A Hard-Sphere Assembly of Crystalline Bosons

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The properties of crystalline quantum hard-sphere systems of bosons at low and high densities are studied. At a very high density, the hard-sphere system approaches close packing (CP) structure. The ground state energy per particle of a many- boson system of particles is calculated for close-packing densities. For a hard-sphere diameter fixed at 2.48Å, it is found that for a ^4He boson system, the low and high densities are 4.23×10^{22} $particles/cm^3$ and 6.15×10^{22} $particles/cm^3$, respectively. Our calculation shows that particle densities decrease with the increase in hard-sphere diameters when the saturation density is fixed at 2.0×10^{28} $particles/m^3$. The energy per particle also increases with hard-sphere diameter, but it decreases with particle density.

1. Introduction

A hard-sphere system is a many body system in which the particles interact via a pair-potential containing short-ranged and very large repulsive part. At low densities, the particles experience the attractive potential only weakly, whereas at high densities the repulsive part predominates and in such a case, the assembly can be considered a hard-sphere system. In general, the hard-sphere system can serve as a reference (or zero-order) system in perturbative theories. For example, this scheme is the familiar thermodynamic perturbative theory [1] in classical statistical physics that describes classical fluids. The Quantum Thermodynamic Perturbative Theory (QTPT) has been developed [2] to obtain the quantum hard-sphere equation of state for physical densities of systems such as ^{4}He. The effort here is to study the properties of quantum hard-sphere systems at different densities, particularly densities resulting in the crystallization of a hard-sphere boson assembly.

At very low density, the energy E of N-identical boson system is given by [3]

$$\frac{E}{N}=\frac{2\pi\hbar^2\rho a}{m}\left[1+C_1\left(\rho a^3\right)^{\frac{1}{2}}+C_2\rho a^3\log\left(\rho a^3\right)+...\right] \qquad (1)$$

Where, ρ is the particle number density $\left(\rho=\frac{N}{V}\right)$, m is the mass of each boson and a is the s-wave scattering length [4] of the pair potential between particles, and $C_1=\frac{128}{15\sqrt{\pi}}$ and $C_2=8\left(\frac{4\pi}{3}-\sqrt{3}\right)$.

For a hard-sphere system, a reduces to hard-sphere diameter C. The series in Eq.1 is not a power series, and it breaks down at moderate and high densities, including the saturation liquid densities of ^4He.

At very high density, the hard-sphere system can go to close packing (CP) independently of statistics. This packing may either be random or regular. For such a system the ground state energy can be written as

$$\frac{E}{N}\underset{\rho\to\rho_{CP}}{\to}A\frac{\hbar^2}{2m}\left(\rho^{\frac{-1}{3}}-\rho_{CP}^{\frac{-1}{3}}\right)^{-2} \qquad (2)$$

Where, A, called the residue, is a dimensionless constant, and ρ_{CP} is the proper CP density. Using the polyhedron cell method [5], the value of A has been predicted theoretically [6] to lie within the rigorous range,

$$1.63\le A\le 27.0 \qquad (3)$$

for regular CP (face-centred-cubic, FCC, or hexagonal-close-packing, HCP) by generalizing the exact calculation for a simple cubic (SC) lattice based on three mutually perpendicular linear lattices. This gives $A=\pi^2$. However, the experimental value of A extracted by Cole [7] from

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the high pressure data of ^3He, ^4He, H_2 and D_2 systems is: $A \cong 15.7 \pm 0.6$ for crystalline branch of the equation of state.

2. Theory

The first attempt to represent the ground- state energy per particle of an assembly of $N >> 1$ boson hard-spheres for all densities is due to London [8], who proposed the analytical equation of state

$$\frac{E}{N} = \frac{2\pi\hbar^2 C}{m}\left(\rho^{\frac{-1}{3}} - \rho_0^{\frac{-1}{3}}\right)^{-2}\left(\rho^{\frac{-1}{3}} + b\,\rho_0^{\frac{-1}{3}}\right)^{-1} \quad (4)$$

