London equation of state for a quantum-hard-sphere system

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The London analytical interpolation equation between zero and packing densities for the ground-state energy of a many-boson hard-sphere system is corrected for the reduced mass of a pair of particles in a "sphere-of-influence" picture. It is thus brought into good agreement with computer simulations and with experimental results extrapolated out to close packing.

The hard-sphere system is a useful first approximation to a many-body system interacting via a pair potential containing a short-ranged repulsive part. This description is better at very low densities where the particles experience weakly the attractive potential tail surrounding the repulsion, or at very high densities where the repulsions are predominant. However, at intermediate densities the attractive potential can be expected to play a significant role.

The hard-sphere system is used as a "reference system" in perturbative theories in the zero order. For instance, familiar from classical statistical thermodynamics is the thermodynamic perturbation theory,[1] which describes classical fluids very successfully. A quantum counterpart, quantum thermodynamic perturbation theory, has been developed[2] and shown that a good quantum-hard-sphere state equation at physical (intermediate) densities is crucial in correctly describing quantum fluids such as ^{3}He, ^{4}He, electron-spin-polarized H, nuclear matter, etc.

At very low density the energy E for an N-boson system[3] is given exactly by

$$\frac{E}{N}=\frac{2\pi\hbar^2\rho a}{m}\{1+C_1(\rho a^3)^{1/2}+C_2\rho a^3\ln(\rho a^3)+\cdots\}\ , \quad (1)$$

where a is the S-wave scattering length of the pair potential between particles, $C_1=128/15\sqrt{\pi}$, $C_2=8(4\pi/3-\sqrt{3})$, $\rho=N/\Omega$ is the particle number density, Ω the system volume, and m the particle mass. For a hard-sphere system a reduces to the hard-sphere diameter c. This "virial-expansion-like" series is clearly not a power series expansion, and at best is an asymptotic series. A similar series exists for an N-identical-fermion system.[4] Unfortunately, both boson and fermion low-density expansions break down at moderate and higher densities, including the all-important saturation (or equilibrium, zero-pressure) density of ^{4}He, ^{3}He, or nuclear matter.

As in the classical-hard-sphere system, a (Kirkwood) fluid-to-crystal phase transition[5] is expected at some intermediate density around which are available the presumably exact Green function Monte Carlo (GFMC) computer simulations[6] for the many-boson hard-sphere system. Four density data points are reported[6] for the fluid branch and five for the crystalline.

At very high density, as in the classical case, one expects the quantum hard-sphere system to approach a close packing density ρ_0. Furthermore, the equation of state can be expected to then become *independent* of statistics (boson or fermion) as in this limit each particle becomes distinguishable by a precise, specific location. The uncertainty principle applied to a single particle then implies a second-order pole in the ground-state energy per particle given by

$$\frac{E}{N}\underset{\rho\to\rho_0}{\longrightarrow} A\frac{\hbar^2}{2m}(\rho^{-1/3}-\rho_0^{-1/3})^{-2}\ , \quad (2)$$

where the "residue" A is a dimensionless constant. The value of A has been predicted[7] to lie in the range

$$1.63\leq A\leq 27.0 \quad (3)$$

for face-centered-cubic close packing, by generalizing the straightforward calculation for a *simple cubic* lattice based on three mutually perpendicular exactly soluble linear lattices, which itself gives $A=\pi^2\simeq 9.87$. The experimental value for the residue extracted by Cole[8] from high-pressure crystalline branch data in ^{3}He, ^{4}He, H_2, and D_2 systems is

$$A\simeq 15.7\pm 0.6\ . \quad (4)$$

An ingenious attempt to analytically represent the ground-state energy per particle of an assembly of $N(\gg 1)$ boson hard spheres for *all* densities goes back to London,[9] who wrote a formula interpolating the two density extremes of the range $0\leq\rho\leq\rho_0$. Explicitly, he gives

$$\frac{E}{N}=\frac{2\pi\hbar^2c}{m}\frac{1}{(\rho^{-1/3}-\rho_0^{-1/3})^2}\frac{1}{(\rho^{-1/3}+b\rho_0^{-1/3})}\ , \quad (5)$$

where $b\equiv 2^{5/2}/\pi-1$. Here, c is the hard-sphere diameter, and $\rho_0\equiv\sqrt{2}/c^3$ is believed[10] to be the ultimate density for a system of classical hard spheres, thought to close pack in a so-called "primitive hexagonal" (e.g., face-centered-cubic) arrangement. (This hypothesis, variously known as Kepler's or Newton's conjecture, appears to have finally been demonstrated.[11]) London's rationale for Eq. (5) is that it reduces smoothly, at both lowest and highest densities, to the limiting expressions

