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THERMODYNAMICS OF INCOMMENSURATE QUANTUM CRYSTAL

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ABSTRACT

The thermodynamic properties of incommensurate quantum crystal at low temperature are studied using commensurability count. Permutation of the sites and atoms is done in the system of bosons where exclusion is done due to identity among the bosons. The count of the whole system is made and by use of starling approximation, the equation is simplified for easy management. From thermodynamics we get a relation between Gibbs free energy and count, which is used to develop Gibbs free energy as temperature dependence. On differentiating the energy, entropy is determined and finally specific heat is determined by dividing entropy with $\log T$ so that maximum and minimum specific heat is observed

Keywords: *Commensurability Count on Properties of Thermodynamics*

INTRODUCTION

The study of thermodynamics properties of incommensurate quantum crystal has been explored using partition function method in statistical mechanics. It is the limitation of determination of entropy and specific heat at low- temperature that led to introduction of commensurability count. Permutation and exclusion of particles and sites leads to easier development of Gibbs free energy hence determination of entropy and specific heat.

There have been experimental (Kim and Chan, 2004), and theoretical (Chandhuri *et al.*, 1999) studies on the properties of crystals of solid ⁴He. The experimental observations and theoretical studies seem to suggest the existence of a ‘supersolid’ phase. In a crystal of bosons, it is believed that the supersolid phase may occur due to the quantum behavior of point defect, namely vacancies and interstitials (Andreev and Lifshitz, 1969; Burns and Goodkind, 1994; Gardner *et al.*, 1973). Previously, a number of experiments had been done to measure the temperature dependence of the vacancy concentration in solid ⁴He, (Renato *et al.*, 2009).

The X- ray measurements on solid hexagonal close packed ⁴He showed that the density of vacancies increases faster than that of interstitials with increasing temperature (Burns and Goodkind, 1994), indicating that Thermal fluctuations favors vacancies more than interstitials. Khanna *et al.*, (2008) in there calculation while studying solid ⁴He under high pressure indicates that crystals moves one behind the other instead of interfusing and that the capillary effect may not be an intrinsic low- temperature property of solid ⁴He. Chelimo (2011) looked at the properties of the crystal. In his work he used partition function of the crystalline particles of super solid ⁴He. He developed Gibbs free energy, entropy and specific heat and determined transition temperature ($T_c=1.25K$) which seemed to be within other results that range from 0.2K to 1,3K but his final equation of specific heat assumed the form; $C_v=AT^3+BT^7$ that has only two terms. The limitation is that he could not determine entropy and specific heat.

The quantitative approach to thermodynamic studies has been embraced in this work. Gibbs energy has been developed from which determination of entropy and specific heat has been done. This work is pegged on development of Gibbs energy which is connected to microscopic properties of the logarithms count while partition is anchored on applications of external heat in the system to bring in temperature variation. ⁴He is used to prevent metals from atmospheric oxidation and as inert gas, in super solid form it is used as a coolant in industries and medical sciences.

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Properties of Incommensurate Crystal

Incommensurability has some effect on thermodynamic properties of ⁴He crystals. In this crystal, sites (N_s) and particles (N) are put in consideration because the ratio of their differences to the sites leads to incommensurability (ε). That is

$$\epsilon = \frac{N_s - N}{N_s} \tag{1}$$

Dealing with bosons, the number of ways we can permute sites and particles is (N+N_s)!. Particles in these systems are identical therefore permutations among them must be excluded by dividing by N!. Similarly permutations among identical sites are excluded by N_s!. Thus the number of ways in which the particles can be distributed among the sites is given as

$$P = \frac{(N+N_s)!}{N_s! N!} \tag{2}$$

The count C for commensurability is then developed as

$$C = \prod_s P = \prod_s \frac{(N+N_s)!}{N_s! N!} \tag{3}$$

The count is a large number therefore to solve it, we take logarithms on both sides because it is simpler to maximize log C than it is with T, that is

$$\log C = \log \prod_s \frac{(N+N_s)!}{N_s! N!} = \sum [(\log N + N_s)! - \log N! - N_s!] \tag{4}$$

