



Thermal physics in the data age—Students judge the applicability of the equipartition theorem

J. D. D. Martin^{a)}

Department of Physics and Astronomy, University of Waterloo, Waterloo, Canada N2L 3G1

(Received 12 February 2023; accepted 4 August 2023)

Providing students of introductory thermal physics with a plot of the heat capacities of many low density gases as a function of temperature allows them to look for systematic trends. Specifically, large amounts of heat capacity data not only allow students to discover the equipartition theorem but also point to its limited applicability. Computer code to download and plot the temperature-dependent heat capacity data is provided. © 2023 Published under an exclusive license by American Association of Physics Teachers.

<https://doi.org/10.1119/5.0146298>

The purpose of this paper is to point out a specific instance in the teaching of thermal physics, where relatively large amounts of *digital data* can help students judge the applicability of a physical concept, namely, the equipartition theorem as it relates to the heat capacities of low-density gases of atoms or molecules. Encouraging students to “weigh the evidence” helps them practice a skill of working scientists, who often have to decide if a paper’s conclusions are warranted by its data.

The organization of this paper is as follows: first, the equipartition theorem is briefly reviewed. Then the common textbook example of its application to H₂ gas is presented. However, the case of H₂ is not representative, as is shown by plotting the heat capacities of numerous molecules as a function of temperature. This limited applicability of the equipartition theorem is discussed in the context of introductory thermal physics courses. Finally, some insight is gained by considering a simple model for the temperature-dependent heat capacity of gaseous CO₂, which is suitable for study in statistical mechanics courses.

The equipartition theorem is a result of *classical* statistical mechanics. For a precise statement and thorough derivation see, for example, Ref. 1. Roughly speaking, the theorem says that each degree of freedom of a system that contributes a quadratic term to the energy adds $k_B T/2$ to the total average energy of the system, where k_B is Boltzmann’s constant and T is the absolute temperature. Following Ref. 2, I denote the number of these contributions as f (per atom or molecule). In that way, a system of N non-interacting atoms or molecules—each with f degrees of freedom contributing quadratic terms to the energy—has a total energy of $U = fNk_B T/2$ and, thus, a temperature-independent constant volume heat capacity of $C_V = fNk_B/2$.

In this paper, discussion will be restricted to non-interacting atoms and molecules; i.e., low-density gases following the ideal gas law. Nevertheless, the equipartition theorem is of broader applicability, most notably here to the heat capacities of single-element solids, as expressed by the Dulong–Petit law, where $f=6$; see, for example, Ref. 3. It also played an important—but sometimes misrepresented⁴—role in the history of understanding thermal electromagnetic radiation; i.e., the Rayleigh–Jeans ultraviolet catastrophe.

The cleanest application of the equipartition theorem is to monatomic ideal gases. Under the assumption that we can ignore their internal structure, there are three quadratic terms in the energy per atom: $U/N = p_x^2/(2m) + p_y^2/(2m) + p_z^2/(2m)$, where p_i are the momenta in three orthogonal

directions and m is the mass of each atom. So $f=3$ and, thus, $C_V = 3Nk_B/2$ for monatomic ideal gases, if the equipartition theorem applies.

However, the equipartition theorem assumes classical—*not* quantum-mechanical—motion. In most cases, the motion of monatomic gases can be understood classically, and thus, the theorem works quite well.⁵ However, once we consider molecules, we are immediately confronted—as were the founders of quantum mechanics—by the limited applicability of the equipartition theorem due to the quantization of molecular rotation and vibration.⁶

An illustrative example of the applicability of the equipartition theorem to low density H₂ gas appears in a popular and well-respected textbook on thermal physics by Schroeder²—see Fig. 1.¹³ Figure 1 shows that below about 100 K, H₂ behaves like a monatomic gas, with only the translational degrees of freedom active. At these low temperatures, molecular rotation is “frozen” out due to quantization of the rotational energy level structure. However, from about 300 to 1000 K—once rotation has been activated—the equipartition theorem appears to be applicable again, but with $f=5$, the two additional quadratic degrees of freedom corresponding to rotation.¹⁴ At about 1000 K, the heat capacity begins to increase again due to the activation of vibrational motion.

