Lecture notes for an undergraduate course in Thermodynamics – A workbook

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PREFACE

This is a one semester course in thermodynamics. Like any course in physics, the precise language of discussion is *mathematics*. A student is expected to freely use this language. Lectures will depend on mathematical logic and you need to follow mathematics as a language like you may follow when someone speaks in English or Spanish.

The topics covered in this book are taken straight out of the required textbook, An introduction to thermal physics by Daniel V. Schroeder. This is an excellent book and the student is urged to read it carefully and work through all the problems in the material covered in class.

The lecture notes are a supplement to the textbook and is in the style of a workbook. A lot of problems are interspersed to help understand the subject. It is necessary to work through the lecture notes to obtain a good understanding of the physics and mathematics. We will need multi-variable calculus for this course. This course is currently being taught by myself in the physics department at Florida International University as PHY 3513 (Fall).

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1 Understanding temperature

Temperature is at the core of thermal physics. As the course develops, we will be able to define temperature from first principles. To start off, a simple way to understand temperature is by expansion and contraction. An object's size usually depend on temperature and we write

$$\frac{dV}{dT} = \beta V. \tag{1}$$

Usually, β, itself mildly depends on temperature.

Problem 1: Water has an interesting property. $\beta < 0$ for $0 < T < 4^oC$ and $\beta > 0$ for $T > 4^oC$. Consider a fixed amount (mass) of water. Show that

$$V(T_1) > V(T_2) \qquad 0 < T_1 < T_2 < 4^oC \quad \Rightarrow \quad \rho(T_1) < \rho(T_2). \tag{2}$$

Use the above result to explain why the temperature of the water will increase to 4^oC as we go down from the surface. Which part of the lake will freeze first? How does this affect the water as we go down the lake from the top? How will the thickness of the ice depend on the surface temperature? ∎

2 Ideal gas law

We will use Newton's law heuristically to derive a simple law for describing thermal physics. We will come back to this law later in the course after we setup thermal physics from first principles and derive it properly.

Consider a gas made up of a single type of molecule and assume that there is no interaction between molecules. Assume that the gas is confined to a box $L_x \times L_y \times L_z$ with solid walls. Since there is no force on a molecule due to other molecules, a molecule with velocity $\mathbf{v}$ will freely move till it comes in contact with the wall.

Problem 2: Consider a molecule that comes in contact with the wall in the $y - z$ plane. Assuming a perfect collision with the wall, if the velocity before collision is (v_x, v_y, v_z), what is the velocity after collision? Assuming it took a small time ΔT for the collision, what is the force on the molecule by the wall? What is the force on the wall by the molecule? Assuming v_y and v_z are not large enough for the molecule to hit the other walls during its back and forth motion, what is the time taken for the molecule to hit the wall again? It is natural to assume this is ΔT. Hence show the pressure (force per unit area) on the wall is

$$P = \frac{F_w}{L_y L_z} = \frac{m v_x^2}{V}; \qquad V = L_x L_y L_z. \tag{3}$$

∎

Since all molecules are identical, we do not expect the velocity of one to be different from the other; we also do not expect the components in the three directions to be different. Let us refer to this average quantity by

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}. \tag{4}$$

Now assume that there are N molecules in the gas.

Problem 3: Show that

$$PV = N m \overline{v_x^2}. \tag{5}$$

Show that the units match on both sides of the equation by independently deriving the units on the left and right side. ∎

We use the Boltzmann's constant

$$k = 1.381 \times 10^{-23} \ \frac{\mathrm{J}}{\mathrm{K}} \tag{6}$$

to convert energy to temperature in Kelvin by saying

$$m\overline{v_x^2} = m\overline{v_y^2} = m\overline{v_z^2} = kT \quad \Rightarrow \quad \overline{K} = \frac{3}{2} kT, \tag{7}$$

where $\overline{K}$ is the average kinetic energy per molecule. This results in the ideal gas law

$$PV = NkT. \tag{8}$$

If we write $N = nN_A$ where N_A is the number of molecules per mole (Avagadro number) and n is the number of moles then

$$PV = nRT. \tag{9}$$

Problem 4: Show that the gas constant R takes on the value

$$R = N_A k = 8.31 \frac{\text{J}}{\text{mol K}}. \tag{10}$$

■

Problem 5: This problem will help you get a feel for pressure and density at a given temperature. The standard atmospheric pressure is 10^5 N/m^2 (Pascals). Assume the palm of your hand is about 10^{-2} m^2 and you hold your out. What is the force on your hand due to air? Is this big or small (should you feel the pressure?) Explain your conundrum. Assume the room temperature is 300 K and calculate the number of molecules per unit volume at standard atmospheric pressure. Then calcuate the volume occupied by one molecule Assume the molecule occupies a sphere and compute the radius of this sphere. How does this compare to the radius of a hydrogen, nitrogen and oxygen atom? Is the air dense? ■

Problem 6: How should the pressure of air change with elevation above sea level if we assume that the temperature does not change with elevation? Apply Newton's law to a slab of air of thickness dz and area A at a height z that is not moving. Show that

$$\frac{dP(z)}{dz} = -\rho g. \tag{11}$$

Let m be the mass of one molecule of air. Use the ideal gas law to show that the density of air is

$$\rho = \frac{mP}{kT} \tag{12}$$

and hence conclude that

$$\frac{dP}{dz} = -\frac{mg}{kT} P. \tag{13}$$

Assuming the temperature does not change with z, show that

$$P(z) = P(0) e^{-\frac{mg}{kT} z}, \tag{14}$$

where $P(0)$ is the pressure at sea level. Obtain an expression for the density as a function of z and explain the physics that results from it. ■

Problem 7: A hot-air balloon is kept steady by heating up the inside to a certain temperature. Let us figure out how this works using ideal gas law. Assume the mass of all things attached to the hot-air balloon is M. Let ρ_0 be the density of air outside the balloon and let ρ be the density of air inside the balloon. Let V be the volume of the balloon. Derive a formula for the upward buoyant force on the balloon. Derive a formula for the the total weight of the balloon. Hence obtain an equation that says the balloon is holding steady. Why should the pressure inside and outside of the balloon be the same? Use this along with the force balance equation to arrive at

$$\frac{1}{T_0} - \frac{1}{T} = \frac{Mk}{mPV}, \tag{15}$$

where m is the mass of one molecule of air. ■

Problem 8: Consider two rooms in your house and let us keep the door open. Why should the pressure in the two rooms have to be the same? Let us assume the two rooms have the same volume. We know from experience than an inside room in Florida on a hot summer day tend to be cooler than a room that has a glass window to the outside. What can you conclude about the number of molecules in the two rooms? Are they the same? Is it larger in one room compared to the other? If so, where is it larger? ■

3 Conservation of energy

Ideal gas law along with conservation of energy can be used to simply understand standard thermodynamic processes. Since $\frac{1}{2}kT$ is the energy associated with motion of one molecule in one direction, we generalize this to a general gas by saying that the total thermal energy is

$$U = Nf\frac{1}{2}kT \tag{16}$$

where f is the relevant degrees of freedom. $f = 3$ for a monoatomic molecule. $f = 5$ usually for a diatomic molecule where rotations of the molecule about the axes perpendicular to the molecule are also included. Sometimes we also need to include two vibrational degrees of freedom and this makes $f = 7$. For now, f, is usually assumed to be given to you but we will see that we can derive f from first principles as we move forward in this course.

How can one change U which is same as changing T? What if we take a gas at T_1 and mix it with a gas at T_2. There will be energy transfer by collision (conduction or convection) resulting in the energy of the two gases to be the same or they will reach the same temperature. What if you have an air-tight gas container but with glass walls. If the outside of the gas is at a higher temperature, the inside gas will increase in temperature. This is tranfer of energy by radiation. All three are called heat transfer since all one did was bring one system in close proximity to the other. By work energy theorem, we know that we can increase the temperature by doing work on the gas. So we write

$$\Delta U = Q + W \tag{17}$$

$Q > 0$ is the heat transferred into the gas and $W > 0$ is the work (mechanical, electrical ...) done on the gas. Although this is called the first law of thermodynamics it is just a statement about the conservation of energy.

If a gas exerting a pressure P on its walls and some type of work was done to change the volume from V to $V + dV$, then the work done on the gas is

$$dW = -PdV. \tag{18}$$

Given a path (closed or open) in the (P, V) diagram, we can compute the total work done on the ideal gas. Since we know the initial and final (P, V), we can also calculate the change in the thermal energy. We can the use the first law to compute the total heat transferred into the gas. The answer to W and Q depends on the path but $\Delta U = Q + W$ only depends on the end points and independent of the path.

We now discuss several basic processes.

1. **Isochoric process:** This is a process where the volume does not change.

   Problem 9: Explain why no work is done is done. Hence show that $\Delta U = Q$. ∎

   If Q enters the gas, its temperature has to go up and vice-versa.

2. **Isobaric process:** This is a process where the pressure does not change. Let us assume $V_f > V_i$ and the gas has expanded at constant pressure.

   Problem 10: Show that

   $$W = P(V_i - V_f) < 0. \tag{19}$$

   Why does the sign make physical sense? Use ideal gas law to show that

   $$\Delta U = \frac{f}{2}P(V_f - V_i) > 0. \tag{20}$$

   Explain why this makes physical sense. Show using conservation of energy that

   $$Q = P\frac{f+2}{2}(V_f - V_i) > 0. \tag{21}$$

   Therefore, heat **must have** entered the system if an ideal gas expanded at constant pressure. Write a sentence that contains heat entering the system and work done of the system to physically describe an isobaric process. ∎

3. **Isothermal process:** This is a very slow process where the temperature does not change.

   Problem 11: Explain why $\Delta U = 0$. Let us assume that the gas expanded from V_i to $V_f > V_i$. Show all steps in detail to arrive at

$$W = NkT \ln \frac{V_i}{V_f}. \tag{22}$$

   Hence show that

$$Q = NkT \ln \frac{V_f}{V_i}. \tag{23}$$

   Write a sentence that contains heat entering the system and work done of the system to physically describe an isothermal process. ■

4. **Adiabatic process:** This is a very fast process where no heat is able to enter or exit the gas. Therefore $Q = 0$.

