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Density Fluctuations at Low Temperatures

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The applicability to a quantum liquid of the standard classical formula connecting the compressibility with the coherent scattering cross section for large wavelengths, questioned by the author in a previous paper, is examined. The correctness of the standard formula is proved (*a*) at absolute zero (the density fluctuations being infranormal); (*b*) under quantum conditions for all temperatures at which the Wigner expansion converges (it is conjectured that for liquid helium the expansion may diverge below the lambda-point); and (*c*) for a one-dimensional crystal for all temperatures. These results, while they stop short of a complete proof of the standard classical formula for all conditions, do extend considerably our knowledge of its range of validity.

1. INTRODUCTION

IN the coherent scattering of radiation by a monatomic liquid, the scattered intensity is proportional to[1]

$$R(|\mathbf{k}_1-\mathbf{k}_2|)=1+\rho\int h(r)e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}}d^3\mathbf{r}, \qquad (1)$$

where ρ is the number density of atoms, supposed uniform over the scattering volume, $1+h(r)=g(r)$ is the normalized radial distribution function, and $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave vectors in the incident and scattered directions. Consequently, for large wavelengths the atomic scattering cross section is multiplied by an interference factor

$$R(0)=1+\rho\int_0^\infty h(r)4\pi r^2dr. \qquad (2)$$

This factor is proportional to the mean square fluctuation of the number of atoms in a fixed region, or "cell," in the liquid, which is given by

$$\langle M^2\rangle-\langle M\rangle^2=\langle M\rangle\left[1+\rho\int_0^\infty h\,4\pi r^2dr\right], \qquad (3)$$

where M is the number of atoms in the cell in a single observation, the bracket $\langle\ \rangle$ denotes an average over a large number of observations, $\langle M\rangle$ is small compared with the total number N of atoms in the assembly, and the linear dimensions of the cell are large compared with the values of a for which $\int_a^\infty r^2hdr$ is appreciable compared with $\int_0^\infty r^2hdr$. By combining (2) and (3) with the Gibbs fluctuation formula

$$\langle M^2\rangle-\langle M\rangle^2=\langle M\rangle\rho\kappa T\chi_T, \qquad (4)$$

where χ_T is the isothermal compressibility and κ is Boltzmann's constant, one obtains the standard relation connecting the scattering factor R with thermodynamic magnitudes:

$$R(0)=\rho\kappa T\chi_T. \qquad (5)$$

In a previous paper[2] (to be referred to here as I) the formula (5) was called in question for the conditions at low temperatures where quantum physics determines the state of the assembly, such as in liquid helium. Formulas (1) and (2), which are derived from a purely geometrical analysis in terms of the reduced probability distribution $n_2(\mathbf{r}_1,\mathbf{r}_2)$ for the positions of a pair of atoms, remain valid irrespective of the mechanism determining that distribution—whether thermal fluctuations or the zero-point motion are dominant. It was argued in I that (4), on the other hand, cannot remain valid as the temperature tends to absolute zero, because the right-hand side then vanishes, while the left-hand side, which then measures the quantum fluctuations of M for the ground state of the assembly, cannot be zero since the observable M (the function F of I) does not commute with the Hamiltonian and is not a constant of the motion. (Stated in another way, the fluctuation of M could be zero only if the distribution function $n_N(\mathbf{r}_1\cdots\mathbf{r}_N)$ were a combination of delta functions giving every atom a fixed position; and this is impossible by the uncertainty principle.) It was suggested that (4) and (5) hold only for temperatures where classical mechanics applies.

Further consideration has shown that the above argument about the limit of (4) as $T\rightarrow 0$ is not a valid one. The vanishing of the factor $\rho\kappa T\chi_T$ may imply merely that the fluctuations in M are *infranormal*: that $\langle M^2\rangle-\langle M\rangle^2$ does not increase "as fast as $\langle M\rangle$" when the volume of the cell, $v=\langle M\rangle/\rho$, increases (together with N) indefinitely.[3] For example, the finite size of a (still large) cell may be taken into account by an extension

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[1] For derivations of formulas (1)–(5), see J. de Boer, Repts. Progr. in Phys. **12**, 305 (1949), Sec. 10; H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, New York, 1952), Secs. 3.1, 3.2; J. Yvon, *Fluctuations en Densité*, Actualités Scientifiques et Industrielles, No. 542 (Hermann, Paris, 1937), Chap. 1.