That a theorem based on *classical* mechanics can be applied to a quantum mechanical system *over limited temperature ranges* is not surprising. After all, although the center-of-mass motion of atoms and molecules should, in principle, be described using quantum mechanics, as far as heat capacities go, the classical picture is normally sufficient; i.e., $C_V = 3Nk_B/2$ if there are no internal excitations of the atoms/molecules. Reif¹ indicates that the criterion for approximate validity of the equipartition theorem is that the spacing of energy levels around the mean energy be small compared to $k_B T$. For typical confining volumes, the translational energy levels may be considered so dense as to be continuous, and thus, the equipartition theorem is virtually always applicable to the translational degrees of freedom of atoms or molecules.

Since the rotational energy level spacings in molecules are larger than those for translation but typically smaller than those for vibration, we might expect a temperature range where the equipartition theorem gives $C_V = (f_t + f_r)Nk_B/2$ with the contribution due to translation of $f_t = 3$ and $f_r = 2$ or $f_r = 3$ due to rotation, depending on whether the molecular geometry is linear ($f_r = 2$; e.g., H₂, CO₂) or non-linear ($f_r = 3$; e.g., H₂O, CH₄).¹⁵ As noted above, H₂ does

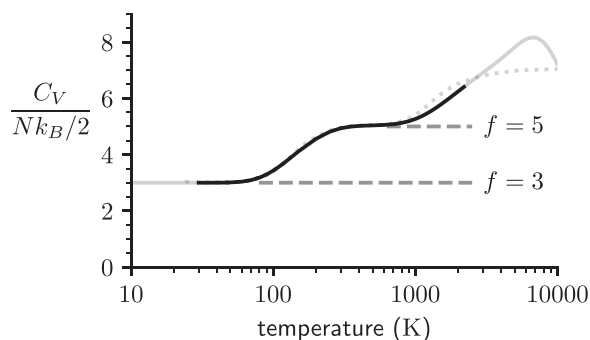


Fig. 1. The scaled heat capacity of low-density gaseous H_2 as a function of temperature (Ref. 7) assuming a constant 3:1 mixture of ortho- and para-hydrogen (so-called *normal hydrogen* (Ref. 8)). This plot is modelled after Fig. 1.13 of Schroeder (Ref. 2) (dark line) but is extended over a larger temperature range (by the light solid line) using the results of Ref. 7. The light dashed line is as shown in Fig. 20.6 from Serway *et al.* (Ref. 9) who do not provide details on its origin.

approximately exhibit a temperature-independent heat capacity $C_V \approx (f_t + f_r)Nk_B/2$ with $f_t = 3$ and $f_r = 2$ from ≈ 300 to ≈ 1000 K.

At higher temperatures, we expect vibration to become important. The simplest model for molecular vibration involves a “linearization” of forces and subsequent decomposition of internal motions into normal modes, each acting as an independent harmonic oscillator.¹⁶ Since harmonic oscillators have two degrees of freedom (momentum and position) contributing quadratic energy terms to the total energy, we might expect from the equipartition theorem that there will be a temperature range for which $C_V \approx (f_t + f_r + f_v)Nk_B/2$ with the contribution due to vibration f_v being equal to twice the number of vibrational modes that a molecule has. For instance, for H_2 , $f_v = 2$, since a diatomic molecule only has one vibrational mode (corresponding to the relative motion of the two nuclei). However, as evident from Fig. 1, there is no extended temperature range over which the heat capacity for H_2 is given by $C_V = fNk_B/2$, where $f = 7$ (as expected from $f = f_t + f_r + f_v$ with $f_t = 3$, $f_r = 2$, and $f_v = 2$). As illustrated in Fig. 1 and discussed later, some textbooks⁹ present plots suggesting that H_2 *does* exhibit a heat capacity plateau corresponding to $f = 7$, at odds with the research literature.⁷

A phenomenologically based discussion of heat capacities is common in first-year general university physics courses and towards the start of upper-year thermal physics courses (before a more in-depth treatment of their statistical mechanical origin).² Some commonly used textbooks^{9,17} show a version of Fig. 1 and briefly discuss the equipartition theorem, without deriving it. In this context, it may be useful to show students many more examples of temperature-dependent heat capacities to help them gauge how general the behavior of Fig. 1 is; i.e., do other molecules have temperature ranges with temperature-independent heat capacities, given by $C_V = fNk_B/2$, with f a positive integer, depending on the temperature range?