   Problem 12: Explain every step in the equation below in detail.

$$dU = dW \quad \Rightarrow \frac{Nfk}{2} dT = -PdV = -\frac{NkT}{V} dV \quad \Rightarrow \frac{dV}{V} + \frac{f}{2}\frac{dT}{T} = 0 \quad \Rightarrow \quad d\left(\ln V + \ln T^{\frac{f}{2}}\right) = 0. \tag{24}$$

   Hence conclude

$$VT^{\frac{f}{2}} = \text{constant} \quad \Rightarrow PV^{\gamma} = \text{constant}; \quad \gamma = \frac{f+2}{f}, \tag{25}$$

   for an adiabatic process. ■

Problem 13: Assume that (P_1, V_1) and (P_2, V_2) are at the same temperature and assume that $V_2 > V_1$. Plot these two points on the $P - V$ diagram. Draw the curve that corresponds to an isothermal process between (P_1, V_1) and (P_2, V_2). Draw the curve that corresponds to an adiabatic process that starts at (P_1, V_1) and ends up with a volume of V_2. Let the final pressure be P_f. Is P_f larger or smaller than P_2? Explain what happens to the temperature in an adiabatic process that undergoes expansion. Show that the work done in the adiabatic expansion is

$$W_a = \frac{(P_f - P_2)V_2}{\gamma - 1}. \tag{26}$$

How does the work done in the adiabatic expansion compare with the isothermal expansion? Discuss the physics by comparing the two processes. ■

Problem 14: Let us go back to the problem of the atmospheric pressure variation as a function of height in Eq. (13). All we have assumed so far is ideal gas law and stability of air. Unless we relate P and T, we cannot proceed forward. In order to get to Eq. (14), we had to assume that the temperature did not vary with height. This is not the case and indeed the temperature drops with the height and this is due to the heating of the ground by sunlight. Let us assume that the pressure and temperature variation is adiabatically maintained – no heat is exchanged between the air masses in contact. Show that

$$\frac{f+2}{2}\frac{dT}{T} = \frac{dP}{P}, \tag{27}$$

for an adiabatic process. Combine this with Eq. (13) to show that

$$\frac{dT}{dz} \leq -\frac{2Mg}{R(f+2)}. \tag{28}$$

where the air mass will rise if it an inequality. Use $M = 0.029$ kg/mol for the molar mass of air and $f = 5$ for air, and show that

$$\frac{dT}{dz} \leq -0.0098 \text{ K/m}. \tag{29}$$

Explain the physics of your result. ■

Problem 15: Sound wave is a pressure wave. In order to define the speed of the wave, one uses the bulk modulus which is

$$B = -V\frac{dP}{dV}. \tag{30}$$

The speed of sound is given by

$$c_s = \sqrt{\frac{B}{\rho}} \tag{31}$$

where ρ is the density of gas. Show that the units work our properly. If the pressure change is isothermal, show that ideal gas law results in

$$B = P. \tag{32}$$

If the pressure change is adiabatic, show that ideal gas law results in

$$B = \gamma P. \tag{33}$$

Compare the speed of sound for the isothermal and adiabatic case. Show that the speed of sound for the adiabatic case is

$$c_s = \sqrt{\frac{\gamma RT}{M}}. \tag{34}$$

Compare this speed with the average speed of the molecule which is $\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3}{\gamma}}c_s$. With $\gamma = \frac{7}{5}$, and $M = 0.029$ kg for air, show that $c_s = 347$ m/s at $T = 300$ K and the average molecular speed is 508 m/s. ■

4 Heat engines and Refrigerators

This is not a course in engineering thermodynamics. Consider a process in the $P-V$ diagram that is closed – it starts and ends in the same point in the diagram.

Problem 16: What can you say about the change in the internal energy in a closed process? Explain your answer. What is the relation between work done **by** the gas and heat **entering** the gas in a closed process? What is the relation between work done **on** the gas and heat **exiting** the gas in a closed process? Explain your answer. ■

If positive work is done by the gas then we call that closed process as a heat engine. If positive heat goes out of the gas we call that closed process as a refrigerator. We will not go beyond these two concepts in the course and we will not address efficiencies at all.

Calculation of work done on the gas and heat entering the gas for each of the segments of a closed cycle is an important type of problems and this includes the physicall interpretation of the close cycle.

Problem 17: A closed cycle for an ideal gas is given by $(P,V) \to (P,aV) \to (bP,aV) \to (bP,V) \to (P,V)$. Assume each segment is connected by a straight line. Evaluate ΔU, W and Q for each of the segments and the closed cycle in terms of P, V, a, b and f, k. Consider all four cases arising from $a > 1$, $a < 1$, $b > 1$ and $b < 1$. Discuss the physics for each of the four cases – what processes describe each of the segments and is the closed cycle a heat engine or a refrigerator. Draw $P - V$ diagrams for each of the four cases to help you explain the physics. ■

Problem 18: A closed cycle for an ideal gas is given by $(P_1,V_1) \to (P_2,V_2) \to (P_3,V_2) \to (P_4,V_1) \to (P_1,V_1)$. You can assume that $V_1 > V_2$. We will consider four cases: the first segment is either isothermal or adiabatic and the third segment is either isothermal and adiabatic. Derive a relation between P_1, P_2, P_3 and P_4 for all four cases. Evaluate ΔU, W and Q for each of the segments and the closed cycle in terms of only the given pressures, volumes and f, k for all four cases. Discuss the physics for all four cases – what processes describe each of the segments and is the closed cycle a heat engine or a refrigerator. ■

Problem 19: An important closed cycle is called the Carnot cycle (sections 4.1 and 4.2). The ideal gas undergoes isothermal compression from (P_1,V_1) to (P_2,V_2) at temperature, T_c with $V_2 < V_1$. The gas then undergoes adiabatic compression from (P_2,V_2) to (P_3,V_3) and the new higher temperature is $T_h > T_c$. The gas then undergoes isothermal expansion from (P_3,V_3) to (P_4,V_4) at T_h and $V_4 > V_3$. Finally the cycle is closed by an adiabatic expansion from (P_4,V_4) back to (P_1,V_1). Using the relation between P and V for isothermal and adiabatic processes show that

$$V_1V_3 = V_2V_4; \quad P_1P_3 = P_2P_4. \tag{35}$$

Evaluate ΔU, W and Q for each of the segments and the closed cycle in terms of only the given pressures, volumes and f, k. Let us call the work done on the gas in the first segment as W_c and let us call the heat into the gas in the third segment as Q_h. Show that

$$W_c = NkT_c \ln \frac{V_1}{V_2} > 0; \qquad Q_h = NkT_h \ln \frac{V_1}{V_2} > 0. \tag{36}$$

■

We make a brief comment on efficiency of a heat engine. We make contact with an engine by saying that the inside of the engine where the fuel is burned is the hot reservoir and the outside environment where the engine operates is the cold reservoir. The total heat into the engine in once cycle is

$$Q = Q_c + Q_h = Nk(T_h - T_c) \ln \frac{V_1}{V_2} \tag{37}$$

and the engine does positive work equal to Q. Ideally, we would want $Q_c = 0$ so that all heat into the engine from the burning of fuel (Q_h) is converted to work done by the engine ($-W$). Since $Q_c \neq 0$, the efficiency of the heat engine is

$$e \equiv \frac{\text{benefit}}{\text{cost}} = \frac{-W}{Q_h} = \frac{Q}{Q_h} = 1 - \frac{T_c}{T_h}. \tag{38}$$

5 Heat capacities

A beginning student in thermal physics is usually confused about the difference between temperature and heat. We have already seen that heat can enter or exit the system while the temperature does not change (isothermal process). We will learn later in the course that the ability for a gas to hold heat is related to its temperature. With that in mind we define the heat capacity and specific heat capacity are defined by

$$C = \frac{Q}{\Delta T}; \qquad c = \frac{C}{m}. \tag{39}$$

respectively.

Problem 20: What is the heat capacity in a adiabatic process? What is the heat capacity in a isothermal process? Based on your answers what processes can be used to measure the heat capacity? ■

Using conservation of energy

$$C = \frac{\Delta U + P\Delta V}{\Delta T}. \tag{40}$$

Problem 21: Consider an isochoric process and show that the heat capacity is

$$C_V = \frac{\Delta U}{\Delta T} = \frac{Nfk}{2}, \tag{41}$$

assuming f does not change in the range of temperature under consideration. Therefore

$$\frac{C_V}{n} = \frac{fR}{2} \tag{42}$$

and provides a way of measuring f. One mole of liquid water weighs 18g and the heat capacity of liquid water is 4.186 J/(K g). Show that

$$\frac{C_V}{n} = 18 \times 4.186\text{J/K} = 9.07 \text{ R}. \tag{43}$$

Since f is never as high as 18, we conclude that much of the thermal energy is stored in inter-molecular interactions. ■

Problem 22: Consider a isobaric process. Show the heat capacity is given by

$$C_P = \frac{Nfk}{2} + Nk = nR\frac{2+f}{2} = nR + C_V. \tag{44}$$

■

Problem 23: If we know the heat capacity of one material, we can measure the heat capacity of an unknown material by the following experiment. Let us assume we have m_k of the known material at temperature T_k and that we have m_u of the known material at temperature T_u. We know all the above quantities and also c_k. Our aim is to find c_u. If we bring the two in contact, they will reach a common temperature T between T_k and T_u which can be measured. Let us assume T_u is greater than T_k. Then the known material gains heat and the unknown material loses heat. Assuming no work was done, show that

$$m_k c_k (T - T_k) = m_u c_u (T_u - T), \tag{45}$$

We can solve for the only unknown, c_u. ■

6 Microstates

Entropy is one of two basic quantities in thermal physics, the other being the energy. Entropy arises from the fact that a gas with a fixed total energy can be in a very large number of microstates. A microstate can be thought of as an asignment of the energy to each of the molecules that make up the gas so that the gas has a fixed total energy. Our aim is to count the number of microstates with a fixed energy for an ideal gas. As it turns out, this counting is not as easy as it seems. So, we will proceed with two simpler examples first and then go to the problem of the ideal gas. Before, we do that we will need to review some mathematics you already should know.

6.1 Math preliminaries

Problem 24: Let us assume we have N boxes and we want to fill $0 \leq q \leq N$ boxes with the same item. Show that the total number of possibilities is

$$\binom{N}{q} = \frac{N(N-1)(N-2)\cdots(N-q+1)}{q(q-1)(q-2)\cdots 1} = \frac{N!}{q!(N-q)!} = \binom{N}{N-q}. \tag{46}$$

To show the above, you have to be able to logically explain where the numerical in the first equality comes from. Then you have to explain the need for the denominator. You have do the appropriate math manipulation to arrive at the third equality. The last equality should be shown in the end and you should the explain logically (in words) why the left hand side of the entire equation is the same as the right hand side of the entire equation. ■

In the above example, q labels a **macrostate** (like a total energy) and

$$\Omega(N, q) = \binom{N}{q} \tag{47}$$

is the **number of microstates** for the particular microstate. The quantity N is akin to the total number of molecules in a gas.

We will use Taylor's series extensively. The definition we will use is

$$f(x) = \sum_{n=0}^{\infty} f_n \frac{(x-a)^n}{n!}; \qquad f_n = \left.\frac{d^n f(x)}{dx^n}\right|_{x=a}. \tag{48}$$

Often, our function might parametrically depend on other variables which will be kept fixed. We will have to terminate at some order and our notation will be $O((x-a)^{k+1})$ to say that all orders with powers greater than or equal to $(k+1)$ are in that remainder term and we have only kept terms up to power k.