For a large number of x, approximation can be used in simplifying such that log x! = x log x - x. Hence equation (3), results to

$$\log C = \sum_s (N + N_s) \log(N + N_s) - (N + N_s) - N \log N + N - N_s \log N_s + N_s$$

this equation simplifies to:

$$\log C = \sum_s (N + N_s) \log(N + N_s) - N \log N - N_s \log N_s \tag{5}$$

From equation (1), we make N_s the subject to get

$$N_s = \frac{N}{1 - \epsilon} \tag{6}$$

Thus definition for N_s in equation (6) requires that ε ≠ 1 at any time. Substituting for N_s in equation (5) gives

$$\log C = \sum_s \left[\left(N + \frac{N}{1 - \epsilon} \right) \log \left(N + \frac{N}{1 - \epsilon} \right) - N \log N - \frac{N}{1 - \epsilon} \log \frac{N}{1 - \epsilon} \right] \tag{7}$$

Making (1-ε) the common multiple of equation (7), it simplifies to:

$$\log C = \sum_s \left[N \left(\frac{2 - \epsilon}{1 - \epsilon} \right) \log N \left(\frac{2 - \epsilon}{1 - \epsilon} \right) - N \log N - \left(\frac{N}{1 - \epsilon} \right) \log \frac{N}{1 - \epsilon} \right]; \tag{8}$$

If N is uniquely determined then it may have only one value for a given crystalline system. Hence the summation over all values of “S” in equation (8) is inconsequential and can be dropped. Hence

$$\log C = \left[N \left(\frac{2 - \epsilon}{1 - \epsilon} \right) \log N \left(\frac{2 - \epsilon}{1 - \epsilon} \right) - N \log N - \left(\frac{N}{1 - \epsilon} \right) \log \frac{N}{1 - \epsilon} \right] \tag{9}$$

Khanna (1986), used the equation below which relates the number of particles(N), the Planck’s constants (h), mass of helium (m), the Boltzmann constant (k), temperature (T), spin (T) and the volume of the container (v)

$$\frac{N h^3}{v g (2 \pi m k T)^{3/2}} = 2.612 \text{ Kg/m}^3 \text{ sk}^0 \tag{10}$$

We consider spinless boson so that there is no interaction among the particles. For spinless boson, g =1, V= volume of the container.

Equating all constants in equation (10) to A, and making N the subject, gives

$$N = A T^{3/2} \tag{11}$$

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$$\text{Where } A = (2.612)V \frac{(2\pi mk)^{\frac{3}{2}}}{h^3} \tag{12}$$

A is an extensive variable that depends on volume and therefore it is a volume charge which is measured in m³. Substituting ‘N’ from equation (11) in equation (9) gives

$$\log C = \left[AT^{\frac{3}{2}} \left(\frac{2-\epsilon}{1-\epsilon} \right) \log AT^{\frac{3}{2}} \left(\frac{2-\epsilon}{1-\epsilon} \right) - AT^{\frac{3}{2}} \log AT^{\frac{3}{2}} - \left(\frac{AT^{\frac{3}{2}}}{1-\epsilon} \right) \log \frac{AT^{\frac{3}{2}}}{1-\epsilon} \right] \tag{13}$$

In thermodynamics, a cooling system gives a relation between the Gibb’s free energy G and entropy S as:

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \tag{14}$$

Separating the variables and integrating gives

$$G = - \int S dT \tag{15}$$

Where ‘G’ is a function of T. Entropy is also given as $S = k \log c$, therefore substituting for S in equation (15) gives

$$G = -K \int \log C dT \tag{16}$$

Using equation (13), equation (16) gives

$$G = -K \int \left[AT^{\frac{3}{2}} \left(\frac{2-\epsilon}{1-\epsilon} \right) \log AT^{\frac{3}{2}} \left(\frac{2-\epsilon}{1-\epsilon} \right) - AT^{\frac{3}{2}} \log AT^{\frac{3}{2}} - \frac{AT^{\frac{3}{2}}}{1-\epsilon} \log \frac{AT^{\frac{3}{2}}}{1-\epsilon} \right] dT \tag{17}$$