For this purpose, Fig. 2 shows the temperature dependence of a large number of heat capacities, downloaded from the National Institute of Standards and Technology (NIST) Chemistry Webbook.¹⁰ Rather than choosing molecules that illustrate the equipartition theorem, all of the available data¹⁸ have been plotted, with just a few species omitted for clarity (which can be added by slightly modifying the plotting code provided in the supplementary material¹²)

Figure 2 shows that, in general, the equipartition theorem is less applicable than one might think from the example of H_2 over the temperature range shown by the dark line in Fig. 1. For the larger polyatomics—unlabeled in Fig. 2—it does not apply at all, at least in the temperature range shown. There are no clearly isolated steps in C_V with temperature because of the variety of low and high vibrational mode frequencies,¹⁹ as will be seen below by examining the case CO_2 in more detail.

In an introductory thermal physics course, one could introduce Fig. 2 in the following ahistorical manner: after derivation of the relationship between the average kinetic energy of a gas molecule and its temperature: $U/N = 3k_B T/2$ (see pp. 10–11 of Ref. 2), Fig. 2 could be examined with the (erroneous) expectation that $C_V = 3Nk_B/2$, independent of temperature. The difference between the atomic and molecular cases will naturally lead to discussion of the additional degrees of freedom of molecules—beyond translation—that result in larger heat capacities. Also deviations from $C_V = 3Nk_B/2$ due to electronic excitations of atoms may be anticipated, although they are not observed for the atoms and temperature ranges of Fig. 2.

From Fig. 2, students will be able to identify that—besides $C_V = 3Nk_B/2$ —there is something special about certain other values of the heat capacity. Specifically, they may observe:

- (1) the transition to $C_V = 5Nk_B/2$ for hydrogen, the propensity to this C_V for other diatomics (within limited temperature ranges), and also
- (2) the labeled triatomics (except for CO_2) show a propensity towards $C_V = 6Nk_B/2$ at low temperatures; i.e., $f = 6$, exhibiting an additional rotational degree of freedom beyond the diatomic case.

With this background, the equipartition theorem can be mentioned, with its limited applicability obvious to students from Fig. 2. Further discussion may then be deferred until statistical mechanics is studied. Until then, the equipartition theorem is just a handy way to remember commonly used heat capacities: $C_V = fNk_B/2$, where $f = 3$ for atomic species without electronic excitation, and $f \approx 5$ for N_2 and O_2 near room temperature, which is particularly useful as so many problems in introductory thermal physics involve the heat capacity of air. (Figure 2 also gives students a sense of the temperature range over which $f \approx 5$ is a good approximation for air.) I have found that, by following this approach, students’ misconceptions regarding the applicability of the equipartition theorem have largely been eliminated.²¹

Once students begin their study of statistical mechanics, they may benefit from a discussion of the role of heat capacities and the equipartition theorem in the historical development of quantum mechanics.^{6,22}

Furthermore, aspects of Fig. 2 are suitable for study in introductory statistical mechanics. For example, to gain some insight into the limited applicability of the equipartition theorem, we may consider a simple model for the temperature dependence of the heat capacity of CO_2 .^{15,16}

The CO_2 molecule has three distinct vibrational mode frequencies, commonly denoted by ν_1 (symmetric stretch), ν_2 (bending), and ν_3 (antisymmetric stretch).²³ Defining corresponding characteristic temperatures $\Theta_i := h\nu_i/k_B$, where h is Planck’s constant, we have $\Theta_1 \approx 2000$ K, $\Theta_2 \approx 960$ K, and $\Theta_3 \approx 3380$ K.²⁴ If we assume that each mode acts as an independent harmonic oscillator, then each makes an