Problem 25: Just like we deal with significant figures when we add and multiply decimal numbers, we will need to figure out the place where we need to terminate when we add or multiply functions. Let $f(x)$ and $g(x)$ be two functions and consider an expansion around $x = 0$. If we want to keep up to x^4 in $f(x) + g(x)$, up to what power do we need to keep in $f(x)$ and $g(x)$? Explain your answer in the form of a logical proof. If we want to keep up to x^4 in $f(x) \times g(x)$, up to what power do we need to keep in $f(x)$ and $g(x)$? Explain your answer in the form of a logical proof. ■

Problem 26: Prove that

$$\frac{1}{1+x} = \sum_{k=0}^{\infty} (-1)^k x^k. \tag{49}$$

■

Problem 27: Prove that

$$\ln(1+x) = \sum_{k=0}^{\infty} (-1)^k \frac{x^{k+1}}{k+1}. \tag{50}$$

■

We will need what is referred to as the Stirling's approximation. It says that

$$\ln(M!) \approx M \ln M - M + \frac{1}{2} \ln(2\pi M) + O\left(\frac{1}{M}\right) \tag{51}$$

where M is a large integer and $O\left(\frac{1}{M}\right)$ means that all the remainder terms go to zero when $M \to \infty$. You can assume this formula for this course without proof. But you will need to understand the terms that are kept. Note that $M \ln M$, M, and $\ln M$ go to infinity as $M \to \infty$.

Problem 28: Show that

$$\lim_{M\to\infty} \frac{1}{\ln M} = 0; \qquad \lim_{M\to\infty} \frac{\ln M}{M} = 0. \tag{52}$$

Use these to explain the order of importance of the three terms as M becomes large. ■

6.2 Two state paramagnet

A simple problem to count the number of microstates is a two state paramagnet. We consider a dipole to have two states – one pointing up and another pointing down. Let us consider a system of N non-interacting dipoles. Consider a **macrostate** with $N_\uparrow$ number of dipoles that point up. Then $N_\downarrow = N - N_\uparrow$. The number of **microstates** follows from Eq. (46) and is

$$\Omega(N_\uparrow, N) = \frac{N!}{N_\uparrow!\ N_\downarrow!}. \tag{53}$$

Our aim is to get a good feel for the number of microstates as a function of the macrostate. Since we are going to consider N to be large, we will assume that it is even.

Problem 29: Show that

$$\frac{\Omega(N_\uparrow + 1, N)}{\Omega(N_\uparrow, N)} = \frac{N - N_\uparrow}{N_\uparrow + 1}. \tag{54}$$

Hence show that

$$\Omega(N_\uparrow + 1, N) > \Omega(N_\uparrow, N) \quad \forall \quad N_\uparrow < \frac{N-1}{2}; \qquad \Omega(N_\uparrow + 1, N) < \Omega(N_\uparrow, N) \quad \forall \quad N_\uparrow > \frac{N-1}{2}. \tag{55}$$

Hence conclude that the number of states has a uniqute maximum when $N_\uparrow = N_\downarrow = \frac{N}{2}$. ■

Next, we want to understand the behavior of $\Omega(N_\uparrow, N)$ close to its maximum and when N is large.

Problem 30: Show that both $N_\uparrow$ and $N_\downarrow$ are also large at the maximum when N is large. Then use the Stirling's approximation in Eq. (51) and show that

$$\ln \Omega(N_\uparrow, N) \approx N \ln N - N_\uparrow \ln N_\uparrow - N_\downarrow \ln N_\downarrow - \frac{1}{2} \ln(2\pi) + \frac{1}{2} \ln \frac{N}{N_\uparrow N_\downarrow}. \tag{56}$$

The symbol $\approx$ says that we have not kept terms that go to zero as $N \to \infty$. ■

Problem 31: To understand the behavior close to the maximum, let $N_\uparrow = \frac{N}{2}(1+x)$. Then show that $N_\downarrow = \frac{N}{2}(1-x)$. With an abuse of notation, we replace $N_\uparrow$ with x in Ω and then show that

$$\ln \Omega(x, N) \approx N \ln 2 - \frac{N}{2} \left[(1+x)\ln(1+x) + (1-x)\ln(1-x)\right] - \frac{1}{2}\ln(2\pi) + \frac{1}{2} \ln \frac{4}{N(1-x^2)}. \tag{57}$$

Finally, show that

$$\begin{aligned} \Omega(x,N) &\approx \frac{2^{N+1}}{\sqrt{2\pi N(1-x^2)}} e^{-\frac{N}{2}[(1+x)\ln(1+x)+(1-x)\ln(1-x)]} \\ \Rightarrow \quad \frac{\Omega(x,N)}{\Omega(0,N)} &\approx \frac{1}{\sqrt{1-x^2}} e^{-\frac{N}{2}[(1+x)\ln(1+x)+(1-x)\ln(1-x)]}. \end{aligned} \tag{58}$$

■

Problem 32: Now comes the crucial observation. Show that

$$\lim_{N\to\infty} \frac{\Omega(x,N)}{\Omega(0,N)}\bigg|_{x\neq 0} = 0. \tag{59}$$

What does this mean physically since N is akin to the number of molecules and is typically a large number like N_A? ■

Problem 33: To understand the previous problem better, define $x = \frac{y}{\sqrt{2N}}$ and show using Taylor expansion,

$$\lim_{N\to\infty} \frac{\Omega\left(\frac{y}{\sqrt{N}}, N\right)}{\Omega(0,N)} = e^{-\frac{1}{2}y^2}. \tag{60}$$

■

Problem 34: Show that we have a plot exactly like Figure 2.7 for the two-state paramagnet. Read the analysis of Figure 2.7 in the book and write your own analysis for this problem. An understanding of this analysis is at the heart of thermal physics. ■

6.3 Einstein solid

We move from a two state problem to an infinite state problem but the states are discrete. You have learned or will learn in quantum mechanics about a simple problem called the quantum Harmonic oscillator. Unlike the classical problem, the energy takes on discrete values, $E_n = nhf$ where f is the frequency of the oscillator, $h = 6.626 \times 10^{-34} \frac{\text{m}^2\ \text{kg}}{\text{s}}$ is the Plank's constant that converts frequency to energy and n take on integer values. We have ignored an addition term of the form $\frac{1}{2}hf$ but this will not be important for us. Let us assume that there are many identical oscillators that do not interact with each other and form a solid, liquid or gas. Let us assume that we have N such particles. The total energy of the system can be anywhere from $E = 0$ to $E = \infty$. We want to know how many possible arrangements of individual energies result in $E = qhf$ where $q \geq 0$.

Problem 35: To find all possible arrangements, start with a fixed q. We need to partition this q into N parts, q_i, $i = 1, \cdots, N$ such that

$$\sum_{i=1}^{N} q_i = q; \qquad q_i \geq 0 \quad \forall \quad i. \tag{61}$$

Let us draw this by drawing q dots and drawing a line after q_1, $q_1 + q_2$, $\cdots$ $q_1 + q_2 + \cdots q_{N-1}$. Explain why this drawing shows a partition of q into N parts. How many lines do you have in your diagram? Thinking of dots and lines as two types of objects, how many objects do we have in our diagram of dots and lines. Now think of choosing q dots from the total number of objects. All possible ways of doing this will give us all solutions to Eq. (61). Explain that the number of ways is

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!}. \tag{62}$$

■

Since we are dealing with thermal physics. we will assume N is very large. What about q? If all the oscillators are in the lowest energy, this is the lowest possible energy of the system and this is where the system will be at zero temperature by definition. Therefore q should be some measure of temperature. Given a temperature, if we increase N, we will expect E to increase proportionally. Therefore, we expect q also to be large or the energy per oscillator, $\frac{q}{N}$, to be non-zero as N goes to infinite.

Problem 36: Using the Stirling's approximation in Eq. (51) and show that

$$\ln \Omega(N,q) = (q+N)\ln(q+N) - q\ln q - N\ln N + \frac{1}{2}\ln\frac{N}{q(q+N)} - \frac{1}{2}\ln(2\pi) \tag{63}$$

■

Problem 37: Let us set $q = fN$ such that as $N \to \infty$, $\frac{q}{N}$ remains fixed. Show that

$$\ln(\Omega(N,f)) = N\left[(1+f)\ln(1+f) - f\ln f\right] - \frac{1}{2}\ln N - \frac{1}{2}\ln[2\pi f(1+f)] \tag{64}$$

and therefore

$$\Omega(N,f) = \sqrt{\frac{1}{2\pi N f(1+f)}}\, e^{N[(1+f)\ln(1+f) - f\ln f]}. \tag{65}$$

■

Problem 38: In order to understand the role played by f at a fixed but large N, describe the function, $(1+f)\ln(1+f) - f\ln f$, as a function of f. Does it has maxima or minima. Does it always increase or decrease as f increases? Based on your analysis, explain why it makes sense to look at the limits of small and large f. ■

Problem 39: Consider the case when $f \ll 1$. What is the physical meaning of this limit? Use the Taylor's series for $ln(1+f)$ to show that

$$(1+f)\ln(1+f) - f\ln f = -f\ln f + f + O(f^2). \tag{66}$$

Hence show that

$$\Omega(N,q) \approx \sqrt{\frac{1}{2\pi q}}\left(\frac{eN}{q}\right)^q; \qquad q \ll N. \tag{67}$$

Provide a heuristic description of the result. ■

Problem 40: Consider the case when $f \gg 1$. What is the physical meaning of this limit? Write $(1+f) = f(1+f^{-1})$ and perform a Taylor's series in powers of f^{-1} and show that

$$(1+f)\ln(1+f) - f\ln f = \ln f + 1 + O(f^{-1}) \tag{68}$$

Hence show that

$$\Omega(N,q) \approx \sqrt{\frac{N}{2\pi q^2}}\left(\frac{eq}{N}\right)^N; \qquad q \gg N. \tag{69}$$

Provide a heuristic description of the result. ■

Problem 41: Compare $\Omega(N,q)$ for $q \ll N$ with $q \gg N$ and explain the physical meaning of your comparision. ■

6.4 The ideal gas

Now we turn to the problem of computing the *number* of microstates for a fixed energy of an ideal gas. Consider a gas of N monoatomic elements enclosed in a volume V. Let the total internal energy of the gas be U. It is a non-interacting monoatomic gas and all the energy comes from its translational kinetic energy.

Problem 42: Clearly explain why the number of microstates is infinite even when N, V and U are finite. ■

Our aim is to see how this *infinity* depends on N – what a strange concept.

