

Six Ideas That Shaped Physics: Unit T

**Sections T4A.4–5
Sections T5A.1–3
(an alternative to the
published textbook)**

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Why the average energy is interesting

The average energy of a quantum system (qs) is interesting for a variety of reasons, but one of the most important is the following. Consider a macroscopic object at temperature T that is comprised of N_{qs} identical quantum systems. If N_{qs} is very large, we can imagine each quantum system to be in contact with a reservoir consisting of the remaining systems. Under these circumstances, the object's total thermal energy U is very nearly

$$U = N_{\text{qs}} E_{\text{avg}} \quad (\text{T4A.26})$$

Therefore, knowing a quantum system's average energy at a given temperature T means that we can calculate the total thermal energy U of an object made up of such quantum systems without having to know anything about the system's multiplicity Ω . Since it is difficult to determine Ω for most systems other than an Einstein solid, this can be *very* useful.

Example T4A.3

Problem: Suppose that a certain kind of molecule in a solution at room temperature can be in one of either of two quantum states, which have energies $E_0 = 0$ and $E_1 = \varepsilon$ respectively, where $\varepsilon = 0.020$ eV. What is the average energy of such a molecule? If the solution contains 10^{22} such molecules, what is the total thermal energy U stored by the excited molecules?

Solution The quantum system in this case is an individual molecule; the reservoir is the rest of the solution. Since each molecule is a quantum system, the number of molecules N is the same as the number of quantum systems N_{qs} . In this case, we can write out the sums in equation T4.25 explicitly:

$$E_{\text{avg}} = \frac{E_0 e^{-E_0/k_B T} + E_1 e^{-E_1/k_B T}}{e^{-E_0/k_B T} + e^{-E_1/k_B T}} = \frac{0 + \varepsilon e^{-\varepsilon/k_B T}}{e^0 + e^{-\varepsilon/k_B T}} = \frac{\varepsilon e^{-\varepsilon/k_B T}}{1 + e^{-\varepsilon/k_B T}} = \varepsilon \left(\frac{1}{e^{\varepsilon/k_B T} + 1} \right) \quad (\text{T4A.27})$$

where in the last step I multiplied top and bottom by $e^{\varepsilon/k_B T}$. At room temperature $k_B T \approx 0.0254$ eV, so $\varepsilon/k_B T = (0.020 \text{ eV}) / (0.0254 \text{ eV}) = 0.79$ here. Therefore

$$E_{\text{avg}} = \varepsilon \left(\frac{1}{e^{0.79} + 1} \right) = 0.313\varepsilon = 0.00625 \text{ eV} \quad (\text{T4A.28})$$

The total thermal energy U associated with N such molecules is

$$U = N E_{\text{avg}} = 0.313 N \varepsilon = 0.31 (10^{22}) (0.020 \text{ eV}) \left(\frac{1.60 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 10.0 \text{ J} \quad (\text{T4A.29})$$

Let's check equation T4A.28 by using equation T4.8 to calculate the states' probabilities directly and then using equation T4A.23 to find the average energy. The probability that the molecule is in the excited state is

$$\text{Pr}(E_1) = \frac{e^{-\varepsilon/k_B T}}{Z} = \frac{e^{-\varepsilon/k_B T}}{e^0 + e^{-\varepsilon/k_B T}} = \frac{1}{e^{\varepsilon/k_B T} + 1} \quad (\text{T4A.30})$$

which is the same as the quantity in parentheses in equation T4A.27. So we see in this case that the atom has a probability of 0.313 of being in the excited state and thus a probability of 0.687 of being in the ground state. The average energy is thus $0 \cdot 0.687 + \varepsilon(0.313) = 0.313\varepsilon$.

T4A.4 Application to the Einstein Solid

The method outlined in the last section provides a powerful tool for connecting models of microscopic quantum systems to the observable thermal behavior of macroscopic systems. In this section, I will illustrate this by considering again the Einstein solid.