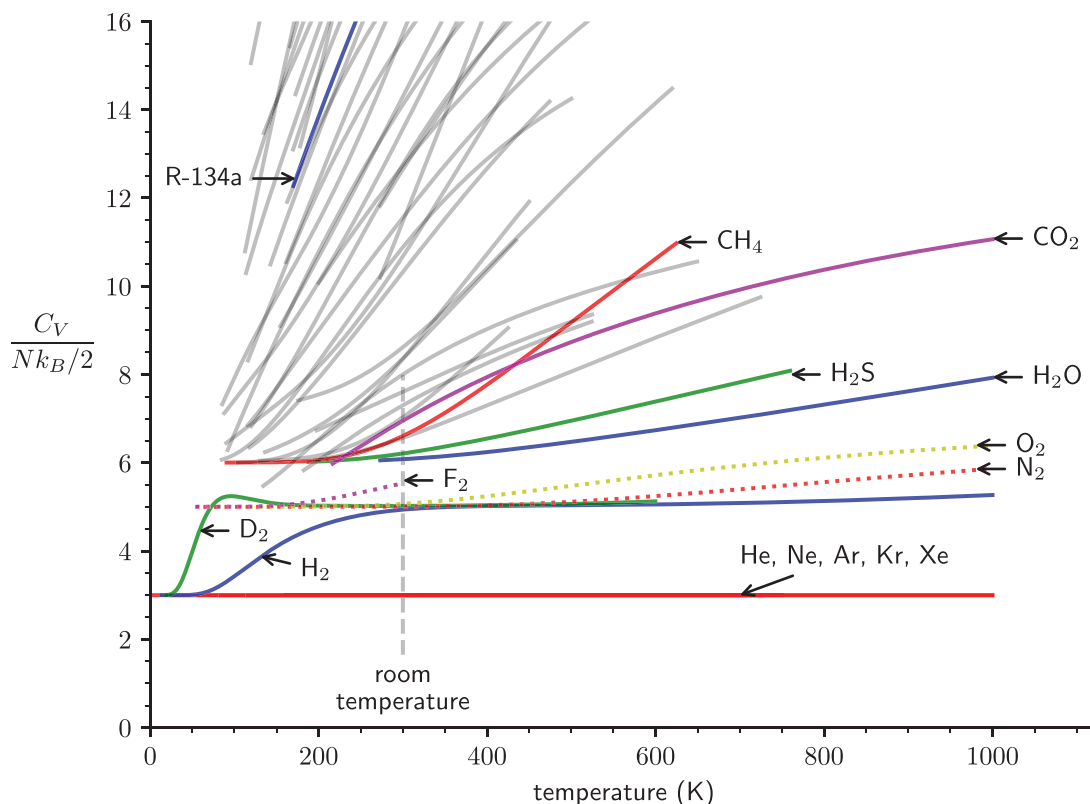


Fig. 2. (Color online) The scaled heat capacities of low density gases as a function of temperature, as obtained from the NIST Chemistry Webbook (Ref. 10) All monatomic and diatomic species are labeled. All unlabeled curves correspond to triatomic or larger species. Many of these molecules are refrigerants, reflecting the technological importance of their thermal properties; see, for example, Ref. 11. For example, the R-134a label on the plot refers to 1,1,1,2-tetrafluoroethane (CH_2FCF_3), once commonly used in automobile air-conditioners. To give an objective view of the validity of the equipartition theorem, all molecules in the database with $C_V/(Nk_B/2) < 16$ are shown, except to prevent crowding, I have omitted carbon monoxide, deuterium oxide, and the ortho- and para- variants of hydrogen and deuterium (the normal mixtures are plotted) (see the supplementary material (Ref. 12) for the PYTHON program to download the data and create this plot).

additive contribution to the heat capacity, given by a standard result often derived in the context of the Einstein solid model (e.g., Eq. 7.7.5 of Ref. 1),

$$\frac{C_{V,i}}{Nk_B/2} = 2g_i \left(\frac{\Theta_i}{T} \right)^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T} - 1)^2}, \quad (1)$$

where the g_i 's are the degeneracies of each mode. The bending mode of CO_2 (ν_2) is doubly degenerate, so $g_2 = 2$; otherwise, $g_1 = g_3 = 1$.