[2] P. J. Price, Phys. Rev. **86**, 495 (1952).

[3] I am indebted to G. Placzek and L. van Hove for drawing my attention to this possibility and its relevance, and for championing the universal validity of (4).

of (3) to

$$\langle M^2\rangle-\langle M\rangle^2=v\cdot\rho\left[1+\rho\int_0^\infty 4\pi r^2 h dr\right]$$
$$+A\cdot\rho^2\int_0^\infty ds\int_s^\infty 2\pi r(s-r)h dr, \quad (3')$$

where A is the surface area of the cell, provided the integrals converge. The coefficient of v may then vanish while the fluctuation of M remains finite, being in the limit of large v proportional to A. However, it remained true that, more generally, (4) *had not been validly proved* except "for classical conditions." If it should nevertheless be correct in general (giving the coefficient of the asymptotic normal part of the fluctuation of M), such a simple connection between the temperature and thermodynamic compressibility, on the one hand, and the quantum fluctuations of M for pure states of the assembly, seemed physically mysterious. It therefore seemed worthwhile to investigate whether (4), and hence (5), could be satisfactorily proved (or disproved) for quantum conditions.

In this paper it is shown that (4) holds certainly for a part, and possibly for the whole, of the range of temperature in which quantum mechanics applies. In Sec. 2 it is proved that the expression (2), $R(0)$, is in fact zero for the ground state, so that (4) and (5) hold at absolute zero (the fluctuation of M being infranormal). In Sec. 3 it is shown that (4) must hold in quantum conditions at all temperatures for which the Wigner expansion, as defined there, converges. The interpretation of these results for liquid helium is discussed. In Sec. 4 we consider a condensed system for which a complete exact solution is possible, namely a one-dimensional *crystal*, and prove that the equivalent of (4) is correct for all temperatures. For absolute zero, the explicit infranormal dependence on $\langle M\rangle$ of the fluctuation of M is obtained. These results stop short of a proof of (4) for all conditions, though they extend considerably our knowledge of its range of validity.

2. ABSOLUTE ZERO

We shall prove that for the ground state of a liquid $R(k)\leqslant(\text{const.})k$,[4] and hence that $R(0)$ is zero. Let the normalized wave functions of the stationary states of the system be $\psi_0, \psi_1, \cdots, \psi_\nu, \cdots$, with energies E_0, $E_1, \cdots, E_\nu, \cdots$, where ψ_0 and E_0 refer to the ground state. Let

$$\phi=\sum_{s=1}^{N}\cos(\mathbf{k}\cdot\mathbf{r}_s), \quad (6)$$

and

$$\phi\psi_0=\psi=\sum_{\nu=0}^{\infty}a_\nu\psi_\nu. \quad (7)$$

Then it follows at once that[5]

$$(\psi|\psi)=(\psi_0|\phi^2|\psi_0)=\tfrac{1}{2}S^xR(k),$$

or

$$\textstyle\sum_\nu|a_\nu|^2=\tfrac{1}{2}S^xR(k). \quad (8)$$

Secondly we note that, with the Hamiltonian of the system of form

$$H=-(\hbar^2/2m)\textstyle\sum_s\nabla_s^2+\Phi(\mathbf{r}_1,\mathbf{r}_2\cdots\mathbf{r}_N) \quad (9)$$

(where Φ may depend also on spin coordinates), the expectation $(\psi|H-E_0|\psi)$ may be transformed, by subtracting a vanishing surface integral, to

$$(\hbar^2/2m)(\psi_0|[\textstyle\sum_s|\nabla_s\phi|^2]|\psi_0),$$

and hence to $(\hbar^2/2m)\frac{1}{2}Nk^2$. Thus,

$$\textstyle\sum_\nu|a_\nu|^2(E_\nu-E_0)=(\hbar^2/2m)\frac{1}{2}Nk^2. \quad (10)$$