As we saw in chapter T2, an Einstein solid is essentially a collection of $3N$ independent quantum oscillators. Let's take a single quantum oscillator as our microscopic system, and consider the other $3N - 1$ oscillators in the solid as a reservoir at temperature T (as long as $N \gg 1$, this should be an excellent approximation). The partition function for a single oscillator is

$$\begin{aligned} Z &= e^{-E_0/k_B T} + e^{-E_1/k_B T} + e^{-E_2/k_B T} + \dots = 1 + e^{-\epsilon/k_B T} + e^{-2\epsilon/k_B T} + \dots \\ &= 1 + x + x^2 + \dots \quad \text{where } x \equiv e^{-\epsilon/k_B T} \end{aligned} \quad (\text{T4A.31})$$

Note that $x < 1$ in this expression. A well-known mathematical identity tells us that when $x < 1$, this infinite power series has a closed-form equivalent:

$$1 + x + x^2 + \dots = \frac{1}{1 - x} \quad (\text{T4A.32})$$

Also note that we can write the sum in the numerator of equation T4.25 as

$$\sum (\epsilon n) e^{-\epsilon n/k_B T} = \epsilon (0 + x + 2x^2 + 3x^3 + \dots) \quad (\text{T4A.33})$$

The sum in parentheses also has a simple value for $x < 1$ (as you can check by looking online or using WolframAlpha):

$$1x + 2x^2 + 3x^3 + \dots = \frac{x}{(1 - x)^2} \quad (\text{T4A.34})$$

Therefore, equation T4.25 implies that the average energy in a quantum oscillator in an Einstein solid is

$$E_{\text{avg}} = \frac{\sum E_n e^{-E_n/k_B T}}{\sum e^{-E_n/k_B T}} = \frac{\epsilon \sum n x^n}{\sum x^n} = \frac{\epsilon x / (1 - x)^2}{1 / (1 - x)} = \frac{\epsilon x}{1 - x} \quad (\text{T4A.35})$$

This means that the total thermal energy in an Einstein solid with N atoms ($3N$ oscillators) must be

$$U = 3N E_{\text{avg}} = \frac{3N \epsilon e^{-\epsilon/k_B T}}{1 - e^{-\epsilon/k_B T}} = \frac{3N \epsilon}{e^{\epsilon/k_B T} - 1} \quad (\text{T4A.36})$$

at *any* absolute temperature T . This is much better than we could do in chapter T3, where we could only get a high-temperature limit.

Now, we define an object's **heat capacity** C to be dU/dT , the ratio of the amount of heat (or other external energy) dU that we put into the object to the differential temperature change dT that results. (The capital C distinguishes heat capacity from *specific* heat c , which is the heat capacity per unit mass.) C is easier to measure experimentally than an object's total thermal energy U . With a bit of work, we can show that an Einstein solid's heat capacity is

$$C \equiv \frac{dU}{dT} = \frac{d}{dT} \left(\frac{3N \epsilon}{e^{\epsilon/k_B T} - 1} \right) = \frac{3N k_B e^{\epsilon/k_B T}}{(k_B T / \epsilon)^2 (e^{\epsilon/k_B T} - 1)^2} \quad (\text{T4A.37})$$

Exercise T4AX.2

Fill in the missing steps in equation T4A.37. (This is just basic calculus.)

The quantity $k_B T / \varepsilon$ is a unitless quantity proportional to the temperature. We can think of it as being a ratio T/T_E where

$$T_E \equiv \frac{\varepsilon}{k_B} = \text{the solid's Einstein temperature} \quad (\text{T4A.38})$$

is a reference temperature that depends on the spacing ε between our particular solid's oscillator energy levels: it is the temperature where $k_B T_E = \varepsilon$. This provides a physical temperature scale for the solid.

Now equation T4A.37 (repeated below using T/T_E for easy reference)

$$\frac{dU}{dT} = \frac{3Nk_B e^{T_E/T}}{(T/T_E)^2 (e^{T_E/T} - 1)^2} \quad (\text{T4A.39})$$

is a pretty complicated function, but fortunately, one can find computer tools (for example, <http://www.wolframalpha.com>) makes plotting even complicated functions pretty straightforward. The solid line in figure T4A.4 shows graphs of this function against experimental data for iron and gold. Note that at high temperatures, equation T4A.39 does imply that $C = dU/dT \approx 3Nk_B$, just as we found in chapter T3. The Einstein model does a decent job of modeling the basic shape of the data, but deviates at both high and low temperatures. This is mostly because at high temperatures, free electrons can store some energy and the atomic oscillators are not perfect harmonic oscillators, and at low temperatures because the assumption that the atoms oscillate independently of each other becomes a poor approximation. Peter Debye in 1912 developed a more complicated model (beyond our scope here) that better describes the low-temperature behavior of solids.

However, the Einstein model does pretty well for a simple model. In particular, it describes two crucial features of the experimental data. The first is that a solid's heat capacity (approximately) levels off at about k_B per oscillator ($3k_B$ per atom) at sufficiently high temperatures. This explains why (noted in chapter T1) the heat capacities of *all* monatomic solids are pretty close to $3Nk_B$ at room temperature.