Problem 43: Each particle can be in any location and therefore explain that the contribution to the total number of states coming from its location is V. The explain that with N particles, the contribution becomes V^N. ■

Problem 44: Let $\mathbf{v}_i = v_{i1}\hat{x} + v_{i2}\hat{y} + v_{i3}\hat{z}$ be the velocity of the i^{th} particle. Show that the total energy of U results in

$$\sum_{i=1}^{N}(v_{i1}^2 + v_{i2}^2 + v_{i3}^2) = \frac{2U}{m}. \tag{70}$$

Explain why the above equation says that the $3N$ components of all the velocity components have to lie on the surface area of a $3N$ dimensional sphere with radius $\sqrt{\frac{2U}{m}}$. Hence argue that the contribution to the total number of states coming from the velocity components is equal to the surface area of a $3N$ dimensional sphere with radius $\sqrt{\frac{2U}{m}}$. ∎

Problem 45: We can compute the surface area of a K dimensional sphere of radius R using the following trick. Explain why the result should be proportional to R^{K-1}? Let us call the proportionally constant $S(K)$. Then show using conversion from cartesian to polar coordianates that

$$\left[\prod_{i=1}^{\infty}\int_{-\infty}^{\infty} dx_i\right] e^{-\sum_{j=1}^{K} e^{-x_j^2}} = S(K)\int_0^{\infty} dr\ r^{K-1}e^{-r^2} \tag{71}$$

Use the integrals,

$$\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}; \qquad \int_0^{\infty} u^{P-1}e^{-u} = \Gamma(P) \tag{72}$$

to arrive at

$$S(K) = \frac{2\pi^{\frac{K}{2}}}{\Gamma\left(\frac{K}{2}\right)}. \tag{73}$$

∎

Problem 46: Putting the contribution from the possible assignment of locations and velocities, we conclude that the total contribution to the number of states should be $V^N S(3N)\left(\frac{2U}{m}\right)^{\frac{3N}{2}}$. We have made the approximation that $3N-1$ is same as $3N$ for large N. Explain why we have over-counted because all particles in the gas are identical. How can we account for this overcounting. The result for the total number of states has to be a number and it cannot have any units. What is the unit of our expression now? Luckily we have a constant that saves us and that is the Planck's constant, h, which has units of kg m^2/s. Show that

$$\Omega(U,V,N) = \frac{2}{N!}\frac{(2m)^{\frac{3N}{2}}}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}\right)}V^N U^{\frac{3N}{2}}. \tag{74}$$

has the correct N dependence on m, V and U and is also unitless. ∎

7 Entropy, thermal equilibrium and temperature

We have found it useful to consider $\ln(\Omega)$ in our analysis of the number of microstates and we will define the entropy of

$$S \equiv k\ln\Omega, \tag{75}$$

where k is the Boltzmann's constant. The need for this constant will become clear now.

Let us consider two systems (two paramagnets, two Einstein solids, two ideal gases with the same molecule) and let us bring them in thermal contact. For this purpose, it will be sufficient to think of $S(N,V,U)$. The two systems before they come in thermal contact have $S(N_A,V_A,U_A)$ and $S(N_B,U_B)$. When the system comes in contact, we will assume they cannot exchange particles nor can their individual volumes change but can exchange energy (you can think of sealed solid window between the two systems through which energy can be exchanged). But the total energy, $U = U_A + U_B$ cannot change since no energy enters or exits the union of the two systems. Different choices of U_A will result in a different number of total microstates for the combined system and we can say that the energy, U_A, where the total number of microstates is maximized will dominate once the two systems reach *equilibrium* (have exchanged the desired amount of energy).

Problem 47: Show that

$$S(N,V,U) = S(N_A,V_A,U_A)+S(N_B,V_B,U_B); \qquad N = N_A+N_B; \qquad V = V_A+V_B; \qquad U = U_A+U_B. \tag{76}$$

Hence show that $S(N,V,U)$ is maximized when

$$\left.\frac{\partial S(N_A,V_A,U_A)}{\partial U_A}\right|_{N_A,V_A} = \left.\frac{\partial S(N_B,V_B,U_B)}{\partial U_B}\right|_{N_B,V_B}. \tag{77}$$

Show that the unit for the above equation is inverse temperature. ∎

The temperature is defined as

$$\frac{1}{T} = \left.\frac{\partial S(N,V,U)}{\partial U}\right|_{N,V} \tag{78}$$

for a thermodynamic system with N particles occupying a volume V and having a total energy, U. We may also say that temperature is *conjugate* to energy in the sense of momentum being conjugate to the position in the Hamiltonian formalism of classical mechanics.

8 Mechanical work and pressure

Consider two systems, A and B, and let us assume that they come in contact in such a way that only their volumes can change but not their energy or number of particles (we assume that the flexible insulating wall connects the two systems).

Problem 48: Show that

$$\left.\frac{\partial S_A}{\partial V_A}\right|_{N_A,U_A} = \left.\frac{\partial S_B}{\partial V_B}\right|_{N_B,U_B}. \tag{79}$$

To understand the meaning of this quantity, first show that at fixed N,

$$dS = \left.\frac{\partial S}{\partial U}\right|_{V,N} dU + \left.\frac{\partial S}{\partial V}\right|_{U,N} dV \tag{80}$$

Now use the definition of temperature and compared with the conservation of energy $\Delta U = Q + W$ to conclude that

$$Q = TdS; \qquad P = T\left.\frac{\partial S}{\partial V}\right|_{U,N}. \tag{81}$$

Show that the units of pressure work out properly. Conclude that the pressure P of the two systems are the same at equilibrium. ∎

The pressure can be thought of as *conjugate* to the volume. We identified Q with TdS and this needs to be understood better. We will wait for the discussion of the ideal gas from entropy to understand this better.

9 Diffusion and chemical potential

Assume that the two systems, A and B, can exchange energy, particles and also change in volume when they come on contact. We extend the change in internal energy to include addition of particle and write

$$\Delta U = Q - PdV + \mu dN \tag{82}$$

where μ is the *chemical potential* per particle of the gas.

Problem 49: Show that

$$\mu = -T\left.\frac{\partial S}{\partial N}\right|_{U,V}. \tag{83}$$

∎

The chemical potential can be thought of as *conjugate* to number of particles.

10 Thermal physics from entropy

We can derive the temperature, pressure and chemical potential starting from the entropy which is just a counting of the number of microstates at a fixed energy, volume and number of particles. Let us now discuss the resulting from this analysis. We will start with the ideal gas, and then proceed to the Einstein solid and finally discuss the two-state paramagnet.

10.1 Ideal gas

Problem 50: Consider two identical ideal gases with the same volume and number of particles but with different energies, U_A and U_B. Show that the total number of states is proportional to $(U_A U_B)^{\frac{3N}{2}}$. Show that this reaches a maximum when $U_A = U_B = \frac{U}{2}$. Let us write $U_A = \frac{U}{2}(1+x)$ $U_B = \frac{U}{2}(1-x)$. Show that the dependence of the number of states on x is given by

$$e^{\frac{3N}{2}\ln\left(1-x^2\right)}. \tag{84}$$

How should x depend on N such that the expression is finite and non-zero as $N \to \infty$? Explain the physics in a manner similar to the discussion in Section 6.2. ■

Problem 51: Show starting from Eq. (74) that

$$S(U,V,N) = Nk\left\{\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3h^2N}\right)^{\frac{3}{2}}\right] + \frac{5}{2}\right\} \tag{85}$$

where we have dropped terms of order $\ln(N)$ and smaller in N. ■

Problem 52: Show that the temperature of the ideal gas is

$$\frac{1}{T} = \frac{3}{2}Nk\frac{1}{U} \tag{86}$$

and rewrite this as an expression for U. What has been shown? Show that the entropy in terms of T, V, and N is

$$S(T,V,N) = Nk\left\{\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}\right\} \tag{87}$$

■

Problem 53: Show that the pressure of the ideal gas is

$$P = TNk\frac{1}{V} \tag{88}$$

Rewrite this equation in the known form for the ideal gas law. Show that the entropy in terms of P, V, and N is

$$S(P,V,N) = Nk\left\{\ln\left[\left(\frac{V}{N}\right)^{\frac{5}{2}}\left(\frac{2\pi mP}{h^2}\right)^{\frac{3}{2}}\right] + \frac{5}{2}\right\} \tag{89}$$

■

Problem 54: Show that the chemical potential is

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right]. \tag{90}$$

Hence show that

$$S(T,N,\mu) = -N\left[\frac{\mu}{T} + \frac{5}{2}k\right]. \tag{91}$$

Assume that the mass of a Helium atom is $m = 6.646\times10^{-27}$ kg and obtain a value for the chemical potential of Helium at room temperature, $T = 300$K, and standard atmospheric pressure, 10^5 N/m^2. Convert your result from Joules to eV using 1 eV $= 1.602\times10^{-19}$ Joules. Compare this value with the first and second ionization energies of Helium. ■

10.1.1 Thermodynamic processes and the relation between Q and TdS

- Adiabatic process

  Problem 55: Show that $\gamma = \frac{5}{3}$ for the ideal gas under consideration. Hence show that S does not change under an adiabatic process. Hence conclude that $Q = TdS$ for an adiabatic process. Note that T is not a constant in this process. ■

- Isothermal process

  Problem 56: Consider an isothermal expansion where the volume changes from V_i to V_f. Show that the change in entropy is

$$S = Nk \ln \frac{V_f}{V_i}. \tag{92}$$

  Hence conclude that $Q = TdS$ for an adiabatic process. ∎

- Isobaric process

  Problem 57: Consider an infinitesimal isobaric expansion where the volume changes from V to $V+dV$. Show that the change in entropy is

$$dS = \frac{5Nk}{2} \frac{dV}{V}. \tag{93}$$

  Hence conclude that $dQ = TdS$ for an infinitesimal isobaric expansion. Why did we have to work with an infinitesimal case? ∎

- Isochoric process

  Problem 58: Consider an infinitesimal isochoric process where the pressure changes from P to $P+dP$. Show that the change in entropy is

$$dS = \frac{3Nk}{2} \frac{dP}{P}. \tag{94}$$

  Hence conclude that $dQ = TdS$ for an infinitesimal isochoric process. Why did we have to work with an infinitesimal case? ∎

Problem 59: This problem will help you understand the possible change in entropy when two gases are mixed. The two cases would be when the two gases are identical and when they are different. Let us assume gas A has $N_A = xN$ atoms where $x \in (0,1)$ and let gas B have $N_B = (1-x)N$ atoms. Let us assume that their atomic masses are m_A and m_B. Let us assume both have the same temperature, T and pressure, P before mixing. Let us assume that the total volume after mixing is the sum of the volumes before mixing (you think of two containers with a common wall that can be removed). If V_A and V_B are their volumes before mixing, show that

$$V_A = xV, \quad V_B = (1-x)V; \quad V = \frac{NkT}{P}. \tag{95}$$

If U_A and U_B are their energies before mixing, show that

$$U_A = xU; \quad U_B = (1-x)U; \quad U = Nf\frac{1}{2}kT. \tag{96}$$

Show that their respective entropy before mixing is

$$S_A^b = xNk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m_A U}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}; \qquad S_B^b = (1-x)Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m_B U}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}. \tag{97}$$

If the two gases are the same, then $m_A = m_B = m$ show that

$$S = S_A^b + S_B^b = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}, \tag{98}$$

before mixing and it is the same after mixing.

