

PHYS 427 - Discussion 02 Solutions

Feb. 4, 2025

1. **2D ideal gas.** In lecture last week, you derived the entropy of a monatomic ideal gas in a 3D box. Steps from that derivation will show up again later in the the course, so we need to understand them well. In this problem, we repeat those arguments for a gas confined to a two-dimensional box¹ (also known as a rectangle).

Our box is a square rectangle with side length L . The gas particles are non-interacting (“ideal”), so at first we just consider one monatomic² particle in the box. From Schrödinger’s equation, one finds that the quantum states of the particle (eigenstates of the Hamiltonian) are uniquely labelled by two numbers $n_x = 1, 2, \dots, \infty$ and $n_y = 1, 2, \dots, \infty$. That is, if you tell me the values of n_x and n_y , I will know exactly what state the particle is in. The particle’s momentum in this state is $\vec{p} = \hbar \vec{k}$ where $\vec{k} = \frac{\pi n_x}{L} \hat{x} + \frac{\pi n_y}{L} \hat{y}$, so the particle’s energy is

$$\varepsilon_{n_x, n_y} = \frac{p^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2), \quad (1)$$

where m is the particle’s mass. This is all the quantum mechanics we will need.

- (a) Draw a graph with axes labelled k_x and k_y (the components of the vector \vec{k}). Draw the possible quantum states of a single gas particle as dots on this graph. Indicate the values of the horizontal and vertical spacings between the dots. How many states are there per unit \vec{k} -space area?

Solution. The dots form a square lattice of equally spaced points in the upper-right quadrant of k_x - k_y the plane (see plot in lecture note 4). The horizontal and vertical spacings between these points are both equal to π/L . There are on average $\frac{1}{(\pi/L)(\pi/L)} = L^2/\pi^2$ states per unit \vec{k} -space area.

- (b) How many states are there with energy between ε and $\varepsilon + d\varepsilon$? *Hint: Use your graph from part (a). You might find yourself drawing two quarter-circles in \vec{k} -space with very similar radii. . .*

Solution. By solving $\varepsilon = \frac{\hbar^2 k^2}{2m}$, we see that the states with energies near ε lie a distance $k = \sqrt{2m\varepsilon}/\hbar$ from the origin of \vec{k} -space. The states with energies between ε and $\varepsilon + d\varepsilon$ lie inside a thin annulus³ in \vec{k} -space. In fact, by taking the differential of $k = \sqrt{2m\varepsilon}/\hbar$, we see that this annulus has approximate thickness $dk = \frac{1}{\hbar} \sqrt{\frac{m}{2\varepsilon}} d\varepsilon$. The area of this \vec{k} -space annulus is approximately its circumference multiplied by its thickness, i.e. $2\pi k dk$, and the number of states in the annulus is its area multiplied by the final result of part (a), i.e. $2\pi k dk \cdot (L^2/\pi^2)$. Inserting the expressions we just found for k and dk , and dividing by 4 to account for the fact that we only consider positive values for k_x and k_y , our final answer is

$$\frac{1}{4} 2\pi k dk \cdot (L^2/\pi^2) = \frac{mL^2}{2\pi\hbar^2} d\varepsilon. \quad (2)$$

Optional challenge: justify the approximations you made⁴.

¹Studying a 2D gas is not only an academic exercise—refinements of this model can describe the mobile electrons trapped on an interface between two different materials. Google “2DEG” after class.

²Our particle isn’t necessarily an atom. It just doesn’t have any internal structure (or such structure must be negligible).

³An annulus is the region between two concentric circles of different radii.

⁴The answer is valid when $\frac{\hbar}{L} \sqrt{\frac{\varepsilon}{m}} \ll d\varepsilon \ll \varepsilon$. It’s possible to find such a $d\varepsilon$ if the box is big enough, namely if $L \gg \hbar/\sqrt{m\varepsilon}$.