Even more importantly, it predicts (at least qualitatively) the observed sharp decrease in a solid's heat capacity as temperature decreases. We can understand this as follows. At $T \gg T_E$, meaning that $k_B T \gg \varepsilon$, the formula tells us that an oscillator's *average* energy approaches $k_B T$. We can consider this the "classical" behavior of the system, that is, its behavior when there is so much energy in each oscillator that the fact that its energy is quantized instead of continuously variable is not significant.

But as the solid's temperature T approaches T_E (meaning that $k_B T$ approaches ε), an average oscillator contains just *one* unit of energy. Now the fact that an oscillator's energy levels are quantized has more effect. Note that an oscillator must have at least one unit of energy to have *any* energy at all. As the temperature continues to fall below T_E , the probability that an oscillator has even *one* unit of energy becomes small, and the number of oscillators having exactly *zero* energy begins to weigh disproportionately in the average energy per oscillator, drawing it down below $k_B T$ and the heat capacity per oscillator below k_B . The Boltzmann factor in fact implies that the probability that an oscillator contains even one unit of energy becomes exponentially suppressed as T becomes much smaller than T_E ($k_B T \ll \varepsilon$), so the ability of the solid to store *any* heat at all also becomes exponentially suppressed. We say that at temperatures $T \ll T_E$, the oscillators are "frozen out" of the normal process of storing energy.

A graph of the heat capacity actually provides a means of estimating the effective spring constant of the forces holding an atom in position in a crystal. As discussed in unit Q, the difference ε between a quantum oscillator's

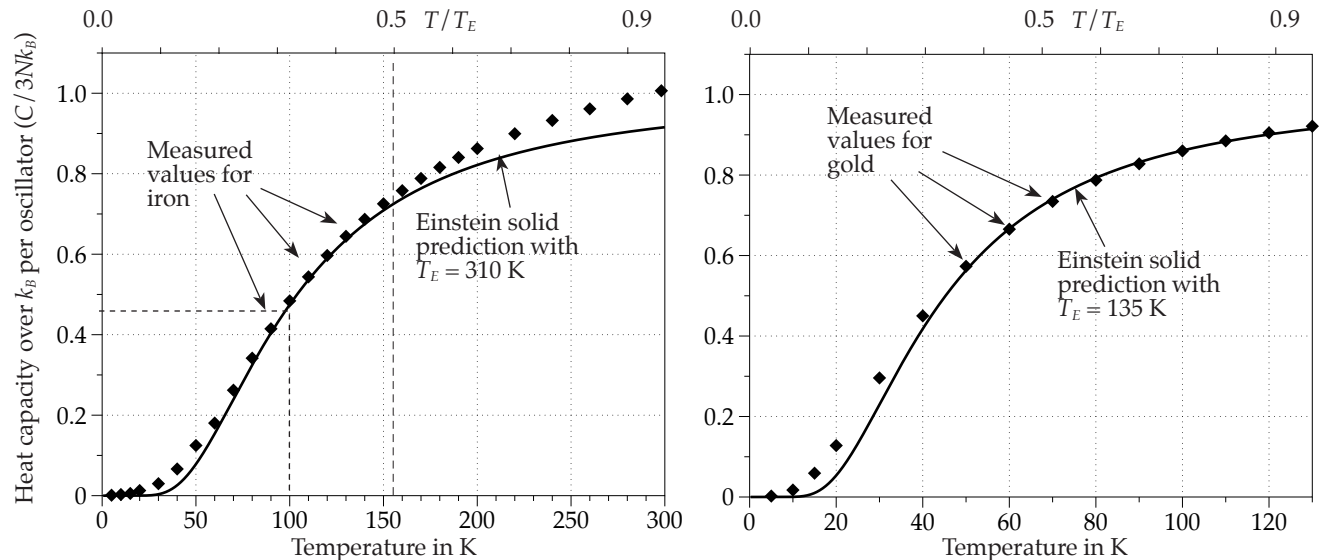


Figure T4A.4

The vertical axis shows heat capacity (in units of k_B per oscillator), while the solid line shows the prediction of the Einstein model. The diamonds show actual measured results. The data for iron is from Desai, *J. Chem. Ref. Data*, **15**, 3, 1986), and that for gold is from the *CRC Handbook* (64th edition, 1983, page D-94). Note that while T_E is different for iron and gold, the basic shape of the graph of experimental heat capacities as a function of T/T_E is nearly the same for both.

energy levels is related to the angular frequency ω at which the oscillator would oscillate classically: $\varepsilon = \hbar\omega$. As we saw in unit N, ω in a classical oscillator is related to the mass of the oscillating object and the spring constant k_s of the spring-like forces that try to hold the object at its equilibrium position: $\omega = (k_s/m)^{1/2}$. We can estimate $T_E = k_B/\varepsilon$ by looking at the curve of a solid's heat capacity and so compute k_s from that, as the example below illustrates.

