and therefore Eq. (29).


1A majority of introductory calculus-based physics textbooks, including many widely used ones, give misleading or incorrect explanations for the failure of the equipartition law to describe correctly the classically expected rotational degrees of freedom in monatomic and diatomic gases. This article outlines typical textbook treatments and reviews the quantum mechanical explanation. © 1996 American Association of Physics Teachers.

Specific heats and the equipartition law in introductory textbooks

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A majority of introductory calculus-based physics textbooks, including many widely used ones, give misleading or incorrect explanations for the failure of the equipartition law to describe correctly the classically expected rotational degrees of freedom in monatomic and diatomic gases. This article outlines typical textbook treatments and reviews the quantum mechanical explanation. © 1996 American Association of Physics Teachers.

I. INTRODUCTION

The law of equipartition of energy is a rigorous consequence of classical mechanics. It states that for any mechanical system, each degree of freedom described by a quadratic term in the energy makes an average contribution to the energy of \( \frac{k}{2} T \), where \( T \) is the absolute temperature and \( k \) is Boltzmann's constant.\(^1\) Nevertheless, as is well-known, measurements of the specific heats of common monatomic and diatomic gases are not consistent with the equipartition law. This conflict between theory and experiment was not resolved until the development of quantum mechanics.

Most calculus-based introductory physics textbooks introduce the equipartition law and relate it to the specific heats of gases. It is an ideal place in introductory physics courses to point out a clear and obvious failure of classical physics that
requires quantum mechanics for its resolution. Consequently, it is disappointing to discover that out of some 27 introductory textbooks surveyed, including many widely used ones, only six correctly describe the predictions of classical equipartition and the reasons for its failure. The rest either do not discuss the topic, or (the large majority) give explanations that are at best misleading and at worst, out-and-out mistaken. In the following sections I will describe this situation in more detail. Section II reviews the predictions of equipartition for ideal gases. Section III describes typical textbook explanations that are misleading or incorrect. Section IV outlines the quantum mechanical reasons for the failure of equipartition. In Sec. V, I offer a few speculations on what might underlie this widespread problem in introductory texts.

II. EQUIPARTITION AND THE SPECIFIC HEATS OF GASES

Consider a monatomic ideal gas, thought of as a collection of “rigid bodies” of finite size. Each atom in such a gas has six degrees of freedom, three translational, and three rotational. Classically, each degree of freedom should have associated with it an average energy of \( \frac{1}{2}kT \), so that the total internal energy per molecule \( U \) should be \( 3kT \). Diatomic molecules should likewise have three translational and three rotational degrees of freedom. For both, the predicted specific heats at constant volume and constant pressure are

\[
\frac{dU}{dT} = 3k,
\]

\[
c_p = c_v + k = 4k.
\]

These values yield a ratio of specific heats

\[
\gamma = \frac{c_p}{c_v} = \frac{4}{3}.
\]

This theoretical prediction is of course in wild disagreement with experiment. The measured value of \( \gamma \) for monatomic gases such as mercury or the noble gases is about 5/3, and for diatomic gases such as oxygen or nitrogen, about 7/5. These measured values correspond respectively to three and five degrees of freedom. It thus appears that monatomic gases have only three translational degrees of freedom; the expected rotational degrees of freedom are missing. Similarly, diatomic molecules apparently have three translational and two rotational degrees of freedom; one rotational degree of freedom is missing, corresponding to rotation about a line joining the two atoms.

A second failure of classical equipartition for diatomic molecules involves two missing vibrational degrees of freedom, corresponding to the potential and kinetic energies of vibrations along a line joining the two atoms. These degrees of freedom do show up at high temperatures (and at lower temperatures in heavier diatomic gases), when the ratio \( \gamma \) falls to a limiting value of about 9/7.

These discrepancies caused widespread bewilderment among the nineteenth physicists who tried to reconcile them with classical mechanics. Maxwell in 1875 said that they constituted “the greatest difficulty yet encountered by the molecular theory.” Lord Kelvin went so far as to question the validity of the equipartition law. Boltzmann, considering only rotation, suggested that molecules might be “smooth” (that is, friction-free), so that collisions could not alter rotational energies about axes of symmetry. Hence, such rotational motions would not affect specific heats. As we now know, no reconciliation is possible: The discrepancies are quantum mechanical in origin. They signal the failure not only of classical equipartition, but of classical mechanics itself.