Solution. For the area of the annulus to be well approximated by its circumference $2\pi k$ multiplied by its thickness dk , we need $k \gg dk$, which is equivalent to $\varepsilon \gg d\varepsilon$. For the number of states in the annulus to be well approximated by its \vec{k} -space area times the density from part (a), the thickness should be much greater than the separation between states, i.e. $dk \gg \pi/L$, which (using $dk = \frac{1}{\hbar} \sqrt{\frac{m}{2\varepsilon}} d\varepsilon$ and discarding numerical factors of order one) is equivalent to $d\varepsilon \gg \frac{\hbar}{L} \sqrt{\frac{\varepsilon}{m}}$. It's possible to find a $d\varepsilon$ satisfying both of these conditions only if $L \gg \hbar/\sqrt{m\varepsilon}$, which we can think of as a “large box” limit. If we use the fact that a typical single-particle energy of interest is of order $k_B T$ (this can be shown a posteriori with the equipartition theorem), then the condition becomes $L \gg \hbar/\sqrt{mk_B T}$. The quantity appearing on the right-hand side is proportional to the *thermal de Broglie wavelength* that will be defined later in the course. Physically, it represents the typical value of the quantum-mechanical de Broglie wavelength of a particle in the gas. At room temperature for a gas of helium atoms, we find that the box must be much much larger than about an angstrom, which is of order the size of an atom. So a gas in any human-scale box should be well described by our theory near human-scale temperatures.

- (c) If you were to divide your answer to part (b) by $d\varepsilon$, you would get the *density of states per unit energy*, denoted $\mathcal{D}(\varepsilon)$. Briefly explain why it deserves this name. We will use this construction very often later in the course. What happens to $\mathcal{D}(\varepsilon)$ as $L \rightarrow \infty$? Does the limit make sense?

Solution. From our calculation in part (b), we see that $\mathcal{D}(\varepsilon)d\varepsilon$ equals the number of states with energies between ε and $\varepsilon + d\varepsilon$. Therefore $\mathcal{D}(\varepsilon)$ is the number of states per unit energy interval. Note that $\mathcal{D}(\varepsilon)$ doesn't depend on ε for our 2D system of a freely moving non-relativistic particle, but this is not true in 3D, or if the particle is moving at relativistic speeds, or if the particle is under the influence of an external field (e.g. if it is trapped in a harmonic potential).

When $L \rightarrow \infty$, $\mathcal{D}(\varepsilon) \rightarrow \infty$. This is a statement of the fact that the spacing between allowed energy levels of a bound quantum system becomes very small when the system becomes very large, i.e. the discrete spectrum approaches a continuum.

Now consider a gas of N particles. The quantum state of the gas is specified by $2N$ positive integers $n_{x1}, n_{y1}, n_{x2}, n_{y2}, \dots, n_{xN}, n_{yN}$. The total energy of the gas in such a state is

$$U_{\{n\}} = \frac{\hbar^2 \pi^2}{2mL^2} (n_{x1}^2 + n_{y1}^2 + n_{x2}^2 + n_{y2}^2 + \dots + n_{xN}^2 + n_{yN}^2). \quad (3)$$

The last factor is the square of the radius of a $2N$ -dimensional sphere. The volume of a D -dimensional sphere with radius R is

$$V_D(R) = \frac{\pi^{D/2}}{\Gamma(\frac{D}{2} + 1)} R^D. \quad (4)$$

For the purposes of this problem, the constants are not important and it is enough to write

$$V_D(R) = \frac{(CR)^D}{N!}, \quad (5)$$

for some constant C .

- (d) How many states does the gas have with energies between U and $U + dU$? *Hint: The particles are indistinguishable, so in your final answer you should include an additional factor of $1/N!$ by hand to compensate for overcounting.*

Solution. Now the states are represented by discretely spaced points in the $2N$ -dimensional space whose coordinates are $k_{x1}, k_{y1}, k_{x2}, k_{y2}, \dots, k_{xN}, k_{yN}$. By arguments analogous to part (a), there are $(L/\pi)^{2N}$ states per unit volume in this $2N$ -dimensional space.