Where, *C*= hard-sphere diameter, $b = \left(\frac{2^{\frac{5}{2}}}{\pi} - 1\right)$, $\rho_0 = \rho_{CP}$ and $\rho_0 = \frac{\sqrt{2}}{C^3}$ is the ultimate density [9] for a system of classical hard-spheres that closes packs in a primitive hexagonal, i.e., a face-centered cubic (FCC) arrangement. Eq. 4 reduces to the well known limiting expressions at both low and high densities

$$\frac{E}{N} \underset{\rho \to 0}{\to} \left(\frac{2\pi\hbar^2}{mb}\right)\rho_0 C \quad (5)$$

At high density,

$$\frac{E}{N} \underset{\rho \to \rho_0}{\to} \left(\frac{\pi^2}{2^{\frac{1}{3}}}\right)\left(\frac{\hbar^2}{2m}\right)\left(\rho^{\frac{-1}{3}} - \rho_0^{\frac{-1}{3}}\right)^{-2} \quad (6)$$

The first term, Eq.5, in the asymptotic form is the well known Lenz [10] term. Eq.6 is precisely the kinetic energy of a point mass m inside a spherical cavity of radius *r-c*, where $r = \left(\frac{\sqrt{2}}{\rho}\right)^{\frac{1}{3}}$ is the separation between two neighboring spheres. These results are obtained by assuming primitive hexagonal close packing, i.e., hcp or fcc, of the N cavities.

Recently it was noted [11] that the derivation of high-density extreme of the original boson by London [8] (see Eq. 4) contains one fundamental error related to the neglect of the effective two-body mass. This correction gives $b = \left(\frac{2^{\frac{3}{2}}}{\pi} - 1\right)$. The new result was designated in [11] as the modified London equation and which continues to satisfy Eq.4. The modified London equation (ML) equation agrees better with the Green Function Monte Carlo (GFMC) computer simulation of both the fluid and crystalline branches of the boson hard-sphere system than the original London equation.

For boson hard-spheres, Eq.1 can be rewritten as,

$$\frac{E}{N} = \frac{2\pi\hbar^2}{m}\rho\, C\, e_0(x) \quad (7)$$

Where, $\rho = \frac{N}{V}$, $x \equiv \left(\rho C^3\right)^{\frac{1}{2}}$ with,

$$e_0(x) = 1 + C_1 x + C_2 x^2 \log x^2 + C_3 x^2 + \mathrm{O}(x^3 \log x^2) \quad (8)$$

Alternatively for $x << 1$, we may write,

$$e_0^{\frac{-1}{2}}(x) \cong 1 + F_1 x + F_2\, x^2 \log x^2 + F_3\, x^2 + \mathrm{O}(x^3 \log x^2) \quad (9)$$

Where, the *F*'s are expressible in terms of the *C*'s, but C_3, F_3 and higher-order coefficients are unknown. For random close packing (RCP), the density $\rho = 0.716\rho_0$, which is roughly ten percent below the classical [13,14] RCP value of $\rho = 0.86\rho_0$. This is thus the highest CP density for quantum hard-sphere fluids in the meta-stable region. Since particles at CP are perfectly localized, they lose their indistinguishability so that the results should be independent of the statistics in the limit. It should be emphasized that a regular close pack (CP) is found in the limit of crystalline helium, ^4He.

For hard-sphere bosons at close packing (CP), i.e., at very low temperatures, $\frac{E}{N}$ is given by Eq.7. For this calculation, we shall use two values of ρ, i.e., $\rho = 0.776\rho_0$ and $\rho = 0.86\rho_0$. For, $e_0(x)$, we shall only use the series up to C_2, since C_3 and higher order terms are either unknown or are very small and of no physical significance. Thus

$$e_0(x) \approx 1 + C_1 x + C_2 x^2 \log x^2 \qquad (10)$$

$$\rho_0 = \frac{\sqrt{2}}{C^3} \quad ; \quad x = \left(\rho C^3\right)^{\frac{1}{2}}$$

C= hard-sphere diameter [15] =2.84 Å.
For, ρ_0, we could also use the value of 2×10^{22} particles/cm^3 and $m = 6.646\times10^{-24}$ gm for ^4He.

