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The Einstein–Stern model for the rotational contribution to the heat capacity of a diatomic gas has recently been resuscitated. In this communication, we show that the apparent success of the model is illusory, because it is based on what has turned out to be an unfortunate comparison with experiment. We also take exception to the possibility of assigning any meaning to the rotational zero-point energy introduced by the model. © *1998 American Institute of Physics.* [S0021-9606(98)02448-9]

I. INTRODUCTION

In a conceptually interesting article from 1913, Einstein and Stern[1] discussed the possible existence of a zero-point energy for a quantum-mechanical vibrator. Planck had presented arguments in favor of such a zero-point energy two years earlier and had replaced his first formula for the temperature-dependent energy of a harmonic vibrator,[2]

$$E_{v1} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}, \tag{1}$$

by a second one,[3]

$$E_{v2} = \frac{h\nu}{2} \frac{e^{\frac{h\nu}{kT}} + 1}{e^{\frac{h\nu}{kT}} - 1} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{h\nu}{2}. \tag{2}$$

Einstein and Stern pointed out that when expanded to second order in $h\nu/kT$, the first formula gives $E_{v1} = kT - h\nu/2$, whereas the second formula gives $E_{v2} = kT$. The two formulas lead, however, to the same expression for the heat capacity[4] of a system of N vibrators, namely,

$$C_v = R \frac{h\nu}{kT} \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1 \right)^2}, \tag{3}$$

with N being the Avogadro constant and R the gas constant. With an additional factor of 3 this is Einstein's expression from 1907 for the heat capacity of a monatomic solid.[5]

As is well known, Einstein's analysis solved the long standing puzzle of the temperature dependence of the heat capacity of solids. According to the equipartition theory of classical statistical mechanics the heat capacity should have the constant value $3R$. But in fact it drops from the value $3R$ at high temperatures to the value 0 at $T=0$, and this is what was accounted for by Einstein's expression.

For a diatomic gas, the heat capacity has a value of about $\frac{5}{2}R$ at ambient temperature. According to classical statistical mechanics, this value is made up of a contribution of $\frac{3}{2}R$ from the translational motion, and a contribution of R from the rotational motion. That the rotational contribution to the

heat capacity might decrease from R to 0 by cooling was, however, considered a realistic possibility around 1912. So, to test this possibility Eucken measured the heat capacity of molecular hydrogen at several temperatures between 273 and 35 K, and indeed found that the heat capacity diminished from 4.84 to 2.98 cal mol^{-1} K^{-1} in that interval,[6] i.e., from 2.44 to 1.50R. Soon thereafter, the temperature-dependent heat capacities of several other gases were also measured, in particular by Scheel and Heuse.[7]

Eucken tried to represent his data by an expression of the form in Eq. (3), augmented by a $\frac{3}{2}R$ term. But he found that this led to too shallow a curve for the heat capacity as a function of T, in comparison with the experimental curve.

This was the starting point for Einstein and Stern's analysis. Their idea was to tie the problem of accounting for the form of the rotational contribution to the heat capacity of a diatomic molecule to the problem of deciding upon the possible existence of a zero-point energy for a vibrator. They treated the molecule as a rigid rotator, with the rotational energy

$$E_r = \frac{1}{2} I (2\pi\nu)^2, \tag{4}$$

where I is the moment of inertia, and ν is the frequency of rotation which is supposed to depend on the temperature. For each temperature, they compared the energy of the rotator with that of a vibrator with the same frequency ν, and required that the two energies be the same. For each of the above energy expressions, E_{v1} and E_{v2}, this uniquely determines ν and hence E_r as a function of T. Finally, the heat capacity of a gas of rotators was determined as

$$C_r = N \frac{dE_r}{dT}. \tag{5}$$

This leads to two expressions for C_r as functions of T. Einstein and Stern compared the graphs based on these expressions with Eucken's experimental graph of the rotational contribution to the heat capacity of molecular hydrogen. They found that only the graph related to the expression (2) could be brought in good agreement with the experimental

graph, and hence concluded that the existence of a vibrational zero-point energy had been made probable.

However, the derivation based on the expression (2) also predicted a rotational zero-point energy. Today we know that this was an incorrect prediction. The Einstein–Stern model has, nevertheless, attracted some recent attention, through the presentation by Milonni[8] and the subsequent discussion by Malta, Marshall, and Santos.[9] Milonni rejected the model because of our present knowledge, that *a molecule has no zero-point rotational energy*. However, the latter authors claim that the agreement with the experimental data can be qualitatively explained in the *Wigner representation*.