The volume of the region between two spheres is

$$\frac{(C[k + dk])^{2N}}{N!} - \frac{(Ck)^{2N}}{N!} \approx \frac{2C^{2N}}{(N-1)!} k^{2N-1} dk, \quad (6)$$

where $k = \sqrt{k_{x1}^2 + k_{y1}^2 + \dots + k_{xN}^2 + k_{yN}^2}$ is the radial coordinate in the $2N$ -dimensional space. In analogy with in part (b), multiplying this by $(L/\pi)^{2N}$ gives the answer we're looking for. We should also use $U = \frac{\hbar^2 k^2}{2m}$ to eliminate k in favor of U , and multiply by an overall factor of $1/N!$ to approximately correct for overcounting, because the particles are indistinguishable. The result is

$$\frac{1}{N!} \frac{C^{2N}}{(N-1)!} \left(\frac{2m}{\hbar^2 \pi^2} \right)^N U^{N-1} L^{2N} dU. \quad (7)$$

- (e) In part (e), you found that there are $\Omega \approx f(N)V^N U^N dU$ states accessible to a gas of N non-interacting particles in a $2D$ box when the energy is restricted to a tiny interval $(U, U+dU)$. Here $V = L^2$ is the “volume” (actually area) of the $2D$ box and $f(N)$ is some complicated function of N that is unimportant for this problem. Compute the temperature $1/T \equiv (\partial S/\partial U)_{V,N}$. If you remember the equipartition theorem from PHYS 213, comment on how it relates to your answer (if you don't remember, don't worry, we'll study it later in the course). Compute the pressure $p \equiv T(\partial S/\partial V)_{U,N}$ of the gas and appreciate how familiar the result is.

Solution. We have

$$S/k_B = \ln \Omega = N \ln V + N \ln U + \text{stuff that only depends on } N. \quad (8)$$

Then

$$\frac{1}{T} = \frac{Nk_B}{U} \implies U = 2 \cdot \frac{1}{2} Nk_B T \quad (9)$$

This way of writing it highlights the connection with the equipartition theorem. The gas has $2N$ quadratic degrees of freedom, the 2 translational degrees of freedom for each of the N particles. The equipartition theorem says each quadratic degree of freedom contributes on average $k_B T/2$ to the total energy. Next,

$$p = k_B T \frac{N}{V} \implies pV = Nk_B T. \quad (10)$$

Ah, nice. Evidently the familiar ideal gas law holds in two dimensions too. Note that V here is really the area L^2 , as mentioned in the problem statement.

2. *Fun with multiplicity functions.* Find the multiplicity Ω for the following closed systems.

- (a) One 3D harmonic oscillator with frequency ω and total energy $U = \hbar\omega\tilde{n}$, where \tilde{n} is a non-negative integer. The microstates of this system are uniquely specified by three integers, n_x , n_y , and n_z , each of which can take any integer value from zero to infinity. The energies of the microstates are given by $\varepsilon_{n_x, n_y, n_z} = \hbar\omega(n_x + n_y + n_z)$.

Solution. We need to find the number of microstates whose energies $\hbar\omega(n_x + n_y + n_z)$ equal the given total energy $\hbar\omega\tilde{n}$. That is, we need to find the number of ways of choosing distinct triplets (n_x, n_y, n_z) of non-negative integers that add up to \tilde{n} , i.e. $\tilde{n} = n_x + n_y + n_z$. The answer is given by the “stars and bars” argument discussed on page 2 of lecture 2, with \tilde{n} stars and $3 - 1 = 2$ bars. The answer is

$$\Omega = \binom{2 + \tilde{n}}{\tilde{n}}. \quad (11)$$

- (b) N non-interacting 3D harmonic oscillators sitting in a row, sharing a total energy $U = \hbar\omega\tilde{n}$. Each oscillator has the same frequency ω . Note that the oscillators are distinguishable (by their position in the row).