If the two gases are not the same, show that their respective entropies after mixing is

$$S_A^a = xNk \left\{ \ln \left[\frac{V}{xN} \left(\frac{4\pi m_A U}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}; \qquad S_B^a = (1-x)Nk \left\{ \ln \left[\frac{V}{(1-x)N} \left(\frac{4\pi m_B U}{3h^2 N} \right)^{\frac{3}{2}} \right] + \frac{5}{2} \right\}. \tag{99}$$

Hence conclude that the change in entropy due to mixing is

$$S^a - S^b = -Nk \left[x \ln x + (1-x) \ln(1-x) \right]. \tag{100}$$

Discuss the sign of the change (does the entropy increase or decrease?). Explain where this change comes from? Note that their masses do not appear in the change. For what value of x is the change extremized and what is that value? ∎

10.2 Einstein solid

Problem 60: Keeping only terms proportional to N, and setting the energy of a single oscillator as $E_i = \epsilon q_i$ where $\epsilon = hf$, show that the entropy of an Einstein solid with N oscillators having a total energy of U is

$$S(U,N) = kN\left[\frac{\epsilon N+U}{\epsilon N}\ln\frac{\epsilon N+U}{\epsilon N} - \frac{U}{\epsilon N}\ln\frac{U}{\epsilon N}\right] \tag{101}$$

■

Problem 61: Use the definition of temperature from entropy and show that

$$U = \frac{N\epsilon}{e^{\frac{\epsilon}{kT}}-1}. \tag{102}$$

Show that the specfic heat is given by

$$C = \frac{dU}{dT} = Nk\left[\frac{\frac{\epsilon}{2kT}}{\sinh\frac{\epsilon}{2kT}}\right]^2. \tag{103}$$

Show that the entropy in terms and T and N is

$$S(T,N) = Nk\left[\frac{\frac{\epsilon}{kT}}{e^{\frac{\epsilon}{kT}}-1} - \ln\left(1-e^{-\frac{\epsilon}{kT}}\right)\right]. \tag{104}$$

■

Problem 62: Show that the chemical potential is

$$\mu = kT\ln\left(1-e^{-\frac{\epsilon}{kT}}\right) \leq 0. \tag{105}$$

■

Problem 63: Can you extract the number of degrees of freedom for an Einstein solid from Eq. (102)? Let us try to understand the physics at very low and very high temperatures. Show that

$$\begin{aligned} &U = NkT; \quad C = Nk; \quad S = Nk\ln\frac{kT}{\epsilon}; \quad \mu = kT\ln\frac{\epsilon}{kT}; \quad \frac{\epsilon}{kT} \ll 1; \\ &U = N\epsilon e^{-\frac{\epsilon}{kT}}; \quad C = Nk\left(\frac{\epsilon}{kT}\right)^2 e^{-\frac{\epsilon}{kT}}; \quad S = \frac{N\epsilon}{T}e^{-\frac{\epsilon}{kT}}; \quad \mu = -kTe^{-\frac{\epsilon}{kT}}; \quad \frac{\epsilon}{kT} \gg 1. \end{aligned} \tag{106}$$

Explain the physics of the above equations. Use the values for h and k to find the range of frequencies such that 5K is considered very high temperature. ■

10.3 Two state paramagnet

We first need to convert $N_\uparrow$ and $N_\downarrow$ to energy units. The physical property of relevance is the magnetic moment of a particle, μ_B which is related to energy by $\epsilon = \mu_B B$ where B is the applied magnetic field. We have used μ_B to say that it is not the same as the chemical potential, μ. The total energy is defined as

$$U = \epsilon(N_\uparrow - N_\downarrow) = \mu_B B(2N_\uparrow - N) \quad \Rightarrow N_\uparrow = \frac{U+N\mu_B B}{2\mu_B B}; \qquad N_\downarrow = \frac{N\mu_B B - U}{2\mu_B B}. \tag{107}$$

Problem 64: Using Eq. (56), the entropy is

$$S(U,N) = -k\left[\frac{U+N\mu_B B}{2\mu_B B}\ln\frac{U+N\mu_B B}{2\mu_B BN} + \frac{N\mu_B B-U}{2\mu_B B}\ln\frac{N\mu_B B-U}{2\mu_B BN}\right]. \tag{108}$$

■

Problem 65: Use the definition of temperature from entropy and show that

$$U = -N\mu_B B\tanh\frac{\mu_B B}{kT}. \tag{109}$$

Show that the specific heat is given by

$$C = \frac{dU}{dT} = Nk \left[\frac{\frac{\mu_B B}{kT}}{\cosh \frac{\mu_B B}{kT}} \right]^2 . \tag{110}$$

Show that the entropy in terms and T and N is

$$S(T,N) = Nk \left(\ln \left[2 \cosh \frac{\mu_B B}{kT} \right] - \frac{\mu_B B}{kT} \tanh \frac{\mu_B B}{kT} \right). \tag{111}$$

■

Problem 66: Show that the chemical potential is

$$\frac{\mu}{kT} = -\ln\left(2 \cosh \frac{\mu_B B}{kT} \right) < 0. \tag{112}$$

■

Problem 67: Can you extract the number of degrees of freedom for a two state paramagnet from Eq. (109)? Let us try to understand the physics at very low and very high temperatures. Show that

$$\begin{aligned} &U = -\frac{N\mu_B^2 B^2}{kT}; \qquad C = Nk \left(\frac{\mu_B B}{kT} \right)^2 ; \\ &S = Nk \left[\ln 2 - \frac{1}{2} \left(\frac{\mu_B B}{kT} \right)^2 \right]; \qquad \mu = -kT \left[\ln 2 + \frac{1}{2} \left(\frac{\mu_B B}{kT} \right)^2 \right]; \end{aligned} \tag{113}$$

for $\frac{\mu_B B}{kT} \ll 1$ and

$$U = -N\mu_B B; \qquad C = 4Nk \left(\frac{\mu_B B}{kT} \right)^2 e^{-2\frac{\mu_B B}{kT}}; \qquad S = \frac{N\mu_B B}{T} e^{-\frac{2\mu_B B}{kT}}; \qquad \mu = -\mu_B B; \tag{114}$$

for $\frac{\mu_B B}{kT} \gg 1$. Explain the physics of the above equations. ■

Problem 68: Show that the specific heat goes to zero as $T \to 0$ and as $T \to \infty$ and it reaches a unique maximum at $T = T_m$ satisfying

$$\frac{\mu_B B}{kT_m} \tanh \frac{\mu_B B}{kT_m} = 1, \tag{115}$$

and show that

$$U_m = -NkT_m; \qquad C_m = \frac{Nk}{\sinh^2 \frac{\mu_B B}{kT_m}}, \tag{116}$$

at the maximum. Explain the physics. ■

11 Canonical ensemble

Enumeration of the number of states with a fixed total energy is a relatively easy problem for a non-interacting system like the three examples we have considered so far. Interactions are of crucial importance in physics and we would like to enumerate the number of microstates for a fixed total energy in a interacting system. This is usually a difficult problem and the approach is conceptually different. In addition, the approach to be discussed in this section is easier to use even for non-interacting systems and we can work out more examples with relative ease and this will help us focus more on the physics concepts. We start my noting that temperature is the variable conjugate to the energy. It will easier to say that we keep the system at a fixed temperature as opposed to a fixed energy. To physically achieve this, we will take our system which is thermodynamically large and keep it in contact with a *thermal reservoir*. The reservoir is a very large system compared to our system and its volume, V, number of particles, N, and temperature, T, are unchanged when it is kept in contact with our system. Our system will reach *thermal equilibrium* with the *thermal reservoir* by only exchanging energy. We will be able to study the thermal properties of our system

once it has reached equilibrium. *This is referred to as the approach using canonical ensemble.* The crucial point to keep in mind is that our system and the reservoir can exchange energy even at equilibrium as long as the temperature is held fixed. This is akin to small fluctuations that are allowed in the total energy such that the ratio of the number of microstates with respect to the energy that maximizes the number of microstates remains finite and non-zero. Consider a small system in thermal equilibrium with a very large system which we will call as a reservoir with temperature T. We will need to set up some notation. We will refer to s as a particular microstate of our system. Let $E(s)$ be the energy of the system at that particular microstate. This fixes the energy of the reservoir to be $U_R(s)$ such that the combined system has the correct total energy at that temperature (we will assume this does not fluctuate). Given, $U_R(s)$, we know $\Omega_R(s)$ which is the total number of microstates of the reservoir with energy $U(s)$ and volume V and N that do not change.

Let us now consider two different microstates of the system, s_1 ans s_2. The associated number of microstates of the reservoir are $\Omega_R(s_1)$ and $\Omega_R(s_2)$. If $p(s_1)$ and $p(s_2)$ are the probabilities of finding the system in s_1 and s_2, we can say that

$$\frac{p(s_1)}{p(s_2)} = \frac{\Omega_R(s_1)}{\Omega_R(s_2)} \tag{117}$$

This equation trades the number of microstates of the system to the number of microstates of the reservoir. Using the definition of entropy

$$\frac{p(s_1)}{p(s_2)} = e^{\frac{1}{k}[S_R(s_1) - S_R(s_2)]}. \tag{118}$$

Using

$$dU_R = TdS_R - PdV_R + \mu dN_R \tag{119}$$

for the reservoir and noting that $dV_R = 0$ and $dN_R = 0$ we have

$$\frac{1}{k}\left[S_R(s_1) - S_R(s_2)\right] = \frac{1}{kT}\left[U_R(s_1) - U_R(s_2)\right] = -\frac{1}{kT}\left[E(s_1) - E(s_2)\right] \tag{120}$$

and we have used that the total energy of the system and reservoir does not change.