In the present communication, we draw attention to the fact that the experimental curve with which Einstein and Stern compared their theoretical curve was the experimental curve for so-called normal hydrogen, which is a nonequilibrium mixture of ortho- and parahydrogen. When a comparison with a proper system is performed, the success of the Einstein–Stern model vanishes, for any diatomic molecule.

In the following, we briefly review the Einstein–Stern model, using a dimensionless representation rather than adopting the somewhat cumbersome units used in Einstein and Stern's article. We then compare the Einstein–Stern expression for C_r with the modern expressions derived from statistical mechanics, and demonstrate the poor agreement between the two descriptions. Finally, we comment on the so-called *angular-momentum dilemma* and the possible existence of a zero-point energy for rotational motion.

II. THE EINSTEIN–STERN MODEL

Let us introduce the rotational and vibrational temperatures, Θ_r and Θ_v, respectively, by the usual definitions

$$\Theta_r = \frac{h^2}{8\pi^2 I k}, \quad \Theta_v = \frac{h\nu}{k}. \tag{6}$$

Θ_r is a constant, whereas Θ_v depends on T through the temperature-dependent frequency ν. Expression (4) for the rotational energy may then be written

$$E_r = \frac{h\nu}{4} \frac{\Theta_v}{\Theta_r}. \tag{7}$$

The condition $E_r = E_{v1}$ becomes

$$\frac{1}{4} \frac{\Theta_v}{\Theta_r} = \frac{1}{e^{\frac{\Theta_v}{T}} - 1}, \tag{8}$$

from which we get

$$\frac{T}{\Theta_r} = \frac{\Theta_v}{\Theta_r} \left[\ln\left(\frac{4}{\Theta_v/\Theta_r} + 1 \right) \right]^{-1}. \tag{9}$$

This equation gives the relation between T and ν, or between τ and x, where

$$\tau = \frac{T}{\Theta_r}, \quad x = \frac{\Theta_v}{\Theta_r}. \tag{10}$$
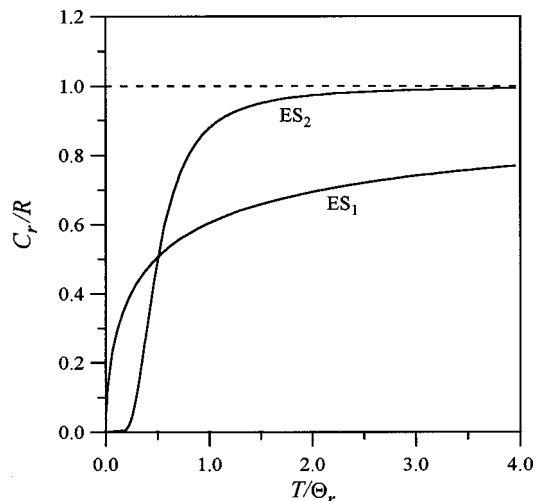
The heat capacity may be written

FIG. 1. Molar constant volume heat capacity of a gas of rigid rotators according to the model of Einstein and Stern. ''ES$_1$'' is based on expression (12), ''ES$_2$'' on expression (15).

$$C_r = \frac{1}{2} R x \frac{dx}{d\tau}, \tag{11}$$

where R is the gas constant. It leads to the expression

$$C_{r1} = R \frac{x^2}{2\tau} \left(1 + \frac{\tau}{\frac{x^2}{4} + x} \right)^{-1} \tag{12}$$

which, through Eq. (9), determines C_r as a function of τ.

Similarly, the condition $E_r = E_{v2}$ becomes

$$\frac{1}{4} \frac{\Theta_v}{\Theta_r} = \frac{1}{e^{\frac{\Theta_v}{T}} - 1} + \frac{1}{2}, \tag{13}$$

from which we get

$$\frac{T}{\Theta_r} = \frac{\Theta_v}{\Theta_r} \left[\ln\left(\frac{4}{\frac{\Theta_v}{\Theta_r} - 2} + 1 \right) \right]^{-1}. \tag{14}$$

This equation gives the new relation between τ and x and leads to the alternative expression

$$C_{r2} = R \frac{x^2}{2\tau} \left(1 + \frac{\tau}{\frac{x^2}{4} - 1} \right)^{-1} \tag{15}$$

for the heat capacity.