Figure 3 shows the individual mode contributions to the heat capacity of CO_2 as computed using this simple model. Over the temperature range plotted, the equipartition theorem applies to the rotational motion, so that the total heat capacity is

$$C_V = (f_t + f_r) Nk_B/2 + \sum_{i=1,2,3} C_{V,i}, \quad (2)$$

with $f_t = 3$ and $f_r = 2$ ($f_r = 2$ instead of 3 since CO_2 is a linear molecule¹⁵) and the $C_{V,i}$'s given in Eq. (1).

In the high-temperature limit, Eq. (1) gives $C_{V,i} = g_i Nk_B$ for g_i harmonic oscillators; i.e., $f = 2$ for each oscillator, as expected from the equipartition theorem.¹ Thus, we expect a jump of $\Delta f = 2g_i$ as each mode is activated with increasing temperature. Since the ν_2 bending mode has the lowest frequency, we expect it to be activated at a lower temperature than the ν_1 and ν_3 modes. However, Fig. 3 shows that the

activation of the ν_1 and ν_3 modes obscure observation of the ν_2 plateau.

Furthermore, the low frequency of the ν_2 bending mode limits the range over which the $f=5$ (translation and rotation) plateau may be seen. This behavior is typical of the larger molecules in Fig. 2, which usually have low frequency bending and hindered internal rotation modes.^{16,25}

In contrast, the limited number of small polyatomics in Fig. 2 that show a propensity to $f=6$ around room temperature (H_2S , H_2O , and CH_4) do not have low-frequency modes (also these molecules all have a non-linear geometry and, thus, rotation contributes $f_r = 3$ in contrast to $f_r = 2$ for CO_2 which is linear¹⁵). For example, the lowest vibrational mode frequency of H_2O has $\Theta_2 \approx 2300$ K in comparison to the lowest for CO_2 : $\Theta_2 \approx 960$ K. The delayed activation of vibration in H_2O facilitates the observation of an $f=6$ plateau.

Now let us consider the high-temperature limit of the simple model for the heat capacity of CO_2 , decomposing the contributions due to translation t , rotation r , and vibration v as: $f = f_t + f_r + f_v$ in $C_V = f Nk_B/2$. From the $T \rightarrow \infty$ limit of Eq. (1) together with the number of modes and their degeneracies, $f_v = 8$. Thus, we expect a heat capacity corresponding to $f=13$ at high temperatures (from $f_t = 3$, $f_r = 2$, and $f_v = 8$). However, as the higher temperature heat capacity data for CO_2 in Fig. 4 shows, this limit is approached and then exceeded as T increases. It is natural to expect this breakdown of the harmonic oscillator model at such high

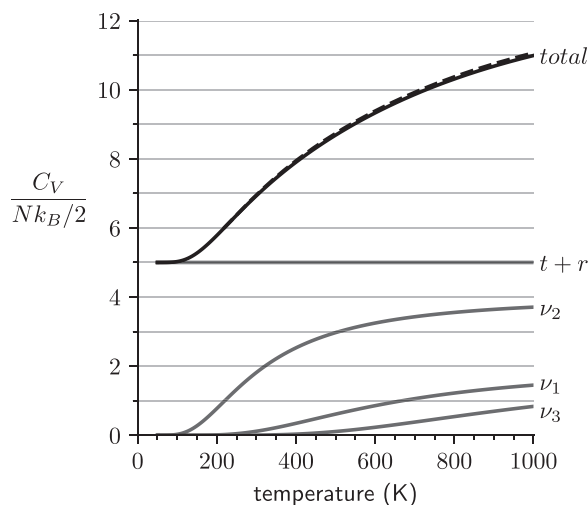


Fig. 3. The scaled heat capacity of low-density gaseous CO₂ (*total*) together with the individual contributions of translation and rotation (*t+r*), and the three vibrational modes (ν_1 , ν_2 , and ν_3) as calculated in a simplified model (see the text). The dashed line is the data from the NIST Chemistry Webbook (Ref. 10).