Using the above mentioned parameters, the ground state energy per particle of a many-boson system of particles can be calculated for close-packing densities. The results can be compared to a recent calculation [14] for ^4He. Thus the value of $\frac{E}{N}$ we have to work with is

$$\frac{E}{N} = \frac{2\pi\hbar^2}{m}\rho C\left[1 + C_1 x + C_2 x^2 \log x^2\right] \qquad (11)$$

The density at which the hard-sphere assembly may form CP crystalline structure may be called the saturation density and denoted by ρ_s. At this density, E will be maximum such that

$$\left(\frac{\partial E}{\partial \rho}\right)_{\rho=\rho_s} = 0 \qquad (12)$$

This will give the value of $\rho = \rho_s$ at which a hard-sphere assembly of bosons can form a crystalline structure. Using this value of $\rho = \rho_s$, we can get $\frac{E}{N}$ per particle when the assembly of bosons, assumed to be composed of hard-spheres, forms a crystalline structure. Using Eq.11, we can write,

$$\frac{\partial E}{\partial \rho} = \frac{2\pi N\hbar^2}{m}\rho C\left[\frac{C_1 C^3}{2}\left(\rho C^3\right)^{-\frac{1}{2}} + C_2 C^3\left(1 + \log \rho C^3\right)\right] \qquad (13)$$

Using Eq.12 and the fact that $\log\left(\rho C^3\right)^{\frac{-1}{2}}$ is very small, we shall get,

$$\frac{C_1^2}{4C_2^2} = \rho_s C^3 \qquad (14)$$

Or,

$$\rho_s = \frac{C_1^2}{4C_2^2 C^3} \qquad (15)$$

In our case, the ultimate density at which an assembly of hard-spheres that close packs (CP) is thus given by ρ_s and it can be compared with the earlier [9] such value ρ_0. Simultaneously, the value of $\frac{E}{N}$ will be calculated from Eq.11 by replacing ρ by ρ_s. By varying the hard-core diameter 'C' we can get different values for ρ_s and $\frac{E}{N}$.

There could be some objection to our using Eq.1 or Eq.7 for studying the properties of an assembly of hard-spheres that forms a crystalline structure since such a system has to be of high density, whereas Eq.7 is applicable to a low density system. But for comparison and rough estimates, we could use Eq.1 or Eq.7 and assume that these equations could be reasonably accurate from zero through physical densities. However, calculations using Eq.6, which is the equation for a high density system, are also given below.

Using Eq.6 we can write,

$$\left(\frac{\partial E}{\partial \rho}\right) = \left(\frac{\pi^2}{2^{\frac{1}{3}}}\right)\left(\frac{N\hbar^2}{2m}\right)(-2)\left(\rho^{\frac{-1}{3}} - \rho_0^{\frac{-1}{3}}\right)^{-3}\left(\frac{-1}{3}\right)\rho^{\frac{-4}{3}} \qquad (16)$$

At $\rho = \rho_s$, $\left(\frac{\partial E}{\partial \rho}\right)_{\rho=\rho_s} = 0$ and hence Eq.16 leads to the result that $\rho = \rho_0$ and this is the fundamental condition for a high density system leading to Eq.6. Hence for a high density system, Eq.6 will be used to get the value of $\frac{E}{N}$ at the density $\rho_s = \rho_0 = \frac{\sqrt{2}}{C^3}$. Again by varying C, we can get different values for $\frac{E}{N}$. From Eq.15, the value of ρ_s for a low density system is

$$\rho_s(low\ density) = \frac{C_1^2}{4C_2^2 C^3} = \frac{0.97}{C^3} \qquad (17)$$

For a high-density system, the value of ρ_s is,

$$\rho_s\,(high\ density) = \rho_0 = \frac{\sqrt{2}}{C^3} = \frac{1.41}{C^3} \qquad (18)$$

