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Specific Heat of the Anisotropic Rigid Rotator

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The exact (numerical) thermal evolution of the specific heat C of the single anisotropic (not necessarily equal inertial momenta $I_x = I_y \equiv I_{xy}$ and I_z) quantum rigid rotator is calculated. For values of I_{xy}/I_z low enough, C presents an unexpectedly high maximum; for sufficiently high values of I_{xy}/I_z a second peak emerges. Also a quite rich $T \to 0$ asymptotic behavior is exhibited.

KEY WORDS: Specific heat; anisotropic rigid rotator; quantum statistics; molecular statistics.

Very few quantum systems exist for which the *exact* energy spectrum is known. Among them we have the symmetric top or anisotropic rigid rotator associated with *two* different momenta of inertia ($I_x = I_y \equiv I_{xy}$ and I_z do not necessarily coincide). This is an important system as it can account, within a first approximation, for the rotational degrees of freedom of molecules whose inertial ellipsoid is oblate ($I_{xy} > I_z$; e.g., HD, NO, HCl, HCN, SCO) or prolate ($I_{xy} < I_z$; e.g., C_6H_6) or spherical ($I_{xy} = I_z$; e.g., CH_4). Surprisingly enough, the calculation of the specific heat C of this system has never, as far as we know, been accomplished for all temperatures, excepting of course the $I_{xy}/I_z \to \infty$ limit which since long is a standard one.[1] The purpose of the present paper is to exhibit the influence of the ratio I_{xy}/I_z on the thermal behavior of C.

The system is characterized by the Hamiltonian

$$\mathscr{H} = \frac{L_x^2 + L_y^2}{2I_{xy}} + \frac{L_z^2}{2I_z} \tag{1}$$

where L_i ($i = x, y, z$) are the components of the angular momentum $\mathbf{L}$, $I_x = I_y \equiv I_{xy}$ and I_z being the corresponding momenta of inertia (the ratio

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I_{xy}/I_z varies, for the rigid rotator, between $1/2$ (extremely prolate) and ∞ (extremely oblate); however, as an obvious analytical extension, we discuss the whole range $[0, \infty]$). The eigenvalues are given[2] by

$$E_{l,m} = \frac{\hbar^2}{2}\left[\frac{l(l+1)}{I_{xy}} + \left(\frac{1}{I_z} - \frac{1}{I_{xy}}\right)m^2\right] \tag{2}$$

where $l = 0, 1, 2, \ldots,$ and $m = l, l-1, \ldots, -l$, each level presenting, because of the possible projections of $\mathbf{L}$ on the intrinsic rotation axis of the rotator, a $(2l+1)$ degeneracy (see Ref. 3 for a discussion of the eigenvalues associated with the general case where all three $\{I_i\}$ are arbitrary). Notice that, in both particular cases $I_{xy}/I_z \to \infty$ (extremely oblate) and $I_{xy}/I_z = 1$ (spherical), the levels follow the $l(l+1)$ law, but while the former presents a $(2l+1)$ degeneracy, the later presents a $(2l+1)^2$ one. In the particular case $I_{xy}/I_z = 0$ the levels are equidistant and present a relatively irregular degeneracy. The canonical partition function Z is given by

$$Z(t) = \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)/t} \sum_{m=-l}^{l} e^{-(I_{xy}/I_z - 1)m^2/t} \tag{3}$$

where $t \equiv 2I_{xy}k_B T/\hbar^2$. Consequently the specific heat is given by

$$\frac{C}{k_B} = \frac{1}{t^2}\left[\frac{V}{Z} - \left(\frac{W}{Z}\right)^2\right] \tag{4}$$

$$V \equiv \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)/t} \sum_{m=-l}^{l} \left[l(l+1) + \left(\frac{I_{xy}}{I_z} - 1\right)m^2\right]^2 e^{-(I_{xy}/I_z - 1)m^2/t}$$

$$W \equiv \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)/t} \sum_{m=-l}^{l} \left[l(l+1) + \left(\frac{I_{xy}}{I_z} - 1\right)m^2\right] e^{-(I_{xy}/I_z - 1)m^2/t}$$