III. TEXTBOOK EXPLANATIONS

A few textbooks give clear, correct explanations for the failure of equipartition in ideal gases. One particularly thorough discussion reads as follows:

Although the equipartition theorem has had spectacular successes in explaining the measured heat capacities of gases and solids, it has had equally spectacular failures. If a diatomic gas molecule rotates about the line joining the atoms, there should be an additional degree of freedom. Similarly, if a diatomic molecule is not rigid, the two atoms should vibrate along the line joining them. We would then have two more degrees of freedom corresponding to kinetic and potential energies of vibration. According to the measured values of the molar heat capacities..., however, diatomic gases apparently do not rotate about the line joining them nor do they vibrate. The equipartition theorem gives no explanation for this, nor for the fact that monatomic atoms apparently do not rotate about any of the three possible perpendicular axes in space....

The equipartition theorem fails because classical mechanics itself breaks down when applied to atomic and molecular systems and must be replaced by quantum mechanics.

Of the 27 books I examined, five others state correctly, if often in less detail, that some rotational degrees of freedom are missing and that quantum mechanics is needed to explain this failure of the equipartition law. The remaining 21 textbooks fall into the following categories.

(i) Five texts argue that since the moment of inertia \( I \) about a line joining the two atoms of a diatomic molecule is “very small” or “negligible,” there will be no contribution to the energy from this degree of freedom.

This argument is simply wrong. There is no corollary to the equipartition law that says the average energy per degree of freedom is \( \frac{1}{2}kT \) unless the moment of inertia is (in some sense) “small!” If the equipartition law were true, there would be a contribution of \( \frac{1}{2}kT \) to the internal energy for any finite \( J \). None of these texts places this explanation in a quantum context, where it might have at least some justification (see Sec. IV).

(ii) Eight texts explicitly assume that the atoms in a gas molecule are mass points; that is, they have no extension. In that case, the moment of inertia about any axis passing through the atom is zero, and hence there can be no contribution to the energy from rotation about such an axis.

This explanation is formally correct: If atoms were point masses, then these rotational degrees of freedom could not be present. But the premise is wrong: atoms are not point masses! Why, then, can this model be used? Why does it give a correct result? These texts don’t say. Certainly they say nothing about a quantum explanation. One purpose of a physical model is to simplify a problem while preserving the essential physics. This model, by contrast, makes an assump-
tion that in this context is unphysical: Molecules are not point masses, and classically, should rotate. Far from clarifying the physics, this explanation tries to define an evident problem out of existence.

(iii) One popular text, which appeared in multiple editions over many years, is difficult to classify: One edition from the 1960s gives a clear and correct discussion of the missing rotational degrees of freedom, along the lines of Ref. 6 above. Earlier and later editions omit this section, and for the most part offer no explanation at all. The most recent editions state (briefly and a little mysteriously) that in “ordinary” collisions, there is no way for rotational motion about an axis of symmetry to change. This account may be a latter-day version of Boltzmann’s argument, or possibly an ambiguous reference to the quantized symmetric top (see below). It is at best obscure.

(iv) Seven books do not call attention to, much less explain, the missing rotational degrees of freedom. Most of these discussions are brief; some do not even mention equipartition or the concept of degrees of freedom. They do not mislead students except by omission, but they do neglect a marvelous opportunity to point out the limitations of classical physics and the need for quantum mechanics. One exception, from the 1950s, gives a detailed and sophisticated account of equipartition and its quantum limitations that puts most others to shame; but it does not bring up the possibility of rotation about an axis of symmetry, stating only that molecules can be thought of as “smooth spheres”—another possible reference to Boltzmann’s model.

Only a handful of these 21 books point out that one must also explain the absence of rotational degrees of freedom in monatomic gases; the discussion focuses almost entirely on diatomic gas molecules.

Physicists often disagree on how best to present physics to beginning students, and differences of approach abound both in textbooks and in discussions around department coffee pots! Out-and-out mistakes in textbooks are far less common. The arguments described above are puzzling for a more specific reason: Many textbooks that discuss equipartition also point out that a diatomic molecule can be thought of as two masses connected by a spring. The potential and kinetic energies connected with this vibrational motion lead to two additional degrees of freedom, predicted by classical equipartition, that do not show up at room temperature. But in striking contrast to the rotational case, most texts treat the vibrational modes correctly: They point out the failure of classical equipartition, and most go on to explain that at higher temperatures, where the energy level spacings become small compared to $kT$, the additional vibrational degrees of freedom do indeed show up in the specific heats. Many texts also point out that the two rotational degrees of freedom in diatomic molecules can be “frozen out” at low temperatures because of quantum effects. It is only in the discussion of rotation about axes through the center of mass of a monatomic molecule, and rotation about an axis joining the two atoms of a diatomic molecule, that textbooks so often resort to incorrect or misleading explanations. Only a handful state clearly that the absence of these classically expected degrees of freedom is likewise quantum mechanical in origin.