temperatures, for, at the very least, all molecules dissociate and, thus, do not have an unbounded vibrational energy level structure (for CO₂ from Ref. 26: $D/k_B \approx 6 \times 10^4$ K, where D is the energy required to break one of the C–O bonds).

Returning to the case of H₂, the situation is similar to that of CO₂: there is no $f=7$ plateau ($f_t=3$, $f_r=2$, $f_v=2$) observed in C_V (the light solid line of Fig. 1), contrary to the misleading depiction in Ref. 9 (the light dotted line of Fig. 1). As illustrated in Fig. 4, the lack of a $f=7$ plateau is quite typical of diatomics. Its absence may be accounted for by a simple model for anharmonicity in the potential describing the interaction of the two atoms.²⁷ This model may serve as a useful computational exercise for students of statistical physics. Taking into account for anharmonicity in polyatomics is significantly more challenging.²⁷

In summary, giving students of introductory thermal physics the opportunity to examine the heat capacities of a variety of molecules allows them to develop a better appreciation of the applicability of the equipartition theorem than is normally the case when the heat capacity of H₂ is presented over a limited temperature range.^{2,9,17} Students of statistical mechanics may explore the deviations from the equipartition theorem in more detail, as illustrated here using a simple model for the heat capacity of CO₂.

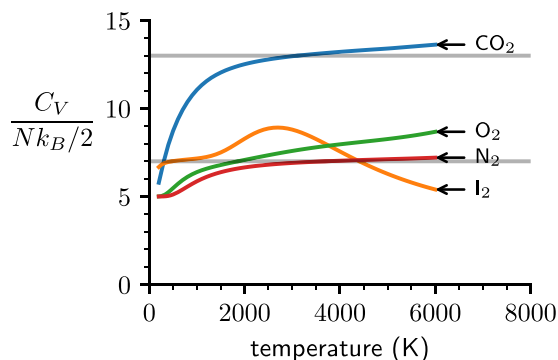


Fig. 4. (Color online) The scaled heat capacities of some low density gases as obtained from the NIST-JANAF database (Ref. 20).

Finally, it is noted that there is a wealth of digital thermodynamic data available for teaching thermal physics. A particularly useful resource is the CoolProp library.²⁸ For example, using the PYTHON interface to CoolProp, students may explore non-ideal fluid properties, such as deviations from the ideal gas law, and predict the thermodynamic efficiencies of refrigerators using different fluids; e.g., Sec. 4.4 of Ref. 2. The examination of digital thermodynamic data—that has only recently become widely available—gives students an active role in judging the applicability of what they are learning.

ACKNOWLEDGMENTS

The author would like to thank J. C. T. Martin, N. Fladd, U. Nandivada, and M. Robbins for comments and V. Koottala for checking the portability of the PYTHON code. This work was supported by NSERC (Canada).

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

^{a)}ORCID: 0000-0003-0306-5830.

¹F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).

²D. V. Schroeder, *An Introduction to Thermal Physics* (Addison Wesley, San Francisco, CA, 2000).

³M. Laing and M. Laing, “Dulong and Petit’s law: We should not ignore its importance,” *J. Chem. Educ.* **83**(10), 1499–1504 (2006).

⁴J. R. Persson, “Evolution of quasi-history of the Planck blackbody radiation equation in a physics textbook,” *Am. J. Phys.* **86**(12), 887–892 (2018).

⁵K. Gottfried and T.-M. Yan, *Quantum Mechanics: Fundamentals* (Springer, NY, 2003); they that with the benefit of hindsight the lack of an electronic contribution to atomic heat capacities (at low temperatures) points to the deficiencies of classical mechanics.