Through Eq. (4) we have numerically calculated C (see Fig. 1). The most remarkable features are: (i) the existence, for *all* values of I_{xy}/I_z, of an important peak which becomes sharper and sharper while I_{xy}/I_z decreases (for $I_{xy}/I_z = 0$ the height almost attains $k_B 5/2$); (ii) the appearance, for I_{xy}/I_z high enough, of a second and smaller peak which, in the $I_{xy}/I_z \to \infty$ limit, becomes the well-known small bump detectable through standard caculation[1]; (iii) the fact that, for any finite I_{xy}/I_z ratio, $\lim_{T\to\infty} C = k_B 3/2$ (classical equipartition associated with three degrees of freedom), whereas $\lim_{T\to\infty}\lim_{I_{xy}/I_z\to\infty} C = k_B$ (only two degrees of freedom, the other one being frozen); (iv) the existence of interesting non uniform convergences in the $T \to 0$ limit, where we verify that

$$\frac{C}{k_B} \sim \frac{6}{t^2}\left[\left(\frac{I_{xy}}{I_z} + 1\right)^2 e^{-(I_{xy}/I_z + 1)/t} + 2e^{-2/t}\right] \tag{5}$$

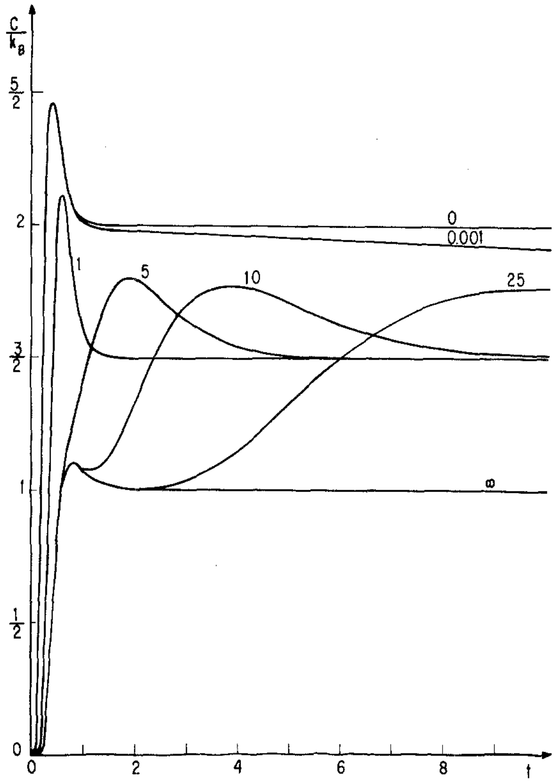

Fig. 1. Reduced specific heat C/k_B as a function of the reduced temperature $t \equiv 2I_{xy}k_BT/\hbar^2$ for typical values of I_{xy}/I_z (numbers parametrizing the curves).

hence (at the leading level)

$$\frac{C}{k_B} \sim \begin{cases} \dfrac{6(I_{xy}/I_z + 1)^2}{t^2} e^{-(I_{xy}/I_z + 1)/t}, & \text{if } 0 \leqslant \dfrac{I_{xy}}{I_z} < 1 \quad (6a) \\ \dfrac{36}{t^2} e^{-2/t}, & \text{if } \dfrac{I_{xy}}{I_z} = 1 \quad (6b) \\ \dfrac{12}{t^2} e^{-2/t}, & \text{if } \dfrac{I_{xy}}{I_z} > 1 \quad (6c) \end{cases}$$

The present results could possibly be of utility for testing theoretical nonexact procedures for calculating specific heats, as well as for the analysis of experimental data on rarefied gases.

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