IV. QUANTUM MECHANICS AND MOLECULAR ROTATION

A. The symmetric rotator

A full quantum mechanical treatment of atomic and molecular rotations is neither trivial nor particularly well known to many physicists. A first step might be to think of both monatomic and diatomic gas molecules as quantized rigid bodies capable of rotation. To be sure, the quantum mechanical “rigid rotator,” which assumes a molecule consisting of two point masses separated by a distance $d$, is a standard textbook problem, frequently encountered in quantum mechanics and statistical mechanics texts. The treatment is straightforward; one finds that the eigenfunctions are spherical harmonics, and that the energy eigenvalues are given by

$$\frac{\hbar^2}{2} \frac{l(l+1)}{I}, \quad l=0,1,2,\ldots,$$

where $I$ is the moment of inertia about the center of mass. This system has two rotational degrees of freedom, and therefore, as is easily shown, contributes $2(\frac{1}{2}kT)=kT$ to the internal energy in the classical limit. Many intermediate and advanced quantum mechanics and statistical mechanics texts use the rigid rotator to describe diatomic molecules; few of them explain why one can make the assumption of point masses.

By contrast, the quantum mechanical “symmetric rotator,” which assumes masses of finite size, is not a standard textbook problem (although, interestingly, it was one of the earliest systems to receive a detailed quantum mechanical treatment). One typically sees it today in physical chemistry or molecular spectroscopy texts. One also sees it in older texts such as Pauling’s Introduction to Quantum Mechanics and Fowler’s Statistical Mechanics. It is often introduced only in discussions of polyatomic molecules, since, as should be evident, the rigid rotator happens to give a perfectly correct result for diatomic molecules.

Moreover, the symmetric rotator is less straightforward mathematically. One must write a Hamiltonian in an Euler angle coordinate system, and the resulting Schrödinger Equation eigenfunctions involve hypergeometric functions. For a symmetric rotator, let $I_s$ be a doubly degenerate moment of inertia (for a diatomic molecule, the moments of inertia about mutually perpendicular axes through the center of mass, and perpendicular to the line joining the two molecules); and let $I_c (<I_s$ in this case) be the moment of inertia about the axis of symmetry (for a diatomic molecule, the line joining the two masses). Then the energy eigenvalues are given by

$$E_{lmj} = \frac{\hbar^2}{2I_c} \frac{l(l+1)}{I_c} + \frac{\hbar^2}{2} \frac{J^2}{I_s} \left( \frac{1}{I_c} - \frac{1}{I_s} \right),$$

where the first term corresponds to rotations about two axes perpendicular to and passing through the center of mass, and the second to rotations about the axis of symmetry. The wave function $\psi_{lmj}$ is described by nonnegative integral quantum numbers $l, m,$ and $J$, which correspond respectively to rotations about the center of mass, the $z$ axis of the fixed coordinate system, and the axis of symmetry of the rigid body.

If one takes the classical limit of this system, one finds three rotational degrees of freedom and a contribution of $\frac{1}{2}kT$ to the specific heat, both for the case considered above ($I_c>I_s$) and for the completely symmetric case (a threefold
degenerate $I_e$) corresponding to a spherically symmetric monatomic gas molecule. This classical limit, however, does not apply to rotations about a line joining the two atoms of a diatomic molecule at room temperature. An order of magnitude calculation for a typical diatomic molecule such as oxygen shows that for the first term in Eq. (4), the lowest excited state has an energy of a few times $10^{-3}$ eV, corresponding to a temperature of a few K. By contrast, the lowest excited state for the second term has an energy of roughly 0.1 MeV, corresponding to a temperature of about $10^9$ K. Hence, at room temperature, the two degrees of freedom corresponding to the first term in Eq. (4) each contribute the $\frac{3}{2}kT$ predicted by classical equipartition. The second term, by contrast, is “frozen out,” and contributes nothing to the internal energy. It is for this reason that the point mass rigid rotator with its two rotational degrees of freedom turns out to give a correct result.

Similar considerations apply to the rotational degrees of freedom for monatomic gases. In this case, the spherical symmetry of the gas molecule ($I_e = I_c$) causes the second term in Eq. (4) to vanish. Thus the energy is the same as for the mass point rigid rotator [Eq. (3)]. Nevertheless, because the degeneracy of the wave functions is different from that of the rigid rotator, the classical limit for the symmetric spherical rotator ($I_e = I_c$) turns out to yield three rotational degrees of freedom. As in the case of the diatomic molecule, the small moment of inertia (in this case, about an axis through the center of the atom) causes the first excited state to be at an energy much greater than can be excited at room temperature.