Which can be worked out to get

$$G = -k \left[\left[\left(\frac{2}{5}(x+y) - \frac{2}{5}z \right) + \frac{2A}{5} \log A - \frac{3A}{2} \right] - \frac{2}{5} \left(\frac{A}{1-\epsilon} \right) \log \frac{A}{1-\epsilon} - \frac{3}{5} \left(\frac{A}{1-\epsilon} \right) \right] T^{\frac{5}{2}} + \left(\frac{2z}{5} + \frac{3A}{5} + \frac{3}{5} \left(\frac{A}{1-\epsilon} \right) \right) T^{\frac{7}{2}} \tag{18}$$

This is the Gibbs free energy.

We introduce the following constants in the Gibbs free energy equation to make it manageable when working with it.

$$\gamma = \left[\left(\frac{2}{5}(x+y) - \frac{2}{5}z \right) + \frac{2A}{5} \log A - \frac{3A}{2} \right] - \frac{2}{5} \left(\frac{A}{1-\epsilon} \right) \log \frac{A}{1-\epsilon} - \frac{3}{5} \left(\frac{A}{1-\epsilon} \right); \alpha = \frac{2z}{5} + \frac{3A}{5} + \frac{3}{5} \left(\frac{A}{1-\epsilon} \right) \tag{19}$$

Then $G = -k \left(\gamma T^{\frac{5}{2}} + \alpha T^{\frac{7}{2}} \right)$ as

From thermodynamics, entropy ‘S’ is given as;

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \tag{20}$$

The system under consideration is a reversible cooling system. Knowing the Gibb’s free energy, entropy can determine as;

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = \left[\frac{k}{2} \left(5\gamma T^{\frac{3}{2}} + 7\alpha T^{\frac{5}{2}} \right) \right] \tag{21}$$

From equation (21) specific heat C_V is calculated as

$$C_V = \frac{S}{\log T} = \frac{S}{T} \quad \text{When } T \ll 1$$

$$\text{Therefore, } C_V = -k \left(\frac{5}{2} \gamma T^{\frac{3}{2}} + \frac{7}{2} \alpha T^{\frac{5}{2}} \right) \cdot \frac{1}{T} = -k \left(\frac{5}{2} \gamma T^{\frac{1}{2}} + \frac{7}{2} \alpha T^{\frac{3}{2}} \right) \tag{22}$$

From which the transition temperature T_c can be developed as:

$$\left(\frac{\partial C_V}{\partial T} \right)_{T=T_c} = 0 = -k \left(\left(\frac{5}{2} \gamma \frac{1}{2} \right) T_c^{-\frac{1}{2}} + \left(\frac{7}{2} \alpha \frac{3}{2} \right) T_c^{\frac{1}{2}} \right) \tag{23}$$

For maximum specific heat, equation (4.38) (22) has a gradient of zero and transition temperature T_c is equal to normal temperature T.

$$\text{Or } k \neq 0 \text{ therefore } \left(\frac{5}{2} \gamma \frac{1}{2} \right) T_c^{-\frac{1}{2}} + \left(\frac{7}{2} \alpha \frac{3}{2} \right) T_c^{\frac{1}{2}} = 0$$

$$\text{Hence } T_c = \frac{5\gamma}{21\alpha} \tag{24}$$

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By first calculating volume $V \approx a^3/8$, then calculate A from equation (11) where m is the mass of ^4He atom and V is the volume of the hexagonal close packed lattice of ^4He . This volume is given as;

$$V \approx \frac{a^3}{8} = \frac{20.23 \text{ cm}^3/\text{mol}}{6.023 \times \frac{10^{23} \text{ molecules}}{\text{mol}}} = 3.359 \times 10^{-29} \text{ m}^3 \quad (25)$$

Given that; $V = 3.359 \times 10^{-29} \text{ m}^3 \pi = 3.142$, $m = 6.68 \times 10^{-27} \text{ kg}$, $k = 1.38 \times 10^{-23} \text{ J/K}$, $h = 6.63 \times 10^{-34} \text{ JS}$

$$\text{Then } A = 2.612V \frac{(2\pi mk)^{\frac{3}{2}}}{h^3} = 0.13260 \text{ per m}^3 \quad (26)$$