Figure 1 shows C_{r1} and C_{r2} as functions of T/Θ_r. As pointed out by Einstein and Stern, the behavior of C_{r1} for small T is qualitatively incorrect. The graph of C_{r2} is more convincing, and Einstein and Stern showed that it could be brought in almost quantitative agreement with the graph representing the experimental values of C_r determined by Eucken, provided a suitable value was assigned to their parameter p. In our notation this parameter is
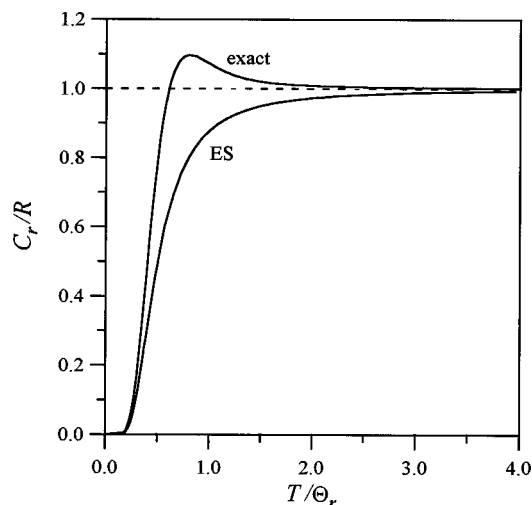
$$p = \frac{h^2}{4\Theta_r k}. \tag{16}$$

FIG. 2. Molar constant volume heat capacity of a gas of rigid rotators. ''Exact'' is based on the partition function of Eq. (18), ''ES'' on the model of Einstein and Stern, expression (15).

FIG. 3. Molar constant volume heat capacity curves for equilibrated hydrogen, orthohydrogen, parahydrogen, and normal hydrogen.

For hydrogen, the determined value for p corresponds to $\Theta_r = 274$ K. This is, however, a very unrealistic value, the correct value for hydrogen being 87.5 K, a discrepancy that has so far been left unnoticed.

As already mentioned in Sec. I, the heat capacity curve by Eucken is the curve for so-called normal hydrogen which is a nonequilibrium mixture of ortho- and parahydrogen. In the following section, we shall therefore make a more appropriate comparison.

III. EXPRESSIONS FOR THE HEAT CAPACITY OF A GAS OF RIGID ROTATORS

According to modern quantum-statistical mechanics, the heat capacity of a gas of rigid rotators is given by the expression[10,11]

$$C_r = R \frac{\partial}{\partial \tau} \left(\tau^2 \frac{\partial}{\partial \tau} (\ln q) \right), \tag{17}$$

where $\tau = T/\Theta_r$ as above, and q is the partition function

$$q = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)/\tau}. \tag{18}$$

Figure 2 shows the graph of expression (17) together with the graph of expression (15). The two graphs have the same limits for low and for high temperatures, but they approach the limits differently, and the general shapes of the graphs are quite different.

When the rigid-rotator model is used to describe the rotation of molecular hydrogen, the statistics of the nuclear spins must be included. This complication was, of course, unknown to Einstein and Stern whose work was published many years before the discovery of spin. It was first properly discussed by Dennison in 1927.[12] As is now well known,[10,11] the presence of the nuclear spins causes the gas to behave like a mixture of two interconvertible gases, orthohydrogen (total nuclear spin one) and parahydrogen (total nuclear spin zero). The partition function for orthohydrogen is obtained by including only odd values of j in the partition function of
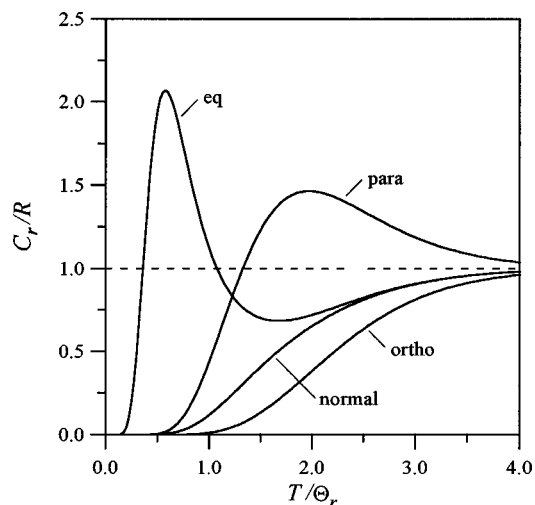
Eq. (18) and subsequently multiplying by a nuclear-spin degeneracy factor of 3, while the partition function for parahydrogen is obtained by including only even values of j in the sum of Eq. (18). In catalytically equilibrated hydrogen, the ortho:para ratio varies with temperature, approaching the value 3:1 for large values of T. So-called normal hydrogen is a hydrogen gas in which the ratio 3:1 is maintained at all temperatures.

Figure 3 shows the heat capacity curves for orthohydrogen, parahydrogen, normal hydrogen, and equilibrated hydrogen (for which the partition function is $q_{para} + q_{ortho}$).