One needs to be explicit about the role of symmetry in this model. As we will see below, for reasons not apparent in the preceding discussion, quantum mechanics prohibits the rotation of systems with full (continuous) spherical or axial symmetry, irrespective of the energy levels. By contrast, rotations of polyatomic molecules with a two- or threefold degenerate moment of inertia but with only $n$-fold rotational symmetry about an axis, are not so restricted. Most textbook discussions of the symmetric rotator do not emphasize this point.

**B. Adequacy of the “symmetric rotator” model**

Some intermediate and advanced texts, particularly older ones, give the above treatment as an explanation for the failure of classical equipartition. Nevertheless, it is not entirely adequate. In particular, an atom or molecule is a complex many-body quantum mechanical system. It is far from obvious that it can be treated as a rigid body, even a quantum mechanical one. How can we justify modeling either a monatomic or a diatomic gas molecule as a symmetric rotator?

We must first ask precisely what is rotating? It is apparent that the electrons cannot participate in any collective rotational mode corresponding to the “rigid body” rotation of the molecule as a whole about an axis of symmetry. If one considers a very simple system—the electronic states of a hydrogen atom—it is apparent that no rotational energy levels of the form

$$\frac{\hbar^2}{2I} (J+1)$$

are possible. If there were any such energy levels, they would appear in the solutions to the Schrödinger equation!

Now in a multielectron atom or molecule, it is in principle possible that a suitable approximation would turn up a collective mode that would appear as a rotational energy spectrum. However, any approximate separation of a Hamiltonian into single electronic states on the one hand, and collective rotational states on the other, would have to rely on something like a Born–Oppenheimer approximation, which requires that rotational energy levels be very different in magnitude from single electronic states. But a rough estimate of the moment of inertia of an orbital electron about the molecular axis of symmetry shows that the rotational energies are on the order of eV—about the same as typical electronic energy states in atoms and diatomic molecules. It therefore appears that one cannot interpret atomic or molecular electronic excited states in terms of collective “rigid body” rotation. (Note, of course, that these electronic states, however regarded, typically have energies $\gg kT$ at room temperature and so cannot contribute to the specific heat.)

Molecular rotations are thus due to nuclear motion. Consider first the two degrees of freedom corresponding to the “tumbling” of a diatomic gas molecule about two perpendicular axes through the center of mass of the molecule. The nuclear mass far exceeds the electron mass, and hence the energies of any nuclear motions are much less than the electronic energies. Here the conditions necessary for the Born–Oppenheimer approximation hold: The electronic energy levels are on the order of eV, the vibrational levels are on the order of 0.1 eV, and the rotational levels are on the order of $10^{-3}$ eV. Moreover, the rotational energies are much less than $kT \approx 0.025$ eV corresponding to room temperatures, and so the equipartition law should apply.

Rotations of diatomic molecules about a line joining the two atoms, and rotations of nuclei in monatomic atoms, are more complex. First, it is evident that there is no coupling between the two nuclei of a diatomic molecule. Thus, although either nucleus might conceivably rotate independently, there can be no collective rotational modes akin to the rigid body rotation of a “dumbbell” around an axis passing through the center of both nuclei.

Atomic nuclei, of course, are no more rigid bodies than are atoms or molecules. Nevertheless, collective “rigid body” modes that lead to nuclear rotational spectra do exist, just as they do for molecular spectra. In principle, therefore, one might expect three rotational degrees of freedom for monatomic gas molecules such as mercury or the noble gases, corresponding to nuclear rotations about three mutually perpendicular axes through the center of the nucleus. These degrees of freedom do not show up for two reasons. First, as argued above, the lowest excited rotational energy state for such systems is on the order of 0.1 MeV, far greater than $kT$, and so the equipartition law could not apply.

A second, more fundamental argument, stemming from the symmetry of the wave function, provides yet another reason not to expect nuclear rotations about axes of symmetry. Consider a wave function $\psi$ that is spherically symmetric. By a well-known theorem in quantum mechanics, such a state must have zero angular momentum. Similar considerations apply to systems that are axially symmetric. This theorem certainly applies to wave functions describing collective “rigid body” motion. Hence for spherically or axially symmetric nuclei, there can be no collective rotation about axes of symmetry. In particular, a symmetric rotator model can describe the rotational states of a spherically or
axially symmetric "rigid body"; but all allowable wave functions for such systems must correspond to zero angular momentum about a symmetry axis \( J = 0 \) in Eq. (4).\(^{23}\) Thus, a spherical nucleus cannot rotate. Similarly, by this theorem, a football-shaped nucleus would have only two rotational degrees of freedom, not the three predicted by classical physics.