⁶C. A. Gearhart, “‘Astonishing successes’ and ‘bitter disappointment’: The specific heat of hydrogen in quantum theory,” *Arch. Hist. Exact Sci.* **64**(2), 113–202 (2010).

⁷R. J. Le Roy, S. G. Chapman, and F. R. W. McCourt, “Accurate thermodynamic properties of the six isotopomers of diatomic hydrogen,” *J. Phys. Chem.* **94**(2), 923–929 (1990).

⁸J. W. Leachman, R. T. Jacobsen, S. G. Penoncello, and E. W. Lemmon, “Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen,” *J. Phys. Chem. Ref. Data* **38**(3), 721–748 (2009).

⁹R. A. Serway, J. W. Jewett, Jr., and V. Peroomian, *Physics for Scientists and Engineers*, 10th ed. (Cengage, Boston, MA, 2017).

¹⁰E. W. Lemmon, I. H. Bell, M. L. Huber, and M. O. McLinden, “Thermophysical properties of fluid systems,” in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, edited by P. J. Linstrom and W. G. Mallard, <<https://webbook.nist.gov/chemistry/fluid/>>, accessed on January 29, 2023.

¹¹M. O. McLinden, J. S. Brown, R. Brignoli, A. F. Kazakov, and P. A. Domanski, “Limited options for low-global-warming-potential refrigerants,” *Nat. Commun.* **8**(1), 14476 (2017).

¹²See supplementary material online for the computer code to reproduce Fig. 2.

¹³Reference 2 gives an early and significant role to the equipartition theorem compared to other textbooks at a similar level; for example, instead of giving the derivation of the formulae for adiabatic, quasistatic compression of an ideal gas in terms of $\gamma := C_P/C_V$, Schroeder uses f , compared to the more conventional usage of γ ; e.g., S. J. Blundell and K. M. Blundell, *Concepts in Thermal Physics*, 2nd ed. (Oxford U. P., Oxford, 2010).

¹⁴C. A. Gearhart, “Specific heats and the equipartition law in introductory textbooks,” *Am. J. Phys.* **64**(8), 995–1000 (1996). As Gearhart notes, an explanation of why the rotation of diatomic molecules only contributes two and not three extra degrees of freedom to f —seemingly avoiding

rotation about the axis connecting the atoms—has been a stumbling block for many textbook authors. A thorough explanation requires a knowledge of quantum mechanics beyond what would be typical of students in an introductory thermal physics course.

¹⁵D. A. McQuarrie and J. D. Simon, *Molecular Thermodynamics* (University Science Books, Sausalito, CA, 1999).

¹⁶G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, reproduced ed. (Krieger, Malabar, FL, 1991).

¹⁷J. Walker, R. Resnick, and D. Halliday, *Halliday & Resnick Fundamentals of Physics*, extended ed. (Wiley, Hoboken, NJ, 2018).

¹⁸I follow NIST's usage of the term "data"; the heat capacities and other tabulated quantities in Ref. 10 are based on mixtures of calculations and empirical data; i.e., some heat capacities are computed using spectroscopically determined energy levels.

¹⁹G. N. Lewis, M. Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2nd ed. (McGraw-Hill, New York, NY, 1961). This book contains illustrative examples of the temperature dependence of gas phase heat capacities.

²⁰*NIST-JANAF Thermochemical Tables*, edited by M. W. Chase and National Institute of Standards and Technology (U.S.), 4th ed. (American Chemical Society, Washington, DC, 1998). Quantities from this database may be accessed using the Python package available at <<https://thermochem.readthedocs.io>>, last accessed on March 19, 2023.

²¹When following Ref. 2 quite closely—giving prominence to Fig. 1—I would frequently observe the appearance of $C_V = fNk_B/2$ as a general

expression for heat capacity in students' work, including situations where the equipartition theorem was not applicable. This misuse was possibly due to the "theorem" terminology, suggesting a good opportunity to discuss the role of precise mathematical results in physics: their premises are often only approximately satisfied in the physical world.