Problem: What is the effective value of the spring constant k_s for iron atoms?

Solution The solid curve in figure T4A.4 was drawn assuming $T_E = 310$ K for iron, but let's estimate T_E assuming we don't know this. The heat capacity per oscillator for iron is about $0.47k_B$ at $T = 100$ K. From the graph, this is about $0.32T_E$, so T_E is about $(100 \text{ K})/0.32 = 310$ K, as claimed. Now note that

$$k_s = m\omega^2 = \frac{m(\hbar\omega)^2}{\hbar^2} = \frac{m\varepsilon^2}{\hbar^2} = \frac{m(k_B T_E)^2}{\hbar^2} = m\left(\frac{k_B T_E}{\hbar}\right)^2 \quad (\text{T4A.40})$$

So to find k_s , we need the mass of an iron atom. Iron's atomic weight M_A is about 56 g, meaning that Avogadro's number $N_A = 6.02 \times 10^{23}$ iron atoms have this mass. So $m = M_A/N_A$, and

$$\begin{aligned} k_s &\approx \frac{M_A}{N_A} \left[\frac{k_B T_E}{\hbar} \right]^2 = \frac{(0.056 \text{ kg})}{6.02 \times 10^{23}} \left[\frac{(1.38 \times 10^{-23} \text{ J/K})(310 \text{ K})}{1.056 \times 10^{-34} \text{ J}\cdot\text{s}} \right]^2 \left(\frac{1 \text{ N}}{1 \text{ kg}\cdot\text{m/s}^2} \right) \\ &\approx 150 \frac{\text{N}}{\text{m}} \end{aligned} \quad (\text{T4A.41})$$

Note that the units work out: k_s expresses the force that a spring exerts when stretched or compressed a certain distance. A macroscopic spring with this k_s would exert 1.5 N of force (≈ 0.35 lb) when stretched or compressed by 1 cm.

Example T4A.3

T5A

The Ideal Gas

Chapter Overview

Introduction

In this chapter, we deploy the techniques developed in the last chapter to explore thermal behavior of gases.

Section T5A.1: Quantum Particles in a One-Dimensional Box

A gas consists of particles bouncing around a mostly empty container. The first step toward modeling this is to consider a particle moving in one dimension between two barriers a distance L apart. Quantum mechanics tells us that the quantized kinetic energy levels for such a particle are given by $E_n = h^2 n^2 / 8mL^2$, where m is the molecule's mass, h is Planck's constant, and n is an integer. In the high-temperature limit, we can evaluate the sums in equation T4.25 by approximating them as integrals. The result is that we find that the particle's average energy when it is in equilibrium with a reservoir at temperature T is $E_{\text{avg}} = \frac{1}{2} k_B T$. If then we imagine N weakly interacting particles in the same one-dimensional box, then we can consider each particle to be a quantum system in equilibrium with a reservoir consisting of the other $N - 1$ particles. The total internal energy of this one-dimensional gas is then

$$U = N E_{\text{avg}} = \frac{1}{2} N k_B T \quad (\text{T5A.6})$$

Section T5A.2: A Three-Dimensional Monatomic Gas

We can make the model more realistic by extending it to three dimensions. Because each particle in a three-dimensional box behaves like independent particles in three one-dimensional boxes (one for each axis direction), we can treat each axis direction for each particle as a quantum system in equilibrium with the reservoir consisting of the other particle axis directions. If we have N particles, we have $3N$ such systems, so the gas's total internal energy and heat capacity at temperature T must be

$$U = 3N E_{\text{avg}} = \frac{3}{2} N k_B T \quad \text{and} \quad \frac{dU}{dT} = \frac{3}{2} N k_B \quad (\text{T5A.8})$$

This is very close to what we observe for *monatomic* gases (see Table T1.2). We call the model we are using of weakly-interacting particles an **ideal gas** model.

