2\pi cV [p_F^4 + (mcp_F)^2] / h^3.$$

So for (a) to be valid we require $p_F \gg mc$ hence

$$\frac{N}{V} \gg \frac{8\pi}{3} \left(\frac{mc}{h} \right)^3$$

which can be satisfied with $N \rightarrow \infty$ for a given V or $V \rightarrow 0$ for a given N .

- (5) In the stated extreme relativistic limit we have $\epsilon = pc$ and $\mu = 0$. Therefore

$$\begin{aligned} \frac{N}{V} &= \left(\frac{4\pi}{(2\pi\hbar)^3} \right) \int_0^\infty \frac{p^2}{e^{pc/k_B T} + 1} dp \\ &= \frac{1}{2\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \int_0^\infty \frac{x^2}{e^x + 1} dx. \end{aligned}$$

The integral is $3\zeta(3)/2 \sim 1.80309$ where ζ is the Riemann-zeta function. The average energy density is

$$\rho = \frac{N}{V} \epsilon = \frac{N}{V} k_B T,$$

and substitute for N/V to obtain the result.