Problem 69: Show that

$$p(s) = \frac{1}{Z}e^{-\beta E(s)}; \qquad Z(\beta) = \sum_s e^{-\beta E(s)}; \qquad \beta = \frac{1}{kT}. \tag{121}$$

This is called the Boltzmann distribution. Explain the physics of the expected distribution of states at low and high temperatures. ∎

The quantity $Z(\beta)$ is called the *canonical partition function.* You should think of $p(s)$ as the normalized histogram of the measurements of the states. We can use this histogram to compute the measured (or average) value of any observable $O(s)$ that depends on s. An example is $E(s)$. The average value of $O(s)$ is

$$\overline{O}(\beta) = \sum_s O(s)p(s) = \frac{1}{Z(\beta)}\sum_s O(s)e^{-\beta E(s)}. \tag{122}$$

In order to compute the variance of this measurement, we have

$$\overline{O^2}(\beta) = \sum_s O^2(s)p(s) = \frac{1}{Z(\beta)}\sum_s O^2(s)e^{-\beta E(s)}; \qquad \sigma_O^2(\beta) = \overline{O^2}(\beta) - \left[\overline{O}(\beta)\right]^2. \tag{123}$$

Problem 70: Show that

$$\overline{E}(\beta) = -\frac{1}{Z(\beta)}\frac{dZ(\beta)}{d\beta}; \qquad \overline{E^2}(\beta) = \frac{1}{Z(\beta)}\frac{d^2Z(\beta)}{d\beta^2}. \tag{124}$$

Then show that

$$\frac{d\overline{E}(\beta)}{d\beta} = \left[\overline{E}(\beta)\right]^2 - \overline{E^2}(\beta) \quad \Rightarrow \quad \sigma_E^2(\beta) = \frac{1}{k\beta^2}\frac{d\overline{E}(T)}{dT}. \tag{125}$$

Hence conclude that the specific heat is

$$C(T) = \frac{1}{kT^2}\sigma_E^2(\beta). \tag{126}$$

∎

11.1 Helmholtz free energy – Extracting thermal physics from the partition function

We saw before that the change in the internal energy

$$dU = TdS - PdV + \mu dN. \tag{127}$$

Let us think of U as a function of (S, V, N) ($U(S, V, N)$) and write

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N}; \qquad P = -\left.\frac{\partial U}{\partial V}\right|_{S,N}; \qquad \mu = \left.\frac{\partial U}{\partial N}\right|_{V,S}. \tag{128}$$

Define the Legendre transformation,

$$F = U - TS. \tag{129}$$

where F is called the Helmholtz free energy.

Problem 71: Show that

$$dF = dU - TdS - SdT = -SdT - PdV + \mu dN. \tag{130}$$

Let us think of F as a function of (T, V, N) ($F(T, V, N)$) and show that

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}; \qquad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}; \qquad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}. \tag{131}$$

■

Note that

$$\left.\frac{\partial F(T,V,N)}{\partial T}\right|_{V,N} = -S(T,V,N) = \frac{F(T,V,N) - U(T,V,N)}{T}; \qquad F(T=0,V,N) = U(T=0,V,N). \tag{132}$$

Problem 72: We will suppress the dependence on (V, N) and focus on the dependence on T. This problem will show that

$$F(T) = -kT \ln Z(T) \tag{133}$$

To show this assume

$$\tilde{F}(T) = -kT \ln Z(T). \tag{134}$$

Then show that

$$\frac{d\tilde{F}(T)}{dT} = \frac{\tilde{F}(T) - \overline{E}(T)}{T}. \tag{135}$$

As $T \to 0$, Z will be dominated by the microstate with the lowest energy, E_0. Show that this results in

$$\tilde{F}(T=0) = E_0; \qquad \overline{E}(T=0) = E_0. \tag{136}$$

■

Therefore, we have shown that

$$F(T, V, N) = -kT \ln Z(T, V, N) \tag{137}$$

is the Helmholtz free energy where the system has a volume V and has a number of particles N. We can compute S, P, μ from $F(T, V, N)$. Before we move on to new examples, let us use the canonical partition function to recompute all the physics for the three examples we have already seen.

Problem 73: If the system under consideration has no interactions, show that the partition function of a system with N particles is just the N^{th} power of the partition function with one particle. Do we need to include a $\frac{1}{N!}$? Think carefully about how we counted the number of microstates for the three examples when you answer this question. ■

11.2 Two state paramagnet

Since this is a non-interacting case, we can start with a single element with two states. The two states have energies, $\pm\mu_B B$.

Problem 74: Show that the partition function for a single element is

$$Z(\beta) = e^{\beta\mu_B B} + e^{-\beta\mu_B B} = 2\cosh(\beta\mu_B B). \tag{138}$$

Show that the previously derived expression for the energy follows from the partition function. Show that the Helmholtz free energy is

$$F(T) = -kT \ln\left[2\cosh\frac{\mu_B B}{kT}\right]. \tag{139}$$

Start from the Helmholtz free energy and show that you arrive at the previously derived expressions for entropy and chemical potential. You need to discuss the factor of N, the number of elements. ∎

11.3 Einstein solid

Since this is a non-interacting case, we can start with a single element with infinite states and energies given by $E_n = n\epsilon;\ n \in [0, \infty]$.

Problem 75: Show that the partition function for a single element is

$$Z(\beta) = \sum_{n=0}^{\infty} e^{-\beta n\epsilon} = \frac{1}{1 - e^{-\beta\epsilon}}. \tag{140}$$

Show that the previously derived expression for the energy follows from the partition function. Show that the Helmholtz free energy is

$$F(T) = kT \ln\left(1 - e^{-\frac{\epsilon}{kT}}\right). \tag{141}$$

Start from the Helmholtz free energy and show that you arrive at the previously derived expressions for entropy and chemical potential. You need to discuss the factor of N, the number of elements. ∎

11.4 Ideal gas

Since this is a non-interacting case, we can start with a single molecule. The energy of the molecule solely comes from the kinetic energy and it is

$$E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2). \tag{142}$$

Do we obtain the partition function by simply integrating over v_x, v_y and v_z? The problem arises since we are supposed to sum over states and a state value does not have units. How can we convert a velocity to a variable that has no units? Remember, we had to find a constant before that matched the units of our counting of states to obtain a number that had no units. We can do the same here by saying that $\frac{h}{mL}$ has units of velocity where $V = L^3$ is the volume. So, we write

$$v_x = \frac{hk_x}{mL}; \qquad v_y = \frac{hk_y}{mL}; \qquad v_z = \frac{hk_z}{mL}; \qquad -\infty < k_x, k_y, k_z < \infty. \tag{143}$$

The variables, k_x, k_y and k_z have no units and we can integrate over them to compute the partition function. It is important to note that it is just a change of variables and should not be confused with wave mechanics. This will come later.

Problem 76: Show that the partition function for a single molecule is

$$Z(\beta) = V\left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}. \tag{144}$$

Show that the energy per molecule equal to $\frac{3}{2}kT$ follows from the partition function. Show that the Helmholtz free energy for a single molecule is

$$F(T,V) = -kT \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right]. \tag{145}$$

Start from the Helmholtz free energy and show that the entropy per molecule is given by

$$S(T,V) = k \left[\ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] + \frac{3}{2} \right]. \tag{146}$$

Compare this with Eq. (87) and explain the differences properly. You need to discuss the factor of N, the number of elements. ∎

11.5 Multistate paramagnet

Instead of two states with energies, $\pm\mu_B B$, materials typically have energies

$$\epsilon_m = 2m\mu_B B; \qquad m = -j, -j+1, \cdots, j-1, j. \tag{147}$$

The two state paramagnet corresponds to $j = \frac{1}{2}$. In general the spin, j, can take on half-integer or integer positive values.

Problem 77: Show that the partition function for a single particle can be written as

$$Z_j(\epsilon) = \sum_{m=-j}^{j} e^{-2\epsilon m}; \qquad \epsilon = \beta\mu_B B. \tag{148}$$

Then prove that

$$Z_j(\epsilon) = \frac{\sinh[(2j+1)\epsilon]}{\sinh \epsilon}. \tag{149}$$

∎

Problem 78: Show that the average energy per particle is given by

$$\overline{E}(\beta) = -\mu_B B \left[(2j+1) \coth[(2j+1)\epsilon] - \coth \epsilon \right]. \tag{150}$$

and show that the average magnetization per particle is given by

$$M(T,B) = -\frac{\partial \ln(Z)}{\partial(\beta B)} = -\mu_B \left[(2j+1) \coth[(2j+1)\epsilon] - \coth \epsilon \right]. \tag{151}$$

This is an odd function of ϵ and therefore B. ∎

Problem 79: Show that for very small temperatures at fixed $B > 0$

$$M(T,B) = -2j\mu_B + 2\mu_B e^{-2\epsilon} + \cdots. \tag{152}$$

Show that for very large temperatures at fixed $B > 0$,

$$M(T,B) = -\frac{1}{3} \left[(2j+1)^2 - 1 \right] \mu_B \epsilon + \cdots. \tag{153}$$

How will your results change for $B < 0$? Explain the physics. ∎

Problem 80: Consider the *classical* limit where $j \to \infty$ and $\mu_B \to 0$ such that $j\mu_B = \mu_c$. Show that

$$M(T,B) = -2\mu_c \coth(2\beta\mu_c B) + \frac{1}{\beta B}, \tag{154}$$

in this limit. Show that for very small temperatures at fixed $B > 0$,

$$M(T,B) = -2\mu_c + \frac{kT}{B} + 4\mu_c e^{-4\beta\mu_c B} + \cdots. \tag{155}$$

and for very large temperatures at fixed $B > 0$,

$$M(T,B) = -\frac{4}{3}\mu_c^2 \beta B + \cdots. \tag{156}$$

How will your results change for $B < 0$? Explain the physics. ∎

12 Grand canonical ensemble

In the discussion in Section 11, we assumed that only energy can be transferred between the reservoir and the system and arrived at Eq. (120). Let us extend this to say that particles can also be exchanged between the reservoir and the system. Then

$$\frac{1}{k}\left[S_R(s_1)-S_R(s_2)\right]=\frac{1}{kT}\left[U_R(s_1)-U_r(s_2)-\mu(N_R(s_1)-N_R(s_2))\right]=-\frac{1}{kT}\left[E(s_1)-E(s_2)-\mu(N(s_1)-N(s_2))\right]. \tag{157}$$

The results in the grand canonical partition function,

$$p(s)=\frac{1}{Z}e^{-\beta(E(s)-\mu N(s))};\qquad Z(\beta)=\sum_s e^{-\beta(E(s)-\mu N(s))}. \tag{158}$$

We can use this partition function to study the behavior of a system as a function of temperature and chemical potential.

We will consider two non-interacting gases. In spite of the simplicity of the models, the physics is quite involved. The two models are free non-relativistic gas of fermions and bosons. The only difference between fermions and bosons is that only one fermion can be in on state but many bosons can be in one state. This affects the computation of the grand canonical partition function and hence the physics.

Problem 81: Let n_k denote the number of particles in a state with energy E_k. Show that the total energy is n_kE_k and the associated partition function (before one considers all possible values of E_k) is

$$Z_k(\beta,\beta\mu)=\begin{cases}\sum_{n_k=0}^{1}e^{-\beta n_k(E_k-\mu)}=1+e^{-\beta(E_k-\mu)} & \text{for fermions}\\ \sum_{n_k=0}^{\infty}e^{-\beta n_k(E_k-\mu)}=\frac{1}{1-e^{-\beta(E_k-\mu)}} & \text{for bosons.}\end{cases} \tag{159}$$

■

Since we are considering non-interacting bosons or fermions, we can say that the total partition function is

$$Z(\beta,\beta\mu)=\prod_k Z_k(\beta,\beta\mu) \tag{160}$$

where the product is over all possible energies.