Comparing Eqs.17 and 18, it is clear that the value of ρ_s for a high-density system is more than that for a low density system as it should be.
For $C = 2.48$ Å, we get

$$\rho_s\,(low\ density) = 4.23\times10^{22}\ particles/cm^3 \qquad (19)$$

$$\rho_s\,(high\ density) = 6.15\times10^{22}\ particles/cm^3 \qquad (20)$$

3. Results and discussion

3.1 Calculation of the variation of particle density ρ with hard-sphere diameter C

The calculations are done for saturation density ρ_s, i.e., the density at which the hard-sphere assembly may form crystalline structure. Considerations are given to both low and high density. Referring to Eqs.17 and 18

$$\rho_s\,(low\,density) = \frac{0.97}{C^3}$$

$$\rho_s\,(high\ density) = \frac{1.41}{C^3}$$

The values of C were taken to vary from 2.1Å to 2.84 Å in steps of 0.025 Å. Table 1 below shows the variation of low density and high density for different values of hard-sphere diameter C.

Table 1

HARD-SPHERE DIAMETER, C (Å)	**LOW SATURATION DENSITY** $\times10^{29}\ particles/m^3$	**HIGH SATURATION DENSITY** $\times10^{29}\ particles/m^3$
2.100	1.047	1.523
2.125	1.011	1.469
2.150	0.976	1.419
2.175	0.943	1.37
2.200	0.911	1.324
2.225	0.8806	1.28
2.250	0.8516	1.238
2.275	0.8238	1.197
2.300	0.7972	1.159
2.325	0.7718	1.122
2.350	0.7474	1.086
2.375	0.7241	1.053
2.400	0.7017	1.02
2.425	0.6802	0.9887
2.450	0.6596	0.9588
2.475	0.6398	0.93
2.500	0.6208	0.9024
2.525	0.6025	0.8759
2.550	0.585	0.8504
2.575	0.5681	0.8258
2.600	0.5519	0.8022
2.625	0.5363	0.7795
2.650	0.5212	0.7577
2.675	0.5068	0.7366
2.700	0.4928	0.7164
2.725	0.4794	0.6968
2.750	0.4664	0.678

The graph below shows the variation of saturation density with the hard-sphere radius.

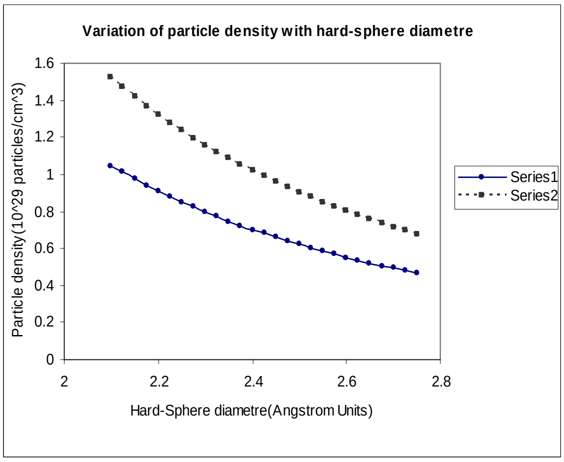

Fig.1: Variation of saturation density with hard-sphere diameter.
Series 1: The curve for low saturation density.
Series 2: The curve for high saturation density.

There is a non-linear decrease in particle density with an increase in hard-sphere diameter. For a uniform volume, an increase in hard-sphere diameter means fewer particles are confined and hence a decrease in the particle densities.

3.2 Calculation of variation of energy per particle $\frac{E}{N}$ with the hard-sphere diameter C

In this calculation, use was made of Eq.11, which is given as

$$\frac{E}{N} = \frac{2\pi\hbar^2}{m}\rho_S C\left[1 + C_1 x + C_2 x^2 \log x^2\right]$$

Where, $x = \left(\rho C^3\right)^{\frac{1}{2}}$.

The following constants were used in the calculations:-

$$C_1 = \frac{128}{15\sqrt{\pi}}$$

$$C_2 = 8\left(\frac{4\pi}{3} - \sqrt{3}\right)$$

$$m = 6.646 \times 10^{-27}\, kg$$

$$\hbar = 1.05457 \times 10^{-34}\, Js$$

In order to study the variation of energy per particle with C, we need to keep the saturation density fixed at some value, say

$$\rho_S = 2.0 \times 10^{28}\ particles / m^3 .$$

The following table was obtained for the variation of energy per particle with hard-sphere diameter C.