Section T5A.3: Diatomic Gases

Gases with multi-atom molecules can store energy in modes *in addition* to their kinetic energy (the kinetic energy per particle is $E_{KE, \text{avg}} = \frac{3}{2} k_B T$ for *all* gases, as found above). In particular, diatomic molecules can store energy in the form of rotational energy. The energy levels for this mode are $E_j = j(j+1)\epsilon$ (where $\epsilon \equiv h^2 / 8\pi^2 I$, h is Planck's constant, and I is the molecule's moment of inertia), and there are $2j + 1$ quantum states per energy level. In the high-temperature limit, we can again approximate the sums in equation T4.25 by integrals. Evaluating the integrals yields $E_{\text{rot, avg}} = k_B T$. This means that the total internal energy and heat capacity of a diatomic gas is

$$U = N(E_{KE, \text{avg}} + E_{\text{rot, avg}}) = \frac{3}{2} N k_B T + N k_B T = \frac{5}{2} N k_B T, \quad \frac{dU}{dT} = \frac{5}{2} N k_B \quad (\text{T5A.14})$$

This is again close to what we observe experimentally (see Table T1.2).

Single atoms are not solid entities that can rotate, so this energy storage mode is not available to atoms in monatomic gases.

(The remaining sections are in the published textbook.)

Section T5.4: The Equipartition Theorem and Its Limits

Note that the average energy per atom in a Einstein solid, the average kinetic energy of a gas molecule, and the average rotational energy of a diatomic molecule are all integer multiples of $\frac{1}{2}k_B T$. The equipartition theorem provides a non-quantum approach to understanding this result.

The equipartition theorem states that if the newtonian expression for the energy of a molecule contains a term that depends on the square of some classical variable q (such as x -position, x -momentum p_x , or the x component L_x of angular momentum), then the average energy associated with that term is $\frac{1}{2}k_B T$. The corresponding variable q is called a **degree of freedom**. The section illustrates how the theorem yields the high-temperature results we have derived earlier. In particular, both the equipartition theorem and our earlier quantum calculations agree that

$$U \approx \frac{f}{2} N k_B T, \quad \frac{dU}{dT} \approx \frac{f}{2} N k_B \quad (\text{T5.21})$$

- **Purpose:** These equations specify the thermal energy U and the heat capacity dU/dT of simple gases containing N particles at temperature T , where f is the gas molecule's "degrees of freedom" ($f=3$ for monatomic gases, $f=5$ for simple diatomic gases) and k_B is Boltzmann's constant.
- **Limitations:** These expressions are approximations valid at sufficiently high temperatures. They also assume that vibrational modes of molecular energy storage either do not exist or are not significant.

However, only the quantum results yield the correct low-temperature behavior. When the temperature falls so low that even the first excited energy level in an energy storage mode is pretty improbable, then that mode has difficulty storing any energy at all and the heat capacity associated with that level goes to zero compared to its high-temperature limit. We say that the mode in such a case is "frozen out."

Section T5.5: The Ideal Gas Law

At normal temperatures, a newtonian model adequately expresses the movement of gas atoms. Such a model implies that gas molecules moving with an average kinetic energy of $\frac{3}{2}k_B T$ bouncing off of the gas container's walls will exert a **pressure** (force per unit area) on those walls such that

$$PV = N k_B T \quad (\text{T5.28})$$

- **Purpose:** This equation gives the pressure P of N molecules of a low-density gas held in a volume V at temperature T , where k_B is Boltzmann's constant.
- **Limitations:** This equation strictly applies only in the zero-density limit (although it is a good approximation for real gases at typical densities). All parts of a gas sample must be in equilibrium for it to have well-defined single values of P and T throughout the volume.
- **Notes:** This is the **ideal gas law**: any gas obeying this law is an **ideal gas**.

Each species in a mixture of gases exerts a partial pressure $P_s = N_s k_B T / V$, and the total pressure is the sum of partial pressures. Also the chemist's ideal gas law is $PV = nRT$, where n is the number of moles and $R = N_A k_B = 8.31 \text{ J/K}$ is the **gas constant**.

T5A.1 Quantum Particles in a One-Dimensional Box

Gases are extremely important systems in thermal physics. We started our exploration of thermal physics with the Einstein solid because one can quite easily determine a macrostate's multiplicity for this particular kind of object. We cannot so easily do this for gases. However, the techniques developed in the last chapter will enable us to do a clever end-run around this problem.

What is a gas?

What is the difference between a gas and a solid? Molecules in a solid are bound together in such a way that a given molecule vibrates around a fixed position in a lattice. The distance between atoms is also basically the same as the size of a molecule. But gas molecules are *not* bound to each other: instead, they may freely roam around whatever container holds the gas. The average separation of gas molecules is typically much larger than the molecule's diameter, meaning that a gas consists mostly of empty space. This means that a gas's volume is not essentially fixed (as a solid's volume is): indeed, specifying a gas's volume V is an important part of specifying its macrostate.

