

On thermodynamics of rigid rotors in the field of centrifugal forces

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Introduction

The thermodynamics and statistical mechanics of rotating system is studied since the works of Maxwell [1]. The fundamental result in the area is the Gibbs distribution for rotating system [2],

$$f(\Gamma) = \frac{1}{Z_0} \exp\left(-\frac{E(\Gamma) - (\mathbf{\Omega}, \mathbf{J}(\Gamma))}{kT}\right); \quad (1)$$

$$Z_0(kT, \mathbf{\Omega}) = \int \exp\left(-\frac{E(\Gamma) - (\mathbf{\Omega}, \mathbf{J}(\Gamma))}{kT}\right) d\Gamma. \quad (2)$$

Here, E is the internal energy, \mathbf{J} is the total angular momentum, T is the temperature, and k is the Boltzmann constant. Both the energy and total angular momentum are supposed to be the function of microscopic state Γ . The quantity Z_0 denotes the partition function, $d\Gamma$ stands for elementary volume element of phase-space. In its own turn, the partition function determines the thermodynamic potential and thermodynamics of the system. The phenomena caused by interaction of proper angular momenta of particles and macroscopic rotation sometimes called the chiral effects [3]. The total angular momentum \mathbf{J} of each particle in the system is given by the sum of orbital and spin angular momentum. The most interesting case has the place when the particle obey a nonzero spin angular momentum. Nevertheless, the formula admits consideration of systems with the orbital angular momentum, for example systems of rigid rotors. The macroscopic rotation excites the rotational degrees of freedom if the product of angular velocity ω and the momentum of inertia of the particle I is at least of order of the Planck constant \hbar ,

$$\omega I \geq \hbar. \quad (3)$$

For small molecules, this inequality requires very high angular velocities of order 10^{10} and higher. For heavy molecules such as fullerenes inequality can be satisfied at much lower angular velocities in the range 10^5 - 10^6 rpm due to their bigger inertia momentum. Such angular velocities accessible with the modern technologies. The aim of the current research is to study the thermodynamics and statistical mechanics and thermodynamics of rigid rotors. We restrict ourselves with the high-temperature expansion for simplicity reasons.

Results and discussions

We consider the statistical mechanics of a single quantum symmetrical rigid rotor with the temperature θ that rotates with constant angular velocity ω around the z -axis of a Cartesian coordinate system. The momenta of inertia of the system with respect to the main axes are denoted by I_x , I_y , I_z . As the rotor is symmetric, without loss of generality we assume $I_x = I_y$. The microscopic state of rotational degrees of freedom of the system is described by the set of quantum numbers l, k, m subjected to conditions

$$l = 0, 1, \dots; \quad k, m = -l, -l+1, \dots, l-1, l. \quad (4)$$

In the state with quantum numbers l, k, m , the kinetic (and total) energy E_{lkm} of rotor and the projection of angular momentum J_z onto z -axis read

$$E_{lkm} = \frac{\hbar^2 l(l+1)}{2I_x} + \frac{\hbar^2 k^2}{2} \left(\frac{1}{I_z} - \frac{1}{I_x} \right), \quad J_z = \hbar m. \quad (5)$$

On substituting these expressions into the Gibbs distribution, we obtain

$$\rho_{lkm} = \frac{1}{Z_0} \exp\left(-\frac{\hbar^2 l(l+1)}{2I_x \theta} + \frac{\hbar^2 k^2}{2\theta} \left(\frac{1}{I_z} - \frac{1}{I_x} \right) + \frac{\hbar m}{\theta}\right). \quad (6)$$

The partition function Z_0 for the rotor has the following form:

$$Z_0 = \sum_{l=0}^{\infty} \sum_{k=-l}^l \sum_{m=-l}^l \exp\left(-\frac{\hbar^2 l(l+1)}{2I_x \theta} + \frac{\hbar^2 k^2}{2\theta} \left(\frac{1}{I_z} - \frac{1}{I_x} \right) + \frac{\hbar m}{\theta}\right). \quad (7)$$

The partition function determines the thermodynamic potential of a single rotor (per rotor) $\Phi = U - \theta S - \omega J$ by the rule

$$\Phi = -\theta \ln Z_0. \quad (8)$$

The thermodynamic potential determines the entropy, and angular momentum by the rule

$$d\Phi = -S d\theta - J d\omega. \quad (9)$$

The entropy and angular momentum of the system are determined as the derivatives of the function Φ ,

$$S = -\left(\frac{\partial \Phi}{\partial \theta}\right)_{\omega}, \quad J = -\left(\frac{\partial \Phi}{\partial \omega}\right)_{\theta}. \quad (10)$$

We are interested in the high temperature expansion of the partition function.