²²M. J. Klein, "Einstein, specific heats, and the early quantum theory," *Science* **148**(3667), 173–180 (1965).

²³P. F. Bernath, *Spectra of Atoms and Molecules*, 3rd ed. (Oxford U. P., Oxford, 2016).

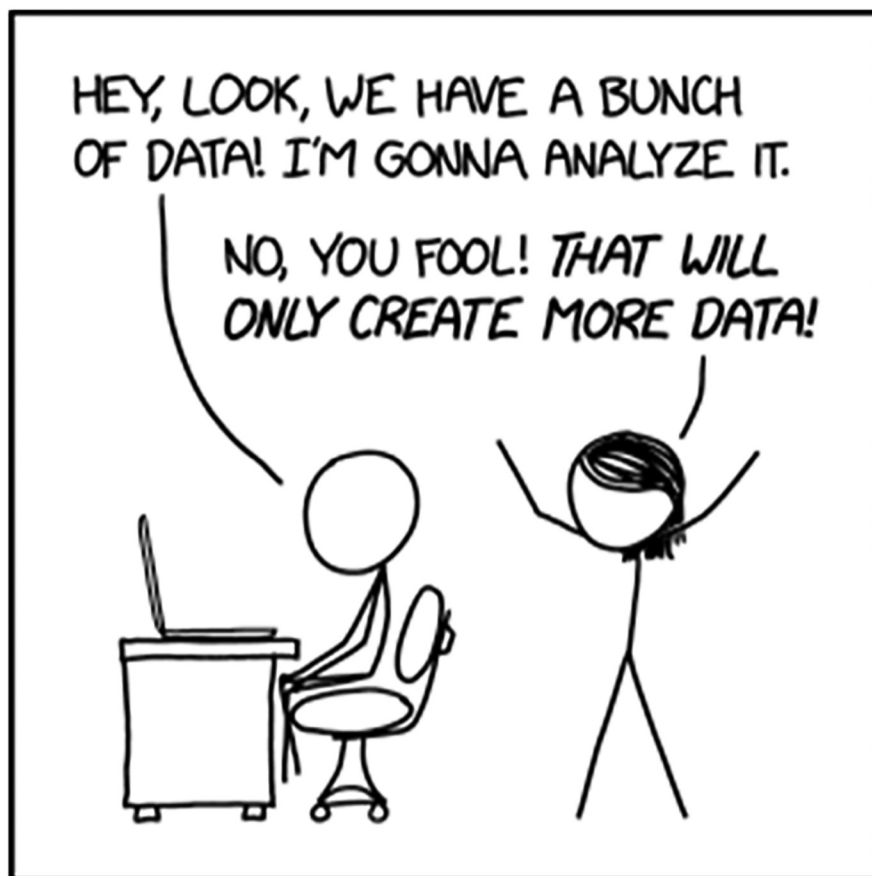
²⁴The mode frequencies are taken from the fundamental bands listed in Table 56 of Herzberg (Ref. 16) as he recommends on p. 504.

²⁵"Hindered internal rotation" refers to the rotation of groups of atoms within a molecule (e.g., a methyl group), where the rotation encounters potential barriers. See, for example, Ref. 16.

²⁶B. Ruscic, "Active thermochemical tables: Sequential bond dissociation enthalpies of methane, ethane, and methanol and the related thermochemistry," *J. Phys. Chem. A* **119**(28), 7810–7837 (2015).

²⁷B. Ruscic and D. H. Bross, "Thermochemistry," in *Computer Aided Chemical Engineering* (Elsevier, Amsterdam, 2019), Vol. 45, pp. 3–114.

²⁸I. H. Bell, J. Wronski, S. Quoilin, and V. Lemort, "Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermo-physical property library CoolProp," *Ind. Eng. Chem. Res.* **53**(6), 2498–2508 (2014), see <<http://coolprop.org>>, last accessed on January 29, 2023.



It's important to make sure your analysis destroys as much information as it produces. (Source: <https://xkcd.com/2582>)