Classical partition function of a rigid rotator
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IV. EXPERIMENTAL CHECK

Figure 2 illustrates some interesting physics. Line C is tangent to curve B at room temperature since there is no heat loss at that temperature. Below room temperature the slope of curve B is greater than that of line C because the calorimeter is absorbing heat from the room which increases $dT/dt$. Likewise as temperatures increase above room temperature, $dT/dt$ of curve B approaches zero. The final equilibrium temperature is the temperature at which $dT/dt$ is zero. According to Eq. (16), $P/J$ is the maximum temperature rise that can be maintained under these experimental conditions. In this experiment $P/J$ equals 31°C. As a final check the calorimeter was heated to 31°C above room temperature and again cranked at 0.5 rev/s. The temperature varied approximately 1°C over a 15-min time interval. Thus it is clear that formula (16) fits well with experimental data.

Equating $K_h$ and $K_e$ from Eq. (5) and (6) gives another formula for the final equilibrium temperature:

$$T_f = \frac{(T_1 - T_2)^2}{(T_1 - T_2 - 2T_2)},$$

where $T_1$, $T_2$, and $T_3$ are three temperatures taken over two equal time periods. This equation is true in any situation where Newton's Law of Cooling applies. It is useful because it is unnecessary to compute a value for $K$ in order to find the equilibrium temperature.


Classical partition function of a rigid rotator

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In a recent note in this Journal,1 it was pointed out that the usual textbook derivations of the classical partition function of a rigid rotator proceed along one of two lines. The first approach2–7 consists in writing the Hamiltonian $H$ as a function of the Euler angles $\phi$, $\theta$, $\psi$ and the conjugate momenta $p_\phi$, $p_\theta$, $p_\psi$ and then integrating $\exp(-\frac{H}{kT})/h^3$ over the phase space $\phi$, $\theta$, $\psi$, $p_\phi$, $p_\theta$, $p_\psi$. This method is straightforward but tedious. The second approach8–10 consists in writing the Hamiltonian $H$ as a function of the components of the angular momentum and then integrating $\exp(-\frac{H}{kT})/h^3$ over the space consisting of these momenta and the associated quasicomponents. This method is quick, obscure, and questionable. Recently, after assigning the determination of the partition function of a rigid rotator as a homework problem without realizing how tedious the direct solution was, I conceived and subsequently discovered in the literature11,12 the following approach, which combines the best features of each of the above methods, being both straightforward and quick.

Let $A$, $B$, and $C$ be the principal moments of inertia of the rigid body with respect to the center of mass, and let $\alpha$, $\beta$, and $\gamma$ be the components of the angular momentum with respect to the associated principal axes. If there are no torques with respect to the center of mass then the rotational kinetic energy $T$, Lagrangian $L$, and Hamiltonian $H$ are all equal and are given by

$$T = H = L = \frac{\alpha^2}{2A} + \frac{\beta^2}{2B} + \frac{\gamma^2}{2C}.$$  

(1)

In terms of the Euler angles, the angular momenta are given by

$$\alpha = A(\phi \sin \theta \sin \psi + \phi \cos \psi),$$  

$$\beta = B(\phi \sin \theta \cos \psi - \phi \sin \psi),$$  

$$\gamma = C(\phi \cos \theta + \psi).$$  

(2)

(3)

(4)

It follows immediately that the generalized momenta are given by

$$p_\phi = \frac{\partial L}{\partial \phi} = \alpha \sin \theta \sin \psi + \beta \sin \theta \cos \psi + \gamma \cos \theta,$$  

$$p_\theta = \frac{\partial L}{\partial \theta} = \alpha \cos \psi - \beta \sin \psi,$$  

$$p_\psi = \frac{\partial L}{\partial \psi} = \gamma.$$  

(5)

(6)

(7)

We can now proceed directly to the evaluation of the partition function as follows:

$$Q = h^{-3} \int \int \int \int \int \exp(-\frac{H}{kT})$$  

$$\times dp_\phi \, dp_\theta \, dp_\psi \, d\phi \, d\theta \, d\psi$$  

$$= h^{-3} \int \int \int \int \int \exp(-\frac{H}{kT})$$  

$$\times \int \left( \frac{P_\phi P_\psi P_\psi}{\alpha \beta \gamma} \right) \, d\alpha \, d\beta \, d\gamma \, d\phi \, d\theta \, d\psi$$  

$$= h^{-3} \int \int \int \int \int \exp(-\frac{H}{kT}) \sin \theta$$  

$$\times d\alpha \, d\beta \, d\gamma \, d\phi \, d\theta \, d\psi$$  

$$= h^{-3} \int_0^{2\pi} d\phi \int_0^{\infty} \sin \theta \, d\theta \int_0^{2\pi} d\psi$$  

$$\times \int_0^{\infty} \exp(-\alpha^2/2AKT) \, d\alpha$$  

$$\times \int_0^{\infty} \exp(-\beta^2/2BT) \, d\beta$$  

$$\times \int_0^{\infty} \exp(-\gamma^2/2CT) \, d\gamma$$  

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\[ 8T^2e^{-3(AB)1/2}(2\pi kT)^{3/2}, \]

where \( J \), the Jacobian for the transformation from the variables \( p_\Theta p_\phi \) to the variables \( \alpha, \beta, \gamma \), was obtained directly from Eqs. (5)–(7). The final expression is the desired partition function.

