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## LETTER TO THE EDITOR

# Quantum melting in a system of rotators

Yu A Freiman†, V V Sumarokov†, A P Brodyanskii† and A Jezowski‡

† Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, 47 Lenin Avenue, 310164 Kharkov, USSR

‡ W Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50–950 Wrocław 2, PO Box 937, Poland

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**Abstract.** We consider a simple system of interacting rotators and show that such a system could display properties of quantum crystals. The possibility of realizing new quantum systems is discussed.

As is well known, as well as usual or classical melting there is also quantum melting which can take place at zero temperature. These two types of melting are caused by two different mechanisms. In classical melting the system state is determined by a competition between the potential energy favoured ordered state and the entropy contribution to the free energy of the system. In this case the kinetic energy of the system plays no decisive role. Quantum melting occurs as a result of the competition between the potential and kinetic energies of the system. In this case the entropy factor is of no importance. Well known examples of systems which exhibit quantum melting are solid  $^3\text{He}$  and  $^4\text{He}$ . In the present work it will be shown that under certain conditions the system of rotators may display an analogous phenomenon—quantum orientational melting.

Let us consider the system described by the Hamiltonian

$$\mathcal{H} = B\mathcal{L}^2 - U\eta P_2(\cos \Theta) + U\eta^2/2. \quad (1)$$

Here  $B\mathcal{L}^2$  is the operator of the kinetic energy of rotation,  $B$  is the rotational constant,  $P_2(\cos \Theta) = \frac{1}{2}(3 \cos^2 \Theta - 1)$ ,  $\eta \equiv \langle P_2(\cos \Theta) \rangle$  is the order parameter, the angular brackets denote a Gibbs average with respect to the Hamiltonian (1), and  $U$  is the molecular field constant.

The Hamiltonian (1) is well known in the theory of molecular cryocrystals [1] where it was used to describe the orientational disordering in such crystals as  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$  [2],  $\text{O}_2$  [3], etc.

The character of the spectrum of the system described by the Hamiltonian (1) is determined by the dimensionless parameter  $V = U/B$ . In the case of large  $V$  the rotator motion is close to harmonic librations. Such a case is realised in the orientationally ordered phases of  $\text{N}_2$ - and  $\text{O}_2$ -type crystals ( $V \sim 100$ ). In the inverse limiting case ( $V \ll 1$ ) Hamiltonian (1) describes the weakly hindered rotation.

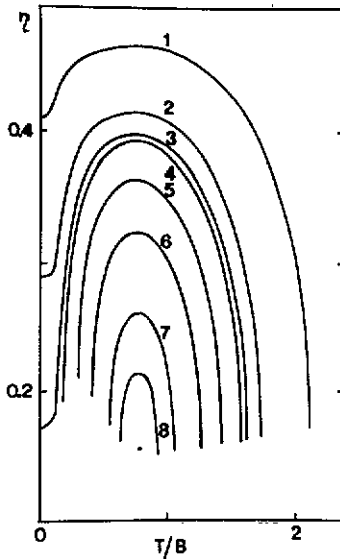


Figure 1. Temperature dependences of the order parameter for various  $V$ : 15 (curve 1), 13.5 (curve 2), 13.106 (curve 3), 13 (curve 4), 12.5 (curve 5), 12 (curve 6), 11.5 (curve 7) and 11.3 (curve 8). The point corresponds to  $V = 11.2$ .

In the present work an intermediate case  $V \geq 1$  is investigated and it is shown that under this condition the system described by the Hamiltonian (1) displays properties of a quantum crystal.

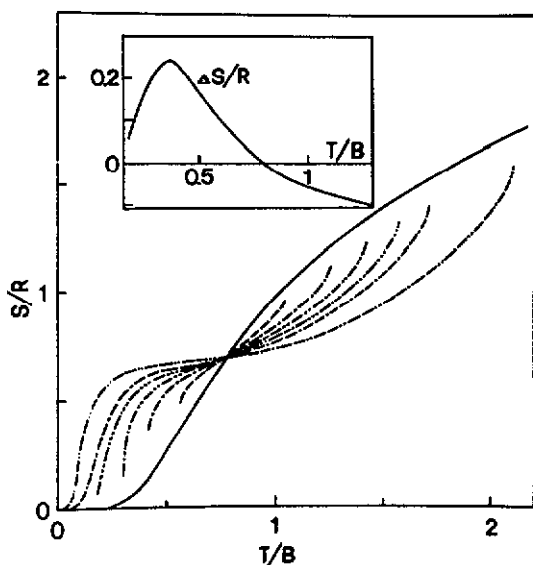
The method of calculation of the spectrum was described in detail in [4]; let us note, however, that in the case  $V \geq 1$  a basis of spherical functions  $Y_{lm}$  in which the kinetic energy operator is diagonal is convenient. In this paper the size of the basis set was limited by the value  $l = 7$ , which was sufficient for calculating the lower levels of a hindered rotator for not very large values of the parameter  $V$ .