Problem 82: Show that the average total energy can be written as

$$-\left.\frac{\partial\ln Z(\beta,\beta\mu)}{\partial\beta}\right|_{\beta\mu}=\frac{E_k}{e^{\beta(E_k-\mu)}\pm 1} \tag{161}$$

and the average number of particles can be written as

$$\left.\frac{\partial\ln Z(\beta,\beta\mu)}{\partial(\beta\mu)}\right|_{\beta}=\frac{1}{e^{\beta(E_k-\mu)}\pm 1} \tag{162}$$

with + for fermions and − for bosons. ■

To proceed further, let us assume that the system is a periodic cube of size L^3. We will assume (using a wave model) that the allowed energies are

$$E_k=\frac{\hbar^2}{2m}k^2;\qquad k^2=k_1^2+k_2^2+k_3^2;\qquad k_i=\frac{2\pi n_i}{L};\qquad n_i\in[0,L-1]\in\mathbf{I}. \tag{163}$$

We need to sum over all possible values of these integers to get the average value for the total energy density, ϵ, and the particle density, ρ, in the system. This sum can be written as a three dimensional integral and if we change variables from k to $p=\hbar k$, the three dimensional integral becomes $\int d^3p\frac{L^3}{8\pi^3\hbar^3}$ and $E_k=\frac{p^2}{2m}$.

Problem 83: Show that the average value for the particle number density is

$$\rho=\frac{1}{2\pi^2\hbar^3}\int_0^\infty\frac{p^2dp}{e^{\beta\left(\frac{p^2}{2m}-\mu\right)}\pm 1}, \tag{164}$$

and that the average value for the energy density is

$$\epsilon(\beta) = \frac{1}{4m\pi^2\hbar^3}\int_0^\infty \frac{p^4 dp}{e^{\beta\left(\frac{p^2}{2m}-\mu\right)} \pm 1}. \tag{165}$$

with the + sign for fermions and − sign for bosons. ∎

12.1 Fermions

The particle number density is given by

$$\rho = \frac{1}{2\pi^2\hbar^3}\int_0^\infty \frac{p^2 dp}{e^{\beta\left(\frac{p^2}{2m}-\mu\right)} + 1}, \tag{166}$$

Let as assume that our volume does not change with temperature and assume that ρ remains the same for all temperature. The above equation becomes a relation between μ and T and we will view $\mu(T)$. Let us refer to $\mu(0)$ as μ_F, called the Fermi energy.

Problem 84: Assuming no restriction on the momentum, p, show that there is no restriction on the range of μ. In other words, show that μ can be any real number. ∎

Problem 85: Consider the system at zero temperature. Show that

$$\rho = \frac{(2m\mu_F)^{3/2}}{6\pi^2\hbar^3}. \tag{167}$$

Given ρ, one can compute the Fermi energy, μ_F. Compute the Fermi energy for electrons in a chunk of copper (problem 7.19 in the book). ∎

Problem 86: We can use the Fermi energy to set the energy scale in the problem. We define,

$$\frac{p^2}{2m} = \mu_F x; \quad \beta = \frac{1}{\mu_F t}; \quad \mu(T) = \mu_F s(t). \tag{168}$$

Derive the units for x, t and $s(t)$. Using the expression for ρ in (167), show that (166) can be rewritten as

$$\frac{3}{2}\int_0^\infty \frac{\sqrt{x}dx}{1+e^{\frac{x-s(t)}{t}}} = 1; \qquad s(0) = 1. \tag{169}$$

which can be solved for $s(t)$. ∎

Fig. 1 shows a plot of $s(t)$ vs t. The chemical potential is a montonically decreasing function.

Problem 87: Let $s(t_F) = 0$. Show that

$$t_F = \left[\frac{3}{2}\int_0^\infty \frac{\sqrt{u}du}{1+e^u}\right]^{-\frac{2}{3}} = \left[\frac{3(\sqrt{2}-1)\sqrt{\pi}}{4\sqrt{2}}\zeta\left(\frac{3}{2}\right)\right]^{-\frac{2}{3}}. \tag{170}$$

Use the integral representation of the Riemann Zeta function to arrive at the second equality. Using $\zeta\left(\frac{3}{2}\right) \approx 2.61237535$, calculate t_F. Define $T_F = \frac{\mu_F t_F}{k}$ as the Fermi temperature. Explain the physics of the change in the energy of the system for $T = T_F$, $T < T_F$ and $T > T_F$. ∎

Problem 88: Let us define $\epsilon(\beta) = \mu_F u(t)$. Show that the energy per particle can be written as

$$\frac{u(t)}{\rho} = \frac{3}{2}\int_0^\infty \frac{x\sqrt{x}dx}{1+e^{\frac{x-s(t)}{t}}}. \tag{171}$$

Then show that

$$\frac{u(0)}{\rho} = \frac{3}{5}; \qquad \frac{u(t_F)}{\rho} = \frac{9}{16\sqrt{2}}(2\sqrt{2}-1)\sqrt{\pi}\zeta\left(\frac{5}{2}\right)t_F^{\frac{5}{2}}; \qquad \zeta\left(\frac{5}{2}\right) = 1.341487. \tag{172}$$

A plot of the energy per particle as a function of the dimensionless temperature is shown in Fig. 2. Explain the physics in the plot. ∎

You are strongly encouraged to work out the details for fermi gas in one and two dimensions.

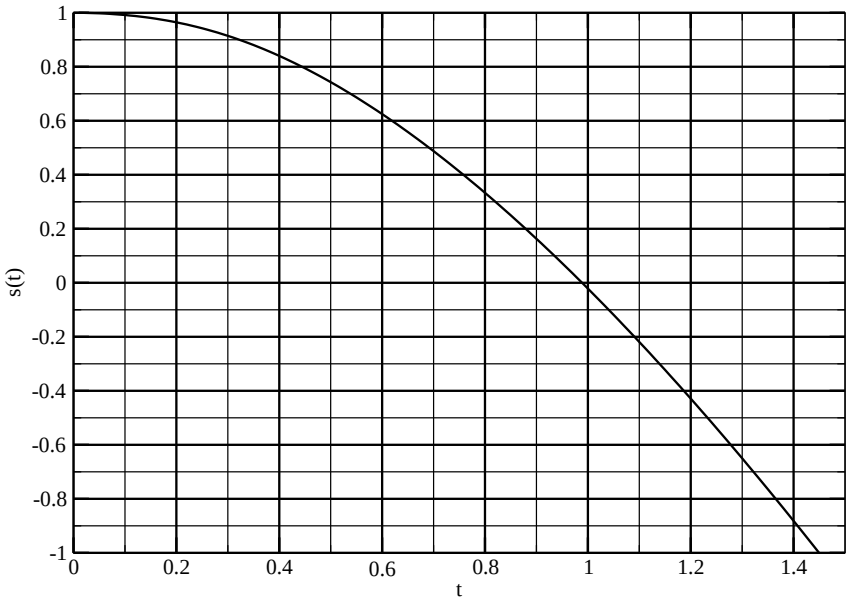

Figure 1: A plot of the dimensionless chemical potential $s(t)$ as a function of the dimensionless temperature, t.

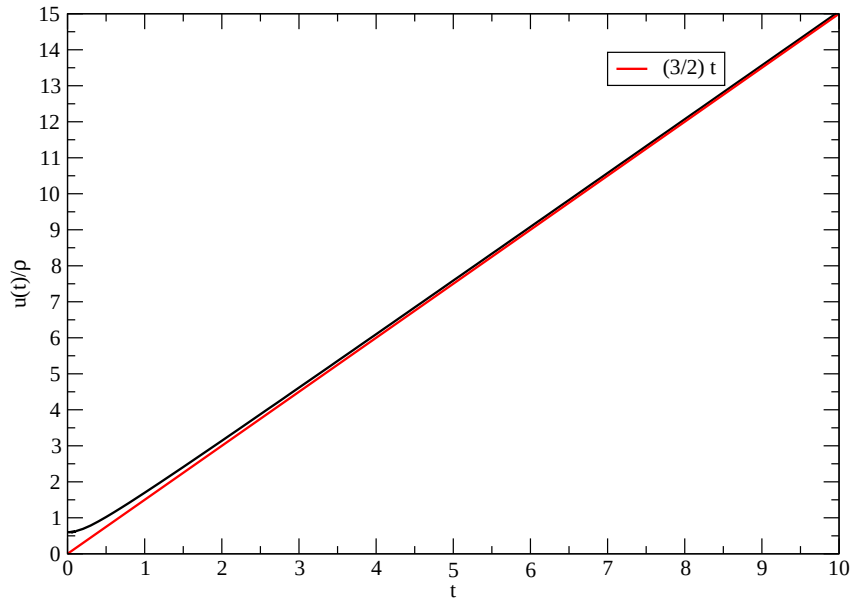

Figure 2: A plot of the energy per particle as a function of the dimensionless temperature, t.

12.2 Bosons

The particle number density is given by

$$\rho = \frac{1}{2\pi^2\hbar^3}\int_0^\infty \frac{p^2 dp}{e^{\beta\left(\frac{p^2}{2m}-\mu\right)}-1}, \tag{173}$$

Like in the case of fermons, let as assume that our volume does not change with temperature and assume that ρ remains the same for all temperature. The presence of the negative sign in the denominator will result in completely different physics compared to fermions.

Problem 89: Assuming no restriction on the momentum, p, show that $\mu \leq 0$. Explain the physics and how it contrasts with fermions. ■

Problem 90: In order to solve for $\mu(T)$ from the above equation, we will set

$$\alpha = e^{\beta\mu} \in [0,1]; \qquad x = \sqrt{\frac{\beta}{2m}}p. \tag{174}$$

What are the units of α and x? Show that the above integral reduces to

$$\rho = \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}} I(\alpha); \qquad I(\alpha) = \frac{4}{\sqrt{\pi}}\int_0^\infty \frac{\alpha x^2 e^{-x^2}}{1-\alpha e^{-x^2}}dx. \tag{175}$$

■

Problem 91: It is necessary to understand the integral, $I(\alpha)$, to proceed further. Using the expression for the geometric series, show the first equality in the equation below:

$$I(\alpha) = \frac{4}{\sqrt{\pi}}\sum_{n=1}^\infty \alpha^n \int_0^\infty x^2 e^{-nx^2}dx = \sum_{n=1}^\infty \frac{\alpha^n}{n^{\frac{3}{2}}} \equiv f_{\frac{3}{2}}(\alpha). \tag{176}$$

Show that the second equality follows from a standard integral. The last equality set the notation for the general function,

$$f_\mu(\alpha) = \sum_{n=1}^\infty \frac{\alpha^n}{n^\mu}. \tag{177}$$

Show that

$$\frac{df_\mu(\alpha)}{d\alpha} = \frac{1}{\alpha}f_{\mu-1}(\alpha). \tag{178}$$