In the conventional approach\(^2\)–\(^7\) the derivation of the partition function is tedious for two reasons. In the first place obtaining the Hamiltonian function \( H(\phi, \theta, \psi, p_\phi, p_\theta, p_\varphi) \) from the Lagrangian function \( L(\phi, \theta, \psi, \phi, \theta, \psi) \) is laborious. In the second place obtaining the partition function \( Q \) from the Hamiltonian function \( H(\phi, \theta, \psi, p_\phi, p_\theta, p_\varphi) \) is also laborious. In the present approach not only is it easy to get the partition function but it is not even necessary to obtain the Hamiltonian function \( H(\phi, \theta, \psi, p_\phi, p_\theta, p_\varphi) \). Nevertheless as an added bonus it is easy to do so; we simply solve Eqs. (5), (6), and (7) for \( \alpha, \beta, \) and \( \gamma \) as functions of \( \phi, \theta, \psi, p_\phi, p_\theta, \) and \( p_\varphi \) and then substitute the results in Eq. (1). In most conventional treatments\(^2\)–\(^6\) the authors ignore this first step, write down the Hamiltonian function \( H(\phi, \theta, \psi, p_\phi, p_\theta, p_\varphi) \) without explanation, and then proceed to evaluate the partition function. It is also apparent that in many cases the Hamiltonian functions used were not derived but simply copied. In Refs. 3–6 the Hamiltonian functions are inconsistent with the given definitions of the Euler angles; the moments of inertia \( A \) and \( B \) should be interchanged. In Ref. 2 the same Hamiltonian function as in Refs. 3–6 appears but the Euler angles are neither directly nor implicitly defined. However, a reference is given to Routh, \(^1\) but the given Hamiltonian is not consistent with Routh’s definitions of \( \phi, \theta, \psi, \) unless the definitions of \( \phi \) and \( \psi \) are interchanged. In all of the above cases the inconsistencies do not affect the value of the partition function. In Ref. 7 the Hamiltonian function \( H(\phi, \theta, \psi, p_\phi, p_\theta, p_\varphi) \) is derived and a correct expression obtained. However the sign of one of the angular velocities occurring in the derivation should be reversed; it does not affect the final result. This unusually large number of inconsequential errors is another indication of the tediousness of the conventional calculation. I hope the present note will relieve some of the tedium.


A note on the thermodynamics of blackbody radiation

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One of the key elements in the thermodynamical treatment of blackbody radiation is the statement that at equilibrium the density \( u \) of radiant energy in a cavity depends only on the temperature of the walls of the cavity, and is otherwise independent of the nature of the walls, and of the shape and volume of the cavity. This statement actually holds for the energy density \( u(\omega)d\omega \) in each infinitesimal interval of frequency, \( \omega \), from \( \omega + d\omega \), and not just for the integrated density

\[ u = \int_{\omega}^{\infty} u(\omega)d\omega. \]  

Most modern textbooks do not prove this statement, leaving sometimes the impression that the result is essentially empirical (at least one book\(^1\) states this explicitly). However the books of Pippard\(^2\) and of Sommerfeld\(^3\) (and maybe other books with which I am not familiar) give a very simple proof, described below. The purpose of the present note is to quibble with this proof.

The proof in question runs as follows. Consider two cavities which are at the same temperature, but which may be made of different materials, be of different volume, or be of different shape. Let now the two cavities be connected by a narrow tube, containing a filter which passes radiation only of frequency close to \( \omega \). Since the energy falling on unit area of the walls in unit time is given by the intensity

\[ I(\omega) = (c/4)n(\omega), \]  

it follows that if \( u(\omega) \) is greater in one cavity than in the other, despite the equality of temperature, there will then be a net flux of radiant energy from one cavity to the other. Therefore, it is concluded, one cavity will cool down and the other heat up, in violation of the Second Law of Thermodynamics.

I contend that this argument is incomplete, since as it stands we could equally well apply it to an ordinary gas of molecules, and conclude that there also, as in a gas of photons, the energy density \( u_{gas} \) depends only on its temperature. This is absurd, of course, since we know that \( u_{gas} \) depends not only on the temperature but also on the number of molecules \( n \) per unit volume, and that the latter can be changed without changing the temperature.

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