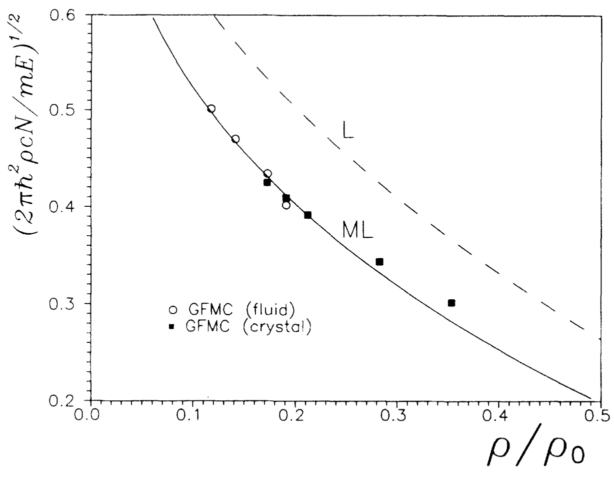

FIG. 1. The dimensionless quantity $(2\pi\hbar^2\rho c N/mE)^{1/2} = [1-(\rho/\rho_0)^{1/3}][1+b(\rho/\rho_0)^{1/3}]^{1/2}$ from the London (L) equation (5) with $b=2^{5/2}/\pi-1$, and from modified London (ML) equation with $b=2^{3/2}/\pi-1$ as discussed in text. This quantity clearly approaches 1 as $\rho/\rho_0 \to 0$, and 0 as $\rho/\rho_0 \to 1$.

$$\frac{E}{N}\underset{\rho\to 0}{\longrightarrow}\frac{2\pi\hbar^2}{m}\rho c \quad \text{(low density)}\ , \tag{6}$$

and

$$\frac{E}{N}\underset{\rho\to\rho_0}{\longrightarrow}\frac{\pi^2}{2^{1/3}}\frac{\hbar^2}{2m}(\rho^{-1/3}-\rho_0^{-1/3})^{-2} \quad \text{(high density)}\ . \tag{7}$$

The asymptotic result Eq. (6) is the leading term in (1) with $a=c$ and is the celebrated Lenz[12] term, calculated by him as the leading correction to the energy due to an "excluded volume" effect. On the other hand, the limiting result equation (7) according to London is just the quantum-mechanical kinetic energy of a point particle of mass m inside a spherical cavity of radius $r-c$, where $r=(\sqrt{2}/\rho)^{1/3}$ is the separation between two neighboring spheres as primitive hexagonal close packing is approached. This can be seen from the Schrödinger equation for the point particle in a spherical cavity of radius $r-c$, whose energy eigenvalues call for the first (nonzero) root of $j_0(x)=\sin x/x$, with $x=k(r-c)$. This is just $k(r-c)=\pi$ so that $\hbar^2k^2/2m=\hbar^2\pi^2/2m(r-c)^2$, which is precisely (7).

Recently, a London equation generalized to describe fermions with ν intrinsic degrees of freedom has been derived[13] which for $\rho\to\rho_0$ becomes independent of statistics, i.e., of ν, and reduces to (7), when $\nu\to\infty$ as it should. From this it follows that according to the London formula (5), and (7), the residue A in (2) for bosons or fermions is the *same* and equal to $(\pi^2/2^{1/3})\simeq 7.83$. This value satisfies the bounds (3) but is roughly only one half the empirical value of (4).

The derivation of the high-density extreme of the original[9] (boson) London equation (5), and consequently of the generalized[13] (fermion) London equation, contains *one fundamental error.* The spherical cavity of radius $r-c$ alluded to above in reality refers to a "sphere of influence" of *two* particles; thus, the particle mass used in obtaining (7) from the lowest Schrödinger equation eigenvalue of a particle in the spherical cavity *should refer to the reduced mass m/2.* This gives the constant $b\equiv 2^{3/2}/\pi-1$ (instead of $2^{5/2}/\pi-1$ as given by London) in (5). The result will be designated the *modified London equation,* which continues to satisfy (6) as this is independent of the constant b in (5). The residue A in (2) is now $2^{2/3}\pi^2\simeq 15.7$ in full agreement with the empirical residue (4). This modified London (ML) equation agrees dramatically better than the original London (L) equation with GFMC computer simulation of both fluid and crystalline branches of the boson-hard-sphere system, Fig. 1. Needless to say, the London interpolation being smooth completely misses the fluid-to-crystalline (first-order) phase transition. The problem examined in this paper is reminiscent of the controversy which raged during the last century between Clausius, Maxwell, and Boltzmann—and finally resolved by the latter—on the correct way to analytically calculate the second virial coefficient for hard spheres in a "sphere-of-influence" picture.

In summary, a correct sphere-of-influence argument taking into account the *reduced* mass of a *pair* of particles modifies the high-density extreme of the ingenious analytical London interpolation formula describing the ground-state energy of a many-boson hard-sphere system. The correction yields both excellent agreement with the experimentally extracted residue at the close-packing-density uncertainty-principle pole in the energy, as well as good agreement with computer simulations at intermediate densities. Clearly, neither of these two tests were available to London.

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