Recent data by Kim and Chan (2004) showed that N_s and N may differ by up to 1% and Since $N_s > N$, N_s is fixed at 100%. From equation (1)

$$\epsilon = \frac{1\%}{100\%} = 0.01 \quad (27)$$

The value of ϵ is used to calculate the values of α and γ from equation (21) as

$$\gamma = \left[\left(\frac{2}{5}(x+y) - \frac{2}{5}z \right) + \frac{2A}{5} \log A - \frac{3A}{2} \right] - \frac{2}{5} \left(\frac{A}{1-\epsilon} \right) \log \frac{A}{1-\epsilon} - \frac{3}{5} \left(\frac{A}{1-\epsilon} \right) = -0.593621797 \quad (28)$$

$$\alpha = \frac{2z}{5} + \frac{3A}{5} + \frac{3}{5} \left(\frac{A}{1-\epsilon} \right) = 0.2402868 \quad (29)$$

$$T_c = -\frac{5\gamma}{21\alpha} = 0.59 \text{ K} \quad (30)$$

At the transition temperature, Gibbs free energy, entropy, specific heat are determined.

$$\text{That is } G = -k \left(\gamma T^{\frac{5}{2}} + \alpha T^{\frac{7}{2}} \right) = -1.67 \times 10^{-24} \text{ J K}^{-1} \quad (31)$$

$$S = -\left(\frac{\partial G}{\partial T} \right)_p = \left[\frac{k}{2} \left(5\gamma T^{\frac{3}{2}} + 7\alpha T^{\frac{5}{2}} \right) \right] = 6.18 \times 10^{-24} \text{ J K}^{-1} \quad (32)$$

$$C_v = k \left(\frac{5}{2} \gamma T^{\frac{1}{2}} + \frac{7}{2} \alpha T^{\frac{3}{2}} \right) = -1.05 \times 10^{-23} \text{ J K}^{-1} \quad (33)$$

The effect of Incommensurability on Transition Temperature (T_c)

The variations of incommensurability and lattice constant have some effect on transition temperature as shown in equation (30) $T_c = -\frac{5\gamma}{21\alpha} = 0.59 \text{ K}$. Equation (18), informs the graph in figure1 from which the value of $T_c = 0.59\text{K}$. This agrees well with the different experimental and theoretical observation made by Kim (2004), Anderson, (2005) and Limo (2011), whose T_c values ranged between 0.2K and 1.3K. The theoretical study of quantum crystal under external pressure by Limo (2011) gives a transition temperature $T_c = 1.25\text{k}$. This information concurs with what is determined in this work and is within acceptable tolerance as depicted in the figures below:

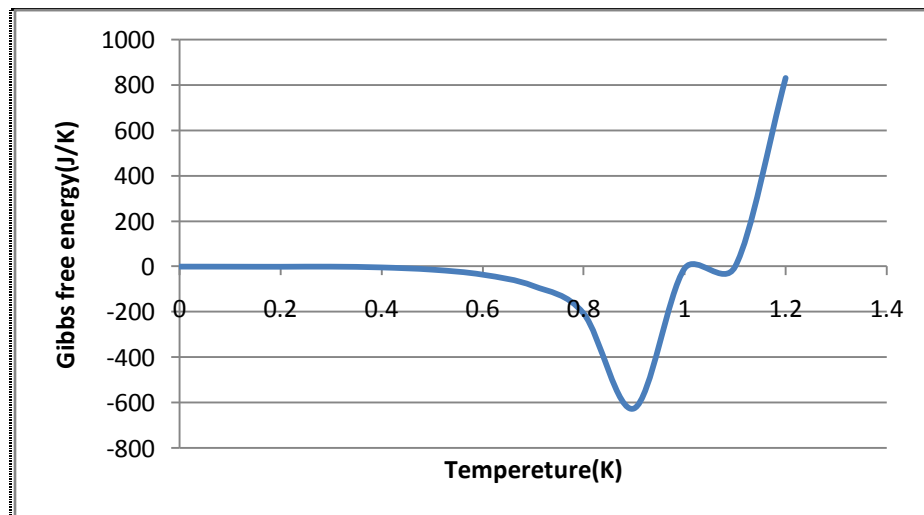


Figure 1: Gibb's Free Energy, G against Temperature, T

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In addition to external energy in a given system, several other useful quantities are present but Gibbs free energy is a potential function of temperature under normal conditions. It is seen to vary linearly with temperature. At constant volume and low temperature, the system experiences dissipative energy that results to negative values of Gibbs as shown in figure 1. Below transition temperature, there are a lot of fluctuations caused by dissipations where maximum dissipation is observed at 0.3K. This is where the free energy is highest and the particles are unstable until beyond transition temperature. After T_c the system is at equilibrium exhibiting the characteristics of canonical ensemble.

The explanation agrees with that of (Anderson, 2005) where quantum fluctuation were strong enough to put the system out of the Mott insulating phase but the ground state remained commensurate because of an approximate vacancy-interstitial symmetry.

Entropy against Temperature

The graph of specific heat capacity against temperature was drawn using equation (21)

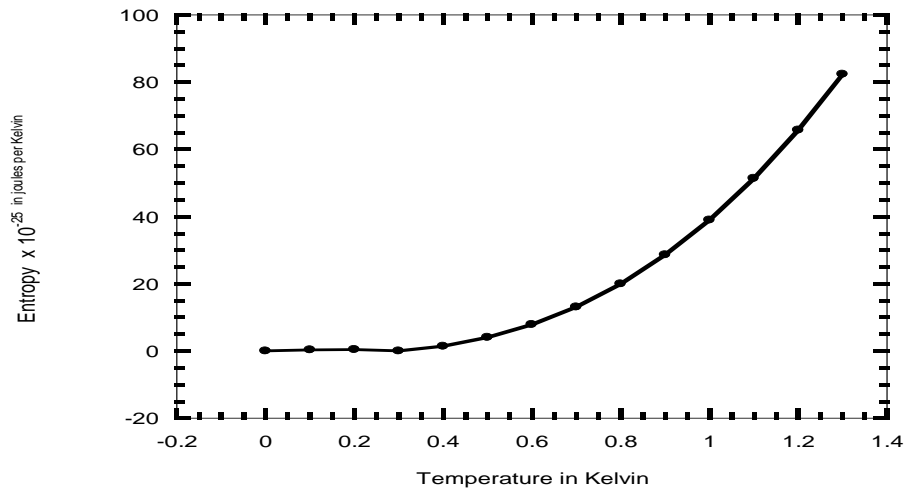


Figure 2: The graph of entropy vs. temperature

Entropy is a measure of disorder in a system. On the graph shown above, entropy is seen increasing instantaneously with increase in temperature. This shows excitation of the particles in the system. The particles in the system do not spin at low temperatures but they gain momentum as the temperature increases. This results tally with that of Ayodo 2008.

Specific Heat Capacity at T_c

The graph of Specific heat capacity against temperature is informed by equation (22) and is shown below.