We estimate (7) the sum over the indices l, m, k by the integral as follows (only leading and sub-leading orders are written out):

$$\sum_{x=a}^b f(x) = \int_{a-\frac{1}{2}}^{b+\frac{1}{2}} f(x) dx - \frac{1}{24} f'(x) dx \Big|_{a-\frac{1}{2}}^{b+\frac{1}{2}} + \dots \quad (11)$$

The high-temperature expansion of the partition function (7) reads

$$Z_0 = \sqrt{\frac{8\pi\theta^3 I_x^2 I_z}{\hbar^6}} \left(1 + \frac{\hbar^2}{\theta} \cdot \frac{(2I_x + I_z)^2 - 2(2I_x^2 + I_z^2)}{24I_x^2 I_z} + \frac{\omega^2}{\theta} \cdot \frac{2I_x + I_z}{6} + o\left(\frac{1}{\theta}\right) \right). \quad (12)$$

Here, the common factor is the partition function of classical rotor in absence of macroscopic rotation, while the expression in bracket accounts quantum and rotational corrections. The first line terms determines the quantum correction to the partition function of non-rotating classical rotor. The second line correction accounts rotational contributions. The leading rotational term is classical because does not include the Planck constant. As we see, the first rotational correction is determined by the average momentum of inertia,

$$I_{avg} = \frac{1}{3}(2I_x + I_z) = \frac{1}{3}(I_x + I_y + I_z). \quad (13)$$

The result has simple explanation. In the weakly rotating system, an orientation of main axis of inertia is almost chaotic. Thus formula (13) involves contributions of each axis of inertia on equal basis.

The high-temperature expansion of the thermodynamic potential (8) reads

$$\Phi = -\theta \ln \sqrt{\frac{8\pi\theta^3 I_x^2 I_z}{\hbar^6}} - \hbar^2 \cdot \frac{(2I_x + I_z)^2 - 2(2I_x^2 + I_z^2)}{24I_x^2 I_z} - \omega^2 \cdot \frac{2I_x + I_z}{6} + o(1). \quad (14)$$

(the contributions that are proportional to the negative powers of θ are not included). The internal energy, entropy, and angular momentum have the following form:

$$U = -\frac{3}{2}\theta - \hbar^2 \cdot \frac{(2I_x + I_z)^2 - 2(2I_x^2 + I_z^2)}{24I_x^2 I_z} - \omega^2 \cdot \frac{2I_x + I_z}{3} + o(1). \quad (15)$$

$$S = \ln \sqrt{\frac{8\pi\theta^3 I_x^2 I_z}{\hbar^6}} + \frac{3}{2}, \quad J = \omega \frac{2I_x + I_z}{3}. \quad (16)$$

As is seen, the internal energy increases with the growth of angular velocity ω . As for the entropy S , it does not depend on angular velocity. The happens because we took

into account first non-trivial correction to the thermodynamic potential. In next order of perturbation theory, the entropy of the system depends on angular velocity. In the classical limit it is determined by the ω^4 -contributions, while in the quantum case $\omega^2 \hbar^2$ -terms are important. The angular momentum J linearly grows with spin. The latter relation has the sense of equation of state (the temperature is involved in higher order corrections). Our result shows that the rotational degree of freedom can be involved in interaction with the thermal degree of freedom. In particular, it is possible to consider the thermodynamic processes in rotating systems of rotors.

It is interesting to study the heat capacities of at constant angular velocity and constant angular momentum. To solve the problem, we need next-order correction to the thermodynamic potential. It is convenient to express the result via the symmetric combinations of inertia momenta, $I_m^n = (2I_x^m + I_z^m)^n$,

$$\Phi = \dots + \frac{1}{72\theta} \left(-\frac{\hbar^4}{10} \cdot \frac{6I_4^1 + I_2^2 I_1^2 - 4I_1^1 I_3^1 - I_2^2}{10I_x^4 I_z^2} - \hbar^2 \omega^2 \frac{I_3^1 - 4I_1^3}{I_x^2 I_z} + \omega^4 I_1^1 \right) + o\left(\frac{1}{\theta}\right). \quad (17)$$

The dots denote contributions given in equation (14). In approximation (19), we get

$$C_\omega = \frac{3}{2} + \frac{1}{36\theta^2} \left(-\frac{\hbar^4}{10} \cdot \frac{6I_4^1 + I_2^2 I_1^2 - 4I_1^1 I_3^1 - I_2^2}{10I_x^4 I_z^2} - \hbar^2 \omega^2 \frac{I_3^1 - 4I_1^3}{I_x^2 I_z} + \omega^4 I_1^1 \right) + o\left(\frac{1}{\theta}\right). \quad (18)$$

For the heat capacity at constant angular momentum, we find

$$C_J = C_\omega - \theta \left(\frac{\partial \omega}{\partial J} \right)_\theta \left(\frac{\partial J}{\partial \theta} \right)_\omega^2 = C_\omega - \frac{3}{2I_x + I_z} \frac{4\omega^2}{72\theta^3} \left(-\hbar^2 \frac{I_3^1 - 4I_1^3}{I_x^2 I_z} + 2\omega^2 I_1^1 \right)^2 + o\left(\frac{1}{\theta^3}\right). \quad (19)$$

Figure 1 shows the heat capacity C_ω at constant angular velocity.