In Fig. 4, we show again the heat capacity curve for normal hydrogen, but with the value 87.5 K inserted for Θ_r. Shown are also the Einstein–Stern curves corresponding to $\Theta_r = 87.5$ and 274 K. Einstein and Stern's analysis corresponds to a comparison of the curve for normal hydrogen at 87.5 K with the Einstein–Stern 274 K curve. Although the two curves are quite similar, the result of such a comparison
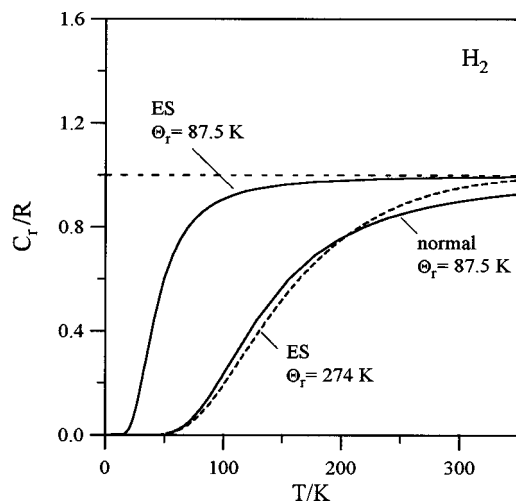

FIG. 4. Molar constant volume heat capacity curve for normal hydrogen compared with heat capacity curves based on the model of Einstein and Stern, expression (15), with $\Theta_r = 87.5$ and 274 K.

is now without meaning, and so is accordingly ''the remarkable agreement between the curves.''

IV. THE ANGULAR-MOMENTUM DILEMMA

As mentioned in Sec. I, Einstein and Stern used their analysis to favor expression (2) for the energy of a vibrator over expression (1). In the light of the present work, according to which the Einstein–Stern model in fact leads to an unacceptable heat capacity curve, this becomes a weak deduction. But then it is not needed anyway, since the correctness of expression (2) follows straightforwardly from modern molecular quantum mechanics. Molecular quantum mechanics also uniquely predicts the energy levels of a rigid rotator to be

$$E_j = \frac{h^2}{8\pi^2 I} j(j+1), \quad j = 0,1,2,\ldots \quad (19)$$

as already used in setting up the partition function of Eq. (18). Expression (19) leads to a vanishing zero-point energy for the rotator.

Relation (13) leads to $\Theta_v = 2\Theta_r$ at $T = 0$. It then follows from the relations (6) and (7) that the Einstein–Stern model predicts a rotational zero-point energy

$$E_{r0} = \frac{h^2}{8\pi^2 I}. \quad (20)$$

In light of our rejection of the validity of the Einstein–Stern model, we need not assign any specific meaning to this result. Yet, we must comment on the remark made by Malta *et al.*,[9] that it can be qualitatively explained in the Wigner representation.

We have discussed the Weyl–Wigner representation and applications of it in several articles. In connection with our work on the electronic Wigner function for the ground state of the hydrogen atom,[13] we discussed what we called the *angular-momentum dilemma* at some length. This is the problem of reconciling the fact that the Bohr theory predicts an angular momentum different from zero for the hydrogen atom's ground state, with the fact that the Schrödinger theory predicts the value zero. As we pointed out in our article, the difference can be qualitatively understood by realizing that the Weyl transform of the *operator* ℓ^2 is the *phase-space*

function $\ell^2 - \frac{3}{2}\hbar^2$, as first noticed by Shewell.[14] Thus, the zero expectation value of the operator ℓ^2 necessarily corresponds to a nonvanishing phase-space average $\frac{3}{2}\hbar^2$ of the function ℓ^2. In their article on the Wigner density of a rigid rotator, Malta et al. turn this argument upside-down by assigning an *a priori* interest to the *phase-space function* ℓ^2. This, then, let them suggest that the proper angular momentum operator be $\ell^2 + \frac{3}{2}\hbar^2$ rather than simply ℓ^2. As a result, the rotator acquires an angular momentum of $\frac{3}{2}\hbar^2$ in its ground state, which in a qualitative way is supposed to explain a nonvanishing zero-point energy. There is, however, no doubt that Eq. (19) is the correct expression for the energy of a molecular rotator and hence, that the operator ℓ^2 correctly accounts for the magnitude of the angular momentum of a rotator.

V. CONCLUSIONS

In the present work, we have shown that the success of the Einstein–Stern model is an illusion, and we have eliminated the incentive to seek a justification of a nonvanishing zero-point energy for rotational motion.

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