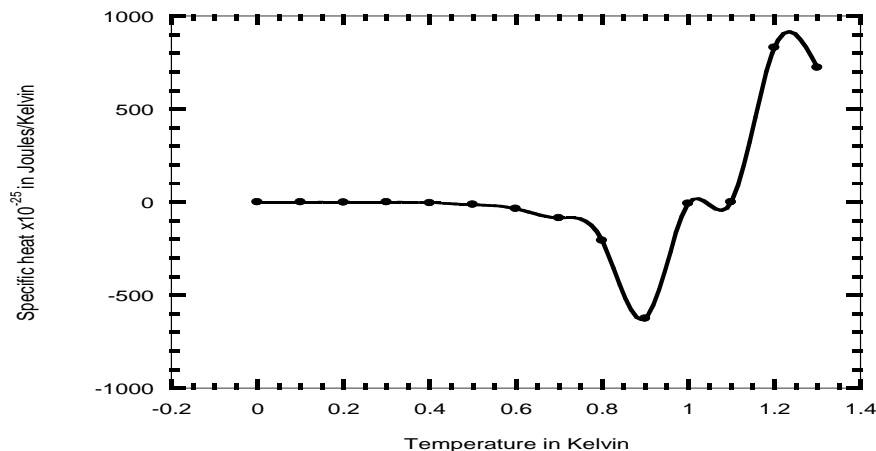


Figure 3: The graph of Specific heat against temperature

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Specific heat is the heat required to raise 1kg of a substance by 1 kelvin. The value of specific heat at transition temperature from equation (22) is $-1.05 \times 10^{-23} \text{ J K}^{-1}$. The value appears to be very low as temperature decreases below 0.597K, majorly because of the microscopic occupation of the ground state. This concurs with what Sakwa *et al.*, (2004) observed for disordered bosons. Thereafter Zero Momentum State (ZMS) remains quite stable as it is sufficiently occupied as from the transition point (Khanna and Sakwa, 2000). In the four –level approximation of the disordered medium by Sakwa *et al.*, (2004), the ZMS was depleted resulting to change of T_c values. After transition temperature, more particles gain energy and a lot of fluctuations are seen thereafter.

Conclusion

The variation of incommensurability and lattice constant of ^4He solid gives transition temperature of 1.097k. This observation has also been seen by Kim (2004), Anderson (2005) and Limo (2011) whose values are in the range of 0.2K to 1.3K. The entropy which is determined statistically, naturally, increases with temperature. From equation (32), the value of S at T_c as $6.18 \times 10^{-24} \text{ J/k}$ and this agrees with the value on the graph. It is found that specific heat increases slightly with temperature and at transition temperature, its value is $-1.05 \times 10^{-23} \text{ J/k}$. There is phase transition because of zero gradient.

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REFERENCES

- Anderson PW, Brinkman WF and Hose DA (2005).** Thermodynamics of Incommensurate quantum crystal. *Science* **310**(5751) 1164-6.
- Andreev AF and Lifshitz IM (1969).** Quantum theory of defects in crystals. *Soviet Physics - JETP USSR* **29** 1107
- Ayodo YK (2008).** Low Temperature Statistical Thermodynamics of a Binary Bose-Fermi System. *PhD. Thesis Moi University.*
- Burns CA and Goodkind JM (1994).** Search of Evidence of Influence of Vacancies on Thermal Conductivity of Solid Helium. *Journal of Low Temperature Physics* **95** 695.
- Chandhuri B, Pederiva F and Chester GV (1999).** Monte Carlo Study of Vacancies in the bcc and hcp phases of ^4He . *Physical Review B* **60** 3271-3278.
- Gardner WR, Hoffer JK and Phillip NE (1973).** Thermodynamic Properties of ^4He , The hcp Phase at Low Densities. *Physical Review A* **7** 10431029.
- Khanna KM (1986).** *Statistical Mechanics and Many Body Problems* (Today and tomorrow printers and publishers) New Delhi 79.
- Khanna KM, Sakwa TW, Chellimo LS and Ayodo YK (2008).** Solid ^4He Under Very High Pressure. *Indian Journal of Pure and Applied Physics* **46** 857-861.
- Kim E and Chan MHW (2004).** Probable observation of Supersolid Helium Phase. *Nature* **427** 225-227.
- Kim E and Chan MHW (2004).** Observation of Superflow in Solid Helium. *Science* **305** 1941.
- Kim E and Chan MHW (2006).** Supersolid Helium at High Pressure. *Physics Review Letters* **97**(11) 115302.
- Limo CD (2011).** Thermodynamic of incommensurate quantum crystal. *PhD. Thesis Moi University.*
- Renato P, de Koning M and Silvio AV (2009).** Zero-Point Vacuum Concentration. *Journal of Statistical Physics* **134**.
- Sakwa TW and Khanna KM (2000).** Occupation of Zero Momentum State, Condensate Fraction and Adsorption of Helium. *Indian Journal of Pure and Applied Physics* **38** 697-701.
- Sakwa TW, Khanna KM, Mueni M, Rotich SK and Torongey PK (2004).** Four Level Approximations in Disorderd Medium. *Indian Journal of Pure and Applied Physics* **42** 355-360.