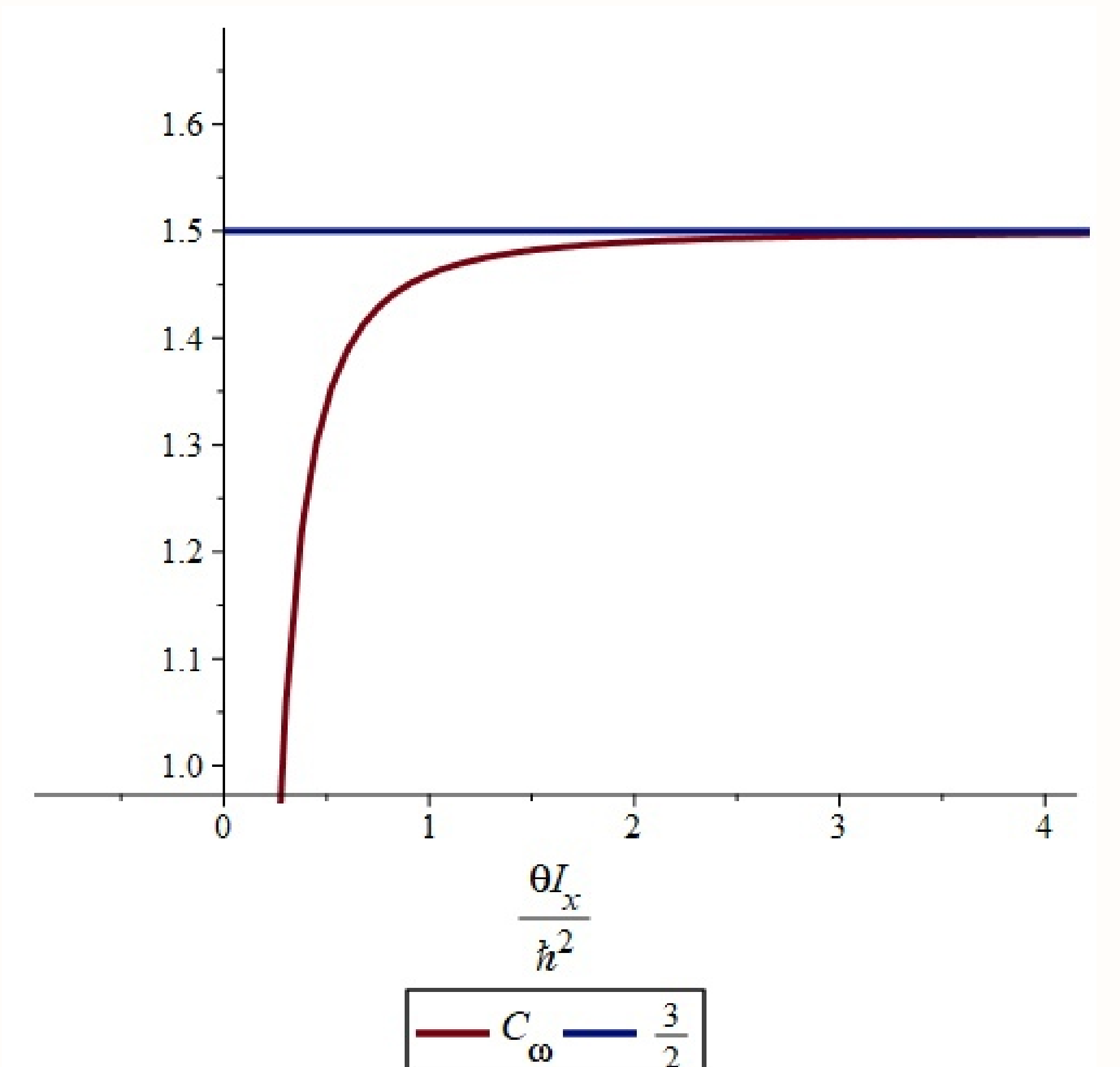


Figure 1: Heat capacity C_ω for $I_x/I_z = 2$.

References

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- [3] K. Fukushima, Extreme matter in electromagnetic fields and rotation, *Prog. in Part. and Nucl. Phys.* 107 (2019) 167.