As it happens, most if not all common monatomic (and diatomic) gases have spherically symmetric nuclei, and hence cannot rotate.\(^{24}\) For gas molecules with nonspherically symmetric nuclei, the high excitation energies described above would prevent the appearance of rotational degrees of freedom.

V. CONCLUSION

We are faced with a puzzling situation: Why is it that so many introductory texts, including many of the most widely used ones, give such a misleading account of molecular rotations? We are missing an outstanding opportunity to point out to students a striking and elementary example of the failure of classical mechanics. We also are discouraging critical thinking by students: It is remarkable, in my own experience, how rarely students ask why a degree of freedom should not appear simply because its corresponding moment of inertia is in some sense "small," or why we can treat atoms as point masses even though we know they are no such thing. Indeed, the authority of the textbook is so great that when these objections are raised, students often actively resist the suggestion than the text might be wrong or incomplete.

I can think of at least three reasons why this state of affairs has persisted:

(i) The quantum explanation for the failure of equipartition is remarkably complex. Moreover, it is likely that most physicists do not in the course of their training routinely encounter the physics that underlies the failure of equipartition for rotations in monatomic and diatomic gases. On one level, the symmetric rotator (unlike the rigid rotator) is not a standard problem in most intermediate and advanced quantum mechanics and statistical mechanics texts. On a second level, a quantum explanation that goes beyond the symmetric rotator involves knowing something of the quantum mechanics of molecular and nuclear rotational spectra. Even among specialists, the usefulness of this quantum mechanical description lies in its ability to explain these spectra. Not surprisingly, texts in molecular or nuclear physics rarely if ever mention how this material applies to the failure of equipartition for rotational degrees of freedom. It is not one of the problems they are interested in!

(ii) Since the advent of quantum mechanics, the predictions of the equipartition law for the specific heats of gases no longer have the status of a mysterious and pressing problem requiring explanation. Some older kinetic theory and statistical mechanics textbooks such as those by Jeans or Fowler clearly remember the challenge that had been posed by the failure of equipartition, and make a point of showing how it can be resolved.\(^{25}\) More recent texts give much less space to this topic. Often, these texts adopt the rigid rotator (with its implicit assumption of point masses) as a model for a diatomic molecule with little or no explanation. Some statistical mechanics texts do not discuss diatomic molecules at all. For this reason as well, many physicists never see, as a part of their undergraduate or graduate education, a careful discussion of the implications of the equipartition theorem for the specific heats of gases—it is no longer a particularly interesting or pressing topic, and there is no shortage of possible substitutes.

(iii) Perhaps most central is the influence of what we might term a "textbook culture." Incorrect and misleading explanations for the failure of equipartition in introductory texts have a long history. The majority of the 27 texts examined here have been published since 1980. But two, both widely used in their day, date from the 1930s, and a number of others are from the 1950s through the 1970s. All but one of these older texts either give no explanation for the failure of equipartition, or give incorrect or misleading explanations similar to those in more recent books. The degree to which our introductory textbooks follow similar patterns in the organization and presentation of material is noteworthy. This organization is to a considerable extent arbitrary and conventional.\(^{26}\) It may be that we retain it, at least in part, merely because as a profession we are comfortable with it, and because both authors and publishers are reluctant to risk challenging established patterns.\(^{27}\) And of course, it is easy for both authors and physics instructors to overlook difficulties with long-established and familiar explanations. The result, in this case, is that as a teaching community we have never settled on a correct and widely accepted account.

Whatever the reasons, it appears that many otherwise first-rate textbooks offer explanations for the failure of equipartition to describe the rotational degrees of freedom in monatomic and diatomic gases that are misleading or simply wrong. It would be desirable for both textbook authors and physics instructors to reconsider their approach to this topic.


DATA ADJUSTMENTS

If one knows the answer, there is a natural tendency to keep on making these corrections until one has the "right" answer and then to stop looking for further corrections. Indeed, the astronomers of the 1919 eclipse expedition were accused of bias in throwing out the data from one of the photographs that would have been in conflict with Einstein's prediction, a result they blamed on a change of focus of the telescope. With hindsight we can say that the British astronomers were right, but I would not be surprised if they had gone on finding corrections until finally their result with all these corrections fit Einstein's theory.