With the aid of the spectrum the free energy  $F$  as a function of the order parameter and temperature was calculated and from the condition  $\partial F / \partial \eta = 0$  the temperature dependence of the order parameter  $\eta = \eta(T)$  was obtained.

Figure 1 shows the temperature dependences of the order parameter calculated for different values of  $V$ . At large  $V$  ( $V \geq 30$ ) the temperature dependence of the order parameter is typical for first-order phase transitions. Decreasing  $V$  leads to an appearance of non-monotonicity on the curves  $\eta(T)$  and beginning with some value of  $V$  the order parameter in a low-temperature range becomes zero. Thus, there is a critical value  $V = V_0$  below which existence of the orientationally ordered phase at  $T = 0$  is impossible. As shown in numerical calculations,  $V = 13.1$ .

Thus, as the case of solid helium required the external pressure to be applied for crystallization at  $T = 0$ , in the system of rotators the orientational localization is possible only with a sufficiently high orientational barrier. Disordering in the rotator system with decreasing barrier height in the range  $V < V_0$  has a quantum nature and is caused by a sharp increase in the zero rotational kinetic energy in a case of orientational localization.

Consider the situation at  $T \neq 0$ . The most interesting observation is the appearance of the ordered phase at  $V < V_0$  with increasing temperature. To elucidate the results depicted in figure 1 let us turn to the analysis of the rotator entropy. As can be seen from figure 2 the entropy of the system has an anomalous character: in the low-temperature range the entropy of the ordered phase is higher than that of disordered one. The



**Figure 2.** Temperature dependences of the entropy of the rotator systems for various  $V$ : —, 0; ----, 11.5; - · - ·, 12; - · · - ·, 12.5; - · · · - ·, 13; - · - · - ·, 13.5; - · · · · - ·, 15. The insert shows  $\Delta S = S - S_0$ , the difference between the entropies of the ordered and disordered phases,  $S$  and  $S_0$ , respectively, as a function of temperature.

quantity  $\Delta S = S - S_0$ , the difference between the entropies of ordered and disordered phases ( $S$  and  $S_0$  respectively) as can be seen from the insert in figure 2, has a complex temperature dependence. Such behaviour of the entropy can be explained by peculiarities in the system spectrum.

In the disordered phase the gap between the ground state and the first excited triplet level is  $2B$ . In the ordered phase the triplet level splits into a singlet and a doublet, and the gap between the ground and singlet states  $\Delta$  is smaller than  $B$  and decreases rapidly with increasing order parameter. Due to the growing population of this level the entropy of the system increases rapidly with temperature. As the population of higher levels grows with further temperature increase, the destabilizing action of the temperature begins to prevail over the stated effect, the  $\Delta S(T)$  curve reaches a maximum and, finally, at higher temperature it changes sign—the entropy of the disordered phase becomes higher than that of the ordered one.

At  $T = 0$  the only ordering factor is the potential energy; with temperature increase the contribution of the entropy factor  $T \Delta S$  to the free energy increases, and at some temperature the sum of the potential energy and the entropy factor levels with the disorder factor, and the kinetic energy, and the phase transition into the ordered phase occurs.

There is a direct correspondence between the temperature dependences of the entropy and the order parameter. In the temperature range where  $\Delta S > 0$  the order parameter increases with temperature, at the point where  $\Delta S = 0$ ,  $\eta(T)$  goes through a maximum and with further temperature increase the order parameter behaves as in a usual order-disorder phase transition. In a low-temperature range on the  $\eta(T)$  curves there is another anomaly. As seen in figure 1, the values of the order parameter at points of the low-temperature phase transition are non-monotonic and go through a maximum. This anomaly in the order parameter corresponds to the anomaly  $\Delta S$  shown in the insert in figure 2.

With further decrease in the parameter  $V$  the temperature range of existence of the ordered phase, is limited between the points of the low- and high-temperature phase transitions, narrows and at the point of intersection of the lines of these transitions ( $V = V_1 = 11.2$ ,  $T/B = 0.78$ ) degenerates into a point. At  $V < V_1$  only the disordered phase can exist.

Thus, at  $V_1 < V < V_0$  the orientationally ordered phase exists in a temperature range limited from above and below. The lower transition has a pure quantum nature and connects with an entropy contribution to the free energy which along with the potential energy stabilizes the ordered phase while the kinetic energy destabilizes it. The upper transition is a usual order-disorder phase transition.

We want to note that the predicted phenomenon—quantum orientational melting—cannot be destroyed by correlation effects neglected in this discussion because the application of the molecular field approximation usually overestimates the stability of the ordered phase.

In conclusion let us discuss the possibility of the experimental realization of the discussed phenomenon. In molecular crystals such as  $N_2$  and  $O_2$  the parameter  $V \sim 100$  and the orientationally ordered phase persists down to zero temperature. The lowering of  $V$  is possible by dissolving inert gases either in the molecular crystals, or in 2D molecular layers. Such systems require separate analysis which will be given elsewhere, but as follows from the present discussion they can claim the role of new quantum systems.

## References

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