Table 2: Values of energy per particle with hard-sphere diameter

HARD-SPHERE DIAMETER ,C (Å)	**ENERGY PER PARTICLE $\frac{E}{N}$,($\times 10^{-22}$ joules)**
2.100	2.0512
2.125	2.0756
2.150	2.1000
2.175	2.1245
2.200	2.1489
2.225	2.1733
2.250	2.1977
2.275	2.2221
2.300	2.2465
2.325	2.2710
2.350	2.2954
2.375	2.3198
2.400	2.3442
2.425	2.3686
2.450	2.3981
2.475	2.4175
2.500	2.4419
2.525	2.4663
2.550	2.4907
2.575	2.5152
2.600	2.5396
2.625	2.5640
2.65	2.5884
2.675	2.6128
2.700	2.6373
2.725	2.6617
2.750	2.6861

Below is the graph that was obtained from the calculations.

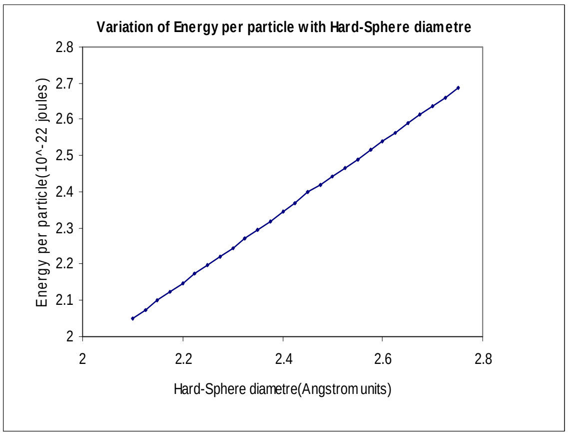

Fig.2: Variation of energy per particle with hard-sphere diameter.

When the hard-sphere diameter is increased, then fewer particles will be confined in a fixed volume. The total energy is then shared by fewer particles resulting in an increase in energy per particle.

3.3. Calculation of variation of energy per particle with particle density

The equations and constants used in this case were similar to those calculations in Sec. 3.2. However, in order to study the variation of energy per particle with particle density, it was necessary to keep C fixed at some value. The chosen value for the hard-sphere diameter was

$$C = 2.84 \times 10^{-10}\, m$$

The table below shows the values that were obtained.

Table 3: Variation of energy per particle with particle density.

DENSITY, ρ **(**$\times 10^{27}$ $particles/m^3$**)**	**ENERGY PER PARTICLE,** $\frac{E}{N}\left(\times 10^{-23}\, joules\right)$
1.62	1.661
1.563	1.681
1.506	1.701
1.449	1.721
1.392	1.741
1.335	1.760
1.278	1.780
1.221	1.800
1.164	1.820
1.107	1.839
1.050	1.859
0.993	1.879
0.936	1.899
0.879	1.919
0.822	1.938
0.765	1.958
0.708	1.978

Below is the graph for the same.

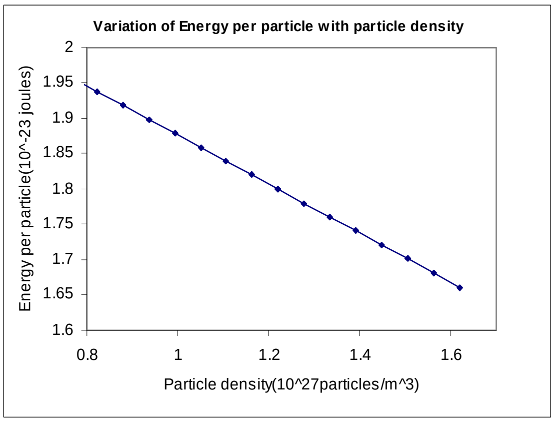

Fig.3: Graph showing the variation of energy per particle with particle density.

An increase in particle density implies that the total energy is divided up among many particles. This results in a decrease in energy per particle with an increase in particle density.

4. Conclusion

For a hard-sphere assembly of crystalline bosons with close packing (CP), particle densities decrease with an increase in hard-sphere diameters for a fixed saturation density. Energy per particle increases with an increase in hard-sphere diameter but decreases with an increase in particle density.

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