■

Problem 92: We will assume without proof that the sum in (177) is convergent for $\mu = \frac{3}{2}$ if $\alpha < 1$. For $\alpha = 1$, show that $\mu = 0$ and $f_{\frac{3}{2}}(1) = \zeta\left(\frac{3}{2}\right) \approx 2.61237535$. Let the corresponding temperature be T_c. Show that

$$T_c = \frac{2\pi\hbar^2}{mk}\left[\frac{\rho}{\zeta\left(\frac{3}{2}\right)}\right]^{\frac{2}{3}}. \tag{179}$$

Set $T = T_c t$ and show that Eq. (175) reduces to

$$1 = t^{\frac{3}{2}}\frac{f_{\frac{3}{2}}(\alpha)}{\zeta\left(\frac{3}{2}\right)}. \tag{180}$$

Use the above result to show that

$$\frac{d\alpha}{dT} = -\frac{3\alpha}{2T}\frac{f_{\frac{3}{2}}(\alpha)}{f_{\frac{1}{2}}(\alpha)}. \tag{181}$$

Explain the range of t where the above equation can be used to solve for μ as a function of T and how will it depend on T. Explain the physics. ■

Problem 93: Since α cannot be greater than unity, explain why it has to stay unity for $0 < t < 1$. What is the physical meaning of this statement? Then show that the right-hand side of Eq. (175) becomes

$\rho t^{\frac{3}{2}}$. But we want the density to remain independent of temperature. Show that the density not accounted for by using $\alpha = 1$ in Eq. (175) is given by

$$\chi(t) = \rho\left(1 - t^{\frac{3}{2}}\right). \tag{182}$$

Go back to the sum over energies defined in Eq. (163) and explain why the conversion to an integral does not quite work and that is the reason for $\chi(t)$. ■

Note that $\chi(1) = 0$ and $\chi(0) = \rho$ and is the amount of the gas that has condensed for $T < T_c$. This phenomenon is referred to as Bose-Einstein condensation.

The energy density is given by

$$\epsilon(\beta) = \frac{1}{4m\pi^2\hbar^3}\int_0^\infty \frac{p^4 dp}{e^{\beta\left(\frac{p^2}{2m}-\mu\right)} - 1}. \tag{183}$$

Problem 94: Using the same procedure as for the particle number density, show that

$$\epsilon(\beta) = \frac{3}{2}\left[\frac{mkT}{2\pi\hbar^2}\right]^{\frac{3}{2}} kT f_{\frac{5}{2}}(\alpha). \tag{184}$$

Plot $\epsilon(\beta)$ as a function of T and discuss its small and high temperature behavior. ■

Problem 95: Show that the specific heat density is given by

$$c = \frac{d\epsilon(\beta)}{dT} = \begin{cases} \frac{15k}{4}\left[\frac{mkT}{2\pi\hbar^2}\right]^{\frac{3}{2}} f_{\frac{5}{2}}(\alpha) - \frac{9k}{4}\rho\frac{f_{\frac{3}{2}}(\alpha)}{f_{\frac{1}{2}}(\alpha)} & t > 1 \\ \frac{15k}{4}\left[\frac{mkT}{2\pi\hbar^2}\right]^{\frac{3}{2}} \zeta\left(\frac{5}{2}\right) & t < 1 \end{cases} \tag{185}$$

■

You are strongly encouraged to consider bosons in one and two dimensions and investigate if one can have Bose-Einstein condensation.

13 A simple model to understand phase transitions

This might seem deceptively close to the paramagnet but it is not. We will introduce interactions but do it in such a way the partition function can be computed easily. Consider an infinite solid arranged in a regular pattern called a lattice. Atoms live on the sites of the lattice and the links of the lattice are the bonds. Let A denote a particular atom. The nearest neighbors of A are the set of atoms attached to A by a bond.

1. One-dimensional lattice: Each atom has two nearest neighbors.
2. Two dimensional square lattice: Each atom has four nearest neighbors.
3. Three dimensional cubic lattice: Each atom has six nearest neighbors.
4. Two dimensional triangular lattice: Each atom has six nearest neighbors.
5. Two dimensional hexagonal lattice: Each atom has three nearest neighbors.
6. Three dimensional body-centered cubic lattice: Each atom has eight nearest neighbors.

Let n denote the number of nearest neighbors. Let the atom be described by a dipole with quantum number j like in the case of the multistate paramagnet in Section 11.5. The atom can therefore be in one of the $(2j+1)$ states with magnetic moment

$$m = -j, -j+1, -j+2, \cdots, j-2, j-1, j. \tag{186}$$

Let $\bar{m}$ denote the average magnetic moment and let the energy of atom A in state m be

$$E = -\epsilon n \bar{m} m, \tag{187}$$

where $\epsilon > 0$ is a unit of energy. Note that E is proportional to the number of nearest neighbors and this is our interaction – it is simple because it does not depend on the explicit state m of the neighbors and only an average. The energy is negative if $\bar{m}$ and m have the same sign and it is positive if $\bar{m}$ and m have the opposite sign. That is to say, the model energetically favors m and $\bar{m}$ to have the same sign and this is our model of an interacting ferromagnet.

Problem 96: Show that the partition function for a single atom is given by

$$Z = \sum_{m=-j}^{j} e^{\beta \epsilon n \bar{m} m}. \tag{188}$$

■

Note that $\beta\epsilon = \frac{\epsilon}{kT}$ is dimensionless and we can set that to $\frac{1}{t}$ such that $T = t\frac{\epsilon}{k}$.

Problem 97: Show that for the model to be consistent, the average magnetic moment obtained using the partition function should be $\bar{m}$:

$$\bar{m} = \frac{1}{Z} \sum_{m=-j}^{j} m e^{\beta \epsilon n \bar{m} m}. \tag{189}$$

Show by explicit computation that

$$\bar{m} = \left(j + \frac{1}{2}\right) \coth\left[\frac{n\bar{m}}{t}\left(j + \frac{1}{2}\right)\right] - \frac{1}{2}\coth\left[\frac{n\bar{m}}{t}\right], \tag{190}$$

where

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}}. \tag{191}$$

■

(190) is called a trancendental equation and one can solve it numerically for a given j, n and t. We can get a feel for the possible solutions by looking at the right hand side of (190).

Problem 98: For small x, Show using the Taylor's series of e^x that

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \cdots. \tag{192}$$

Using this show that the right hand side of (190) leads off as $\frac{j(j+1)n\bar{m}}{3t}$ for small $\bar{m}$. Also show independently that the right hand side of (190) approaches j as $\bar{m} \to \infty$. Then show that $\bar{m} = 0$ is a solution to this equation and will be the case as $t \to \infty$. Show that there is also a non-zero solution to $\bar{m}$, if $\frac{j(j+1)n}{3t} > 1$. ■

The behavior observed above is called a phase transition. the system undergoes a phase transition at the critical temperature $t_c = \frac{j(j+1)n}{3}$. As the system is cooled, the system moves from a demagnetized phase ($\bar{m} = 0$ for $t > t_c$) to a spontaneously magnetized phase ($\bar{m} \neq 0$ for $t < t_c$). Note that the critical temperature is proportional to $j(j+1)$ and n.

Problem 99: Pick one value for j and n. Plot the left-hand side and right-hand side of Eq. (190) as a function of $\bar{m}$. Graphically explain how spontaneous magnetization occurs. Explain why there are three possible solutions below t_c. Explain why the $\bar{m} = 0$ solution is not physical for $t < t_c$. This is a caricature of spontaneous magnetization. ■

14 Blackbody radiation – The need for the quantization of energy

Planck's law has its orgins in thermodynamics, namely black body radiation. From the solutions of the electromagnetic wave equation in vacuum (no matter), we know that we can have electric and magnetic field in vacuum with any energy, E, and any frequency, f. The vacuum will absorb any radiation directed toward it and it can be treated as a black body. Let T be the temperature of vacuum. Since $P(E) \propto e^{-\beta E}$ and all values of E are equally likely,

$$Z = \int_0^\infty dE e^{-\beta E} = \frac{1}{\beta}. \tag{193}$$

Problem 100: Show that

$$\overline{E} = -\frac{d}{d\beta} \ln Z = kT. \tag{194}$$

Explain the physics. ∎

The frequency of the electromagnetic wave can be written as $f = cn$ where c is the speed of light and n is the wavenumber which has units of inverse length. The total number of waves in unit volume with wavenumber n is $2 \times 4\pi n^2 dn$ where the first factor of 2 comes from the two possible solutions to the wave equation for a fixed $\vec{n}$ and the second factor of $4\pi n^2 dn$ is the volume of a thin spherical shell of radius n and thickness dn.

In order to find the total energy density radiated by a blackbody at a certain temperature, T, we need to take our expression for the total number of waves per unit volume and multiply by the average energy, $\overline{E}$ of a wave with wavenumber n and then integrate over all values of n.

Problem 101: Put it together and show that the energy density radiated (or absorbed) by a blackbody at a temperature, T, is equal to

$$8\pi kT \int_0^\infty n^2 dn = \infty \tag{195}$$

demonstrating the failure of classical mechanics. ∎

Let us convert the integral in (193) to a Riemann sum with the aim of keeping the result finite. Let us write, $E = jhf$ where $j = 0, 1, 2, \cdots, \infty$ and hf is the width of each bin in the Riemann sum. We can think of h as a small parameter than needs to to be taken to zero in order to convert the Riemann sum to an integral. The single factor of f in the bin width will become clear at the end of the calculation.

Problem 102: Show that partition function becomes a sum and is

$$Z = \sum_{j=0}^{\infty} e^{-\beta jhf} = \frac{1}{1 - e^{-\beta hf}}. \tag{196}$$

Then show that the average energy becomes,

$$\overline{E} = -\frac{d}{d\beta} \ln Z = \frac{hf}{e^{\beta hf} - 1}. \tag{197}$$

Show that $\lim_{h\to 0} \overline{E} = kT$ but our aim is not take this limit yet. ∎

Problem 103: Let us take the expression for $\overline{E}$ in (197) and compute the energy density radiated (or absorbed) by a blackbody at temperature, T. Using $f = nc$, show that the result is

$$8\pi hc \int_0^\infty \frac{n^3}{e^{\beta hnc} - 1} dn = \frac{8\pi k^4}{(hc)^3} \frac{\pi^4}{15} T^4 = \sigma T^4; \qquad \sigma = \frac{8\pi^5 k^4}{15 h^3 c^3}. \tag{198}$$

You should have used the known integral

$$\int_0^\infty \frac{u^3}{e^u - 1} du = -2\pi^4 B_4 = \frac{\pi^4}{15}, \tag{199}$$

where B_4 is a Bernoulli number, to arrive at the result. ∎

We have obtained a finite result that is proportional to T^4 as long as $h \neq 0$. The constant of proportionality called the Stefan-Boltzmann constant, obtained from experiment, can be used to fix the *physical* value of h, the Planck's constant, since we know k and c.

Problem 104: Show that changing $E = jhf$ to $E = jhf^p$ where p is some arbitrary power will result in a temperature dependence of the form $T^{\frac{p+3}{p}}$. Hence show that only $p = 1$ gives the correct power of T obtained by experiments. ∎