An idealized one-dimensional gas model

Let's begin with the simplest possible quantum model of such a situation. Suppose that we have N gas particles that are moving completely freely back and forth in a *one-dimensional* container between two impenetrable barriers a distance L apart. Also assume that the particles simply pass through each other without interacting as they move back and forth, so that each particle behaves as if it were *alone* in the container, interacting only with the barriers. We call a gas of non-interacting particles an **ideal gas**.

If our gas particle is a completely structureless mathematical point, the only energy it can have is kinetic energy. Assuming that the particle is non-relativistic and has mass m , we learned in unit Q that its energy is

$$E_n = \frac{h^2 n^2}{8mL^2} \quad (\text{T5A.1})$$

where n is an integer. (The energy is *quantized* because we must fit an integer number of half-wavelengths of the particle's quantum wavefunction between the impenetrable: see unit Q for the details.)

Now we can use the equation T4.25 to calculate the average energy this gas particle will have if it is in equilibrium with a reservoir at temperature T . That equation tells us that this particle's average energy will be

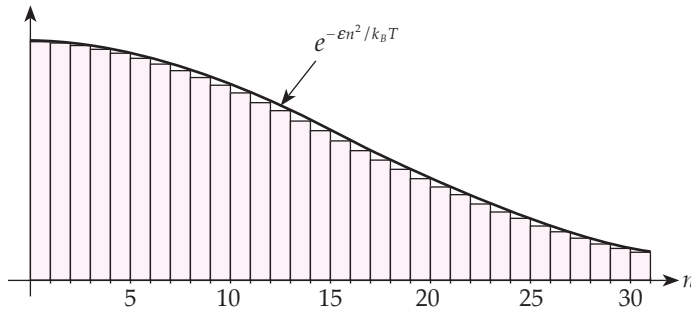
$$E_{\text{avg}} = \frac{\sum E_n e^{-E_n/k_B T}}{\sum e^{-E_n/k_B T}} = \frac{\epsilon \sum n^2 e^{-\epsilon n^2/k_B T}}{\sum e^{-\epsilon n^2/k_B T}} \quad \text{where } \epsilon \equiv \frac{h^2}{8mL^2} \quad (\text{T5A.2})$$

Approximating the partition function using an integral

The infinite sums look difficult to do, but, we can *approximate* them pretty easily in the high-temperature limit. Suppose we draw a graph where we represent the values of $e^{-\epsilon n^2/k_B T}$ at a given temperature T but different values of n as a sequence of bars of width $\Delta n = 1$ (see figure T5A.1). If $\epsilon \ll k_B T$, so that the exponential decays very slowly as n increases, then the value of the bottom sum is approximately equal to the value of the area under the curve of the exponential function from 0 to infinity. Therefore, we can approximate the sum as an integral:

$$\sum_{n=1}^{\infty} e^{-\epsilon n^2/k_B T} \Delta n \approx \int_0^{\infty} e^{-\epsilon n^2/k_B T} dn \quad \text{if } \epsilon \ll k_B T \quad (\text{T5A.3a})$$

This is actually a superb approximation at room temperature. You can show that for a helium atom ($m \approx 6.7 \times 10^{-27}$ kg) trapped between barriers only a micron apart ($L = 10^{-6}$ m), then $\epsilon/k_B T \approx 2 \times 10^{-9}$ at room temperature. This means that n^2 must be $\sim 10^8$ ($n \sim 10^4$) for $e^{-\epsilon n^2/k_B T}$ to fall significantly below 1 even in this extreme case. The exponential therefore decreases *very* slowly with increasing n (indeed, the actual curve is *much* flatter than in the figure).

**Figure T5A.1**

The area under the curve of the function $e^{-\epsilon n^2 / k_B T}$ is approximately equal to the area of the bars, which is equivalent to the sum in the partition function. Note that if ϵ were even smaller, the curve would become flatter, and the approximation improves (the neglected areas between the bars and curve become even smaller).

Exercise T5AX.1

Verify that $\epsilon / k_B T \approx 2 \times 10^{-9}$ for helium in a micron-sized container at room temperature. Also argue that $\epsilon / k_B T$ will be even smaller if m and/or L are larger (note that helium is the lightest possible monatomic gas).