Solution. Now we need to find the number of ways of choosing non-negative integers $(n_{x1}, n_{y1}, n_{z1}, n_{x2}, n_{y2}, n_{z2}, \dots, n_{xN}, n_{yN}, n_{zN})$ adding up to \tilde{n} . Note that rearrangements of these integers do *not*

correspond to the same state, because the oscillators are distinguishable. We have $3N - 1$ bars and \tilde{n} stars, so

$$\Omega = \binom{3N - 1 + \tilde{n}}{\tilde{n}} \quad (12)$$

This is the Einstein model of the vibrations of a 3D solid consisting of N ions.

- (c) One quantum dumbbell⁵ with moment of inertia I and total energy $U = \frac{\hbar^2}{2I} \tilde{\ell}(\tilde{\ell} + 1)$, where $\tilde{\ell}$ is a non-negative integer. A quantum dumbbell is a rod with two equal weights on the end. It can rotate about its center in two independent directions, but it cannot spin about the rod's axis. From the Schrödinger equation, one finds that the microstates of a quantum dumbbell are uniquely specified by two integers, ℓ and m , where $\ell = 0, 1, 2, \dots, \infty$ and $m = -\ell, -\ell + 1, \dots, \ell - 1, \ell$. The energies of the microstates only depend on ℓ ; they are given by $\varepsilon_{\ell m} = \frac{\hbar^2}{2I} \ell(\ell + 1)$.

Solution. Note that the quantum number ℓ is fully determined by the energy. Therefore only the microstates with $\ell = \tilde{\ell}$ are accessible. There are $2\tilde{\ell} + 1$ such microstates, because that's the number of possible choices for the value of m .

$$\Omega = 2\tilde{\ell} + 1. \quad (13)$$

- (d) Two quantum dumbbells sitting in a row, sharing a total energy $U = \frac{\hbar^2}{2I} \tilde{n}$, where \tilde{n} is a non-negative integer. Each dumbbell has the same moment of inertia I . Note that the dumbbells are distinguishable (by their position in the row). First, explicitly work out the multiplicities when $\tilde{n} = 0, 2, 4, 6, 8, 10$, then do it for arbitrary \tilde{n} . *Hint: Give up on this problem when you become convinced that it is very difficult (probably impossible) for arbitrary \tilde{n} ! We have learned: 1) a small adjustment of an easy counting problem can make it impossibly hard, which means 2) the microcanonical ensemble (i.e. the multiplicity-based approach for closed systems), which relies on counting large numbers of arrangements, is difficult to work with for all but the simplest models. That said, a collection of N quantum dumbbells can be studied with relative ease using the so-called canonical ensemble, which will be introduced soon in the lectures.*

Solution. We need to count the number of quantum states $([\ell_1, m_1], [\ell_2, m_2])$ such that

$$\ell_1(\ell_1 + 1) + \ell_2(\ell_2 + 1) = \tilde{n}. \quad (14)$$

If there is no energy in the system, i.e. if $\tilde{n} = 0$, we have no choice but to have $\ell_1 = \ell_2 = 0$, and then we have no choice but to have $m_1 = m_2 = 0$. That is, there is only one state, so $\Omega = 1$.

When $\tilde{n} = 2$, we can have $\ell_1 = 1$ and $\ell_2 = 0$, in which case we can have $m_1 = -1, 0, 1$ but we must have $m_2 = 0$. This accounts for three states. We can also have $\ell_1 = 0$ and $\ell_2 = 1$, in which case we must have $m_1 = 0$ but we can have $m_2 = -1, 0, 1$. This accounts for three more states. There are no other possibilities. So, denoting the multiplicity as $\Omega(\tilde{n})$, we have $\Omega(2) = 6$.

Following similar reasoning, I find: $\Omega(4) = 9$, $\Omega(6) = 10$, $\Omega(8) = 16$, $\Omega(10) = 0$. I can't discern a pattern... can you?

3. **Einstein solid.** Consider the system defined in problem 2(b). We say that n quanta are shared among the oscillators. A *quantum* refers to a packet of energy equal to $\hbar\omega$. Assume $N, n \gg 1$, but do not assume any relationship between N and n .