Similarly, we can approximate the sum in the numerator by

$$\epsilon \sum_{n=1}^{\infty} n^2 e^{-\epsilon n^2 / k_B T} \Delta n \approx \epsilon \int_0^{\infty} n^2 e^{-\epsilon n^2 / k_B T} dn \quad \text{if } \epsilon \ll k_B T \quad (\text{T5A.3b})$$

Note that in both integrals, we are treating n not as an integer but as a continuous variable. We can put it into a more evocative form if we rename n to u (a variable without integer connotations) and define $a^2 \equiv \epsilon / k_B T$: then

$$E_{\text{avg}} \approx \frac{k_B T a^2 \int_0^{\infty} u^2 e^{-a^2 u^2} du}{\int_0^{\infty} e^{-a^2 u^2} du} \quad \text{where } a^2 \equiv \frac{\epsilon}{k_B T} \quad (\text{T5A.4})$$

The two integrals are easy to find online (or to calculate using WolframAlpha): the results are:

$$E_{\text{avg}} \approx \frac{k_B T a^2 (\sqrt{\pi} / 4a^3)}{\sqrt{\pi} / 2a} = \frac{k_B T}{2} \quad (\text{T5A.5})$$

Now consider a gas consisting of N weakly interacting identical particles in the same one-dimensional box. We can consider each particle to be a quantum system in contact with a reservoir consisting of all of the other particles. The particles must interact at least weakly so that each particle can exchange energy with the reservoir represented by the others, but if the interactions are sufficiently weak, we can still reasonably model each particle quantum mechanically as if it were alone in the box. In this circumstance, the total thermal energy of the gas will simply be N times the average energy of each particle:

$$U = N E_{\text{avg}} = N \left(\frac{k_B T}{2} \right) = \frac{1}{2} N k_B T \quad (\text{T5A.6})$$

We have therefore successfully determined the gas's total thermal energy without having to calculate the gas's multiplicity or entropy!

The average energy of a particle in a one-dimensional gas

T5A.2 A Three-Dimensional Monatomic Gas

The next step is to make our model more realistic by allowing our particles move in three dimensions. Suppose that we have structureless gas particles moving in a *three*-dimensional cubic container whose sides have length L .

Generalizing to three dimensions

Quantum mechanics implies that we can treat each coordinate axis *independently*: we must fit an integer number of half-wavelengths of a given particle's quantum wavefunction along each coordinate axis, but those integer numbers (call them n_x , n_y , and n_z) are arbitrary and are not correlated. The total energy of each particle is just the sum of the energies we would get if we treated *each dimension* as a particle in a one-dimensional box:

$$E_{3D} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2} = \epsilon n_x^2 + \epsilon n_y^2 + \epsilon n_z^2 \quad (\text{T5A.7})$$

We can treat *each dimension* of a particle's motion as an independent particle in a 1D box

This means that we can model each dimension of each particle's motion as an independent quantum system in contact with the reservoir. When we have N particles, we have $3N$ systems, and since they are identical, they have the same average energy $E_{\text{avg}} = \frac{1}{2}k_B T$. So the total internal energy of an N -particle ideal gas whose particles move in three dimensions must be simply

$$U = 3NE_{\text{avg}} = N\left(\frac{3}{2}k_B T\right) = \frac{3}{2}Nk_B T \quad (\text{T5A.8a})$$

The heat capacity of an ideal monatomic gas

The heat capacity of such a gas will therefore be

$$\frac{dU}{dT} = \frac{3}{2}Nk_B \quad (\text{T5A.8b})$$

This is *exactly what we observe* experimentally for *monatomic* gases (such as helium, argon, krypton, and so on): see Table T1.2. The reason that this still-simplistic model works well for these noble gases is that their atoms really do interact only weakly, so that model assumption is sound. For reasons that we will discuss in the next section, such atoms have no other accessible ways of storing energy, so the atoms of a noble gas really do behave pretty much as if they were non-interacting structureless particles!

T5A.3 Diatomic Gases

The kinetic energy of any kind of gas molecule is still $\frac{3}{2}k_B T$

The difference between monatomic gases and other gases is that multi-atom molecules can store energy in modes *other* than their kinetic energy. Because these modes are almost always independent of the molecules' center-of-mass kinetic energy, the results of the previous section ensure that a molecule's average *kinetic* energy is $K_{\text{avg}} = \frac{3}{2}k_B T$ for *all* gases. But for multi-atom molecules, this is no longer the entire energy.