- (a) Compute the entropy using Stirling's approximation. (You can use your results from Homework 1).

Solution. This is essentially one of the homework problems. The answer is just what you found in the homework, but with N replaced by $3N$.

- (b) Compute the number of quanta per oscillator as a function of N and the temperature T . Observe the appearance of the *Bose-Einstein distribution function* $f(x) = 1/(e^x - 1)$ in your answer. This function is important and it will appear a lot in this course. What are the limits of your answer

⁵More precisely, a quantum mechanical linear rigid rotor. This is a model for the rotational states of a diatomic molecule.

when T is big or small? (Compared to what? Always ask yourself this when someone claims a dimensionful quantity is big or small.)

Solution. This is also essentially a homework problem. The answer is

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/k_B T} - 1}. \quad (15)$$

The total number of quanta n , by definition, is the total number of packets of size $\hbar\omega$ that make up U . That is, $n = U/\hbar\omega$. The number of quanta per oscillator is

$$\frac{n}{N} = \frac{3}{e^{\hbar\omega/k_B T} - 1}. \quad (16)$$

As you found in the homework, when $k_B T/\hbar\omega \gg 1$, we have $n/N \approx 3\hbar\omega/k_B T \gg 1$. When $k_B T \ll 1$, we have $n/N \approx 3 \exp(-\hbar\omega/k_B T) \ll 1$.

- (c) Compute the heat capacity⁶ at constant volume, $C_V = (\partial U/\partial T)_{V,N}$. Show that $\lim_{T \rightarrow \infty} C_V = 3Nk_B$, which is the celebrated Dulong-Petit law. The Dulong-Petit law agrees well with experiments, but the Einstein solid fails to predict the experimentally observed C_V at low temperatures. We'll do better later in the course with the so-called Debye model.

Solution. From part (b), we have

$$C_V = \frac{\partial}{\partial T} \left(\frac{3N\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \right) \quad (17)$$

$$= -\frac{3N\hbar\omega}{(e^{\hbar\omega/k_B T} - 1)^2} e^{\hbar\omega/k_B T} \left(-\frac{\hbar\omega}{k_B T^2} \right) \quad (18)$$

$$= 3Nk_B (\hbar\omega/k_B T)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \quad (19)$$

$$= 3Nk_B \frac{x^2 e^x}{(e^x - 1)^2}, \quad (20)$$

where I defined $x = \hbar\omega/k_B T$. We want the limit as $k_B T \gg \hbar\omega$, i.e. $x \ll 1$. The denominator is approximately $(e^x - 1)^2 \approx (1 + x - 1)^2 = x^2$. This cancels the x^2 in the numerator, and the remaining e^x asymptotes to 1. So we get $C_V \rightarrow 3Nk_B$. Another way of stating this law is to say $U \approx 3Nk_B T$ at high temperatures. That's the equipartition theorem for a system with $6N$ quadratic degrees of freedom. Those are the 6 quadratic degrees of freedom in the Hamiltonian for each of the N ions. Three of those terms are the translational kinetic energy terms proportional to p_x^2 , p_y^2 , p_z^2 , and the other three are the potential energy terms proportional to x^2 , y^2 , and z^2 .

The Einstein model has the right number of degrees of freedom for a solid consisting of N ions, and the equipartition theorem says that the number of quadratic degrees of freedom is the only thing that determines C_V in the high-temperature (classical) limit. But the Einstein model gets the microscopic physics of those degrees of freedom wrong, which makes a difference for C_V at finite temperatures.

⁶Quick review of heat capacity from PHYS 213. Let dQ be the amount of heat we need to add to the system to change the temperature by dT . The heat capacity is *defined* as the ratio $C \equiv dQ/dT$. If we perform the heating process while keeping the volume (and particle number) constant, then work done by the system on its surroundings is $dW = -pdV = 0$, so the 1st law of thermodynamics tells us the change in internal energy is $dU = dQ + dW = dQ$. That's why $C_V = (\partial U/\partial T)_{V,N}$.