Rotational energy states in quantum mechanics

Multi-atomic gas molecules, for example, can store internal energy in the form of rotational energy. Quantum mechanics tells us that if a molecule has a moment of inertia I , its rotational energy levels are

$$E_j = j(j+1)\epsilon \quad \text{where } j = 0, 1, 2, \dots \quad \text{and} \quad \epsilon = \frac{h^2}{8\pi^2 I} \quad (\text{T5A.9})$$

There are also $2j+1$ distinct quantum states corresponding to each energy level E_j , corresponding to different orientations of the rotation without changing its energy. (The derivation of these results is a topic for an upper-level quantum physics class, so we'll simply accept them here as given.) So the average energy associated with these rotational quantum states is

$$E_{\text{rot,avg}} = \frac{\sum E_j (2j+1) e^{-j(j+1)\epsilon/k_B T}}{\sum (2j+1) e^{-j(j+1)\epsilon/k_B T}} = \frac{\sum [j(j+1)\epsilon] (2j+1) e^{-j(j+1)\epsilon/k_B T}}{\sum (2j+1) e^{-j(j+1)\epsilon/k_B T}} \quad (\text{T5A.10})$$

To evaluate this sum, we apply the same trick that we did in section T5A.1: as long as $\epsilon \gg k_B T$, then we can approximate each sum by an integral:

$$\sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\epsilon/k_B T} \Delta j \approx \int_0^{\infty} (2j+1) e^{-j(j+1)\epsilon/k_B T} dj \quad (\text{T5A.11a})$$

$$\sum_{j=0}^{\infty} \epsilon j(j+1)(2j+1) e^{-j(j+1)\epsilon/k_B T} \Delta j \approx \int_0^{\infty} \epsilon j(j+1)(2j+1) e^{-j(j+1)\epsilon/k_B T} dj \quad (\text{T5A.11b})$$

where $\Delta j = 1$ in each sum, but j in each integral is no longer an integer but a continuous variable. Even for diatomic molecules with fairly small moments of inertia I , the value of ϵ/k_B turns out to be a few kelvins, so at room temperature, $\epsilon/k_B T \approx 100$. Therefore, the exponential still varies pretty slowly and the integral is a good approximation to the sum (though not as good as it was in section T5A.1). Most diatomic gases (except for hydrogen) become liquids before the temperature would be low enough so that this is much of an issue.

These integrals *look* much harder than those considered in section T5A.1, but they are actually easier. Define $u = \epsilon j(j+1)/k_B T$ and note that $du = \epsilon(2j+1) dj/k_B T$, which means that $(2j+1) dj = (k_B T/\epsilon) du$ and $\epsilon j(j+1) = k_B T u$. Substituting these values into equation T5A.11a yields

$$\int_0^{\infty} (2j+1) e^{-j(j+1)\epsilon/k_B T} dj = \frac{k_B T}{\epsilon} \int_0^{\infty} e^{-u} du = -\frac{k_B T}{\epsilon} [e^{-\infty} - e^{-0}] = \frac{k_B T}{\epsilon} \quad (\text{T5A.12a})$$

and doing the same for the integral in equation T5A.11b yields:

$$\int_0^{\infty} \epsilon j(j+1)(2j+1) e^{-j(j+1)\epsilon/k_B T} dj = \frac{(k_B T)^2}{\epsilon} \int_0^{\infty} u e^{-u} du = \frac{(k_B T)^2}{\epsilon} \quad (\text{T5A.12b})$$

(where I did look up the last integral, though one can also use integration by parts). The average energy stored by a rotating molecule therefore

$$E_{rot,avg} = \frac{(k_B T)^2/\epsilon}{k_B T/\epsilon} = k_B T \quad (\text{T5A.13})$$

The total internal energy of N molecules moving in three dimensions and rotating is therefore

$$U = N E_{avg} = N(E_{KE,avg} + E_{rot,avg}) = N\left(\frac{3}{2}k_B T + k_B T\right) = \frac{5}{2}k_B T \quad (\text{T5A.14a})$$

and the heat capacity of such a gas is

$$\frac{dU}{dT} = \frac{5}{2}Nk_B \quad (\text{T5A.14b})$$

Again, this is pretty close to what we observe for diatomic gas molecules, as noted in table T1.2. The main complication is that gas molecules, especially those involving more bonds than the simplest diatomic molecules, can also store energy in the form of various kinds of flexing vibrations. Therefore the heat capacities of all but the simplest diatomic molecules tend to be somewhat higher than $\frac{5}{2}Nk_B T$.

Note that a single atom *cannot* store rotational energy in this way. A single atom is simply an electron cloud surrounding a tiny nucleus, and the electron cloud is not a solid thing that can rotate as a unit like a ball can. We can increase the angular momenta of the cloud's individual electrons, but this involves moving the electrons to energy levels so high that they are simply not accessible at normal temperatures.

(Now read the remaining sections of chapter T5 in the published text.)

Evaluating the integrals

The internal energy and heat capacity of a gas whose molecules can rotate

Why single atoms cannot store rotational energy