To obtain the third relation which is required together with (8) and (10), we imagine the system perturbed by the addition of a *small* potential $\Omega\phi$, where ϕ is given by (6) and Ω is a constant. The Hamiltonian of the perturbed system is then $H'=H+\Omega\phi$. An "ordinary" liquid behaves like an ideal elastic fluid in that the change in the internal energy $E=\langle H\rangle$, on perturbation by a potential field, may be expressed in terms of the redistribution of the number density ρ:

$$E-E_0=\int[\epsilon(\rho')-\epsilon(\rho)]d^3\mathbf{r}$$
$$=\tfrac{1}{2}\epsilon''(\rho)\int(\rho'-\rho)^2d^3\mathbf{r}+\cdots, \quad (11)$$

and hence the *total* perturbation energy in this case—the minimum of $E-E_0+\Omega\int\rho\cos(\mathbf{k}\cdot\mathbf{r})d^3\mathbf{r}$—would be:

$$\text{perturbation energy}=[V/4\epsilon''(\rho)]\Omega^2+O(\Omega^3), \quad (12)$$

where $V=N/\rho$ is the volume occupied by the assembly. A justification of (12) for the ground state of a quantum liquid is given in the appendix. Then, comparing (12) with the standard formula of second-order perturbation theory, we have

$$\textstyle\sum_\nu{}^{(0)}|a_\nu|^2/(E_\nu-E_0)=\frac{1}{4}N/\rho\epsilon''(\rho), \quad (13)$$

where the sum $\sum_\nu{}^{(0)}$ excludes $\nu=0$.

Now,

$$\textstyle\sum_\mu{}^{(0)}|a_\mu|^2(E_\mu-E_0)\sum_\nu{}^{(0)}|a_\nu|^2/(E_\nu-E_0)$$
$$=\sum_\mu{}^{(0)}\sum_\nu{}^{(0)}|a_\mu|^2|a_\nu|^2\left[1+\frac{(E_\mu-E_\nu)^2}{2(E_\mu-E_0)(E_\nu-E_0)}\right]$$
$$\geqslant(\textstyle\sum_\nu{}^{(0)}|a_\nu|^2)^2.$$

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[4] This inequality, and the outline of the derivation presented here, are due to L. Onsager (private communication, 1953).

[5] The relation (8), and hence the inequality (15), is actually true only when $\mathbf{k}$ takes one of the "spectrum values," which are those for which the integral of ϕ over the volume of the ensemble vanishes. However, the spectrum values may be made as close as we please by choosing N large enough (at constant ρ); and $R(0)$, given by (2), is to be understood as the limit of $R(k)$ as $\mathbf{k}$ tends to zero *through spectrum values*.

With **k** one of the spectrum values,[5] $a_0=0$ and hence we have

$$\textstyle\sum_\mu |a_\mu|^2(E_\mu-E_0)\sum_\nu{}^{(0)}|a_\nu|^2/(E_\nu-E_0) \geqslant [\sum_\mu |a_\mu|^2]^2. \quad (14)$$

Substituting (8), (10) and (13) into (14), we obtain Onsager's inequality:

$$R(k)\leqslant \hbar(4m\rho\epsilon'')^{-\frac{1}{2}}k, \quad (15)$$

for the ground state. In terms of the calculated velocity of sound c, given by

$$mc^2=(\chi\rho)^{-1}=\rho\epsilon'',$$

(15) may be written

$$R(k)\leqslant (\hbar/2mc)k. \quad (15')$$

It follows from (15) that $R(0)$—the coefficient of the normal density fluctuations, and the scattering factor for long wavelengths—vanishes at absolute zero. The above proof is independent of the symmetry—Bose, Fermi or classical Boltzmann—of the wave functions (which simply determines the definition of the $\{\psi_\nu\}$), and of the spin of the atoms. It clearly applies equally to one (monatomic) component of a mixture.

3. FINITE TEMPERATURES: THE WIGNER SERIES

In this section we set out the proof of (4) for a *classical* liquid, and then examine how far this proof may be extended to temperatures at which quantum mechanics must apply. For a classical liquid, the probability distribution of atomic configurations $(\mathbf{r}_1,\cdots \mathbf{r}_N)$ is

$$n_N(\mathbf{r}_1,\cdots \mathbf{r}_N)=(\lambda^N/N!)\exp[(F-\Phi)/\kappa T], \quad (16)$$

where Φ is the interaction potential and F the free energy, and λ is a function of the temperature T only. The free energy is accordingly given by

$$N!\exp(-F/\kappa T) =\lambda^N\int d^3\mathbf{r}_1\cdots\int d^3\mathbf{r}_N\exp(-\Phi/\kappa T), \quad (17)$$

where the N integrations are each taken over the volume of the assembly. For N large, F is given by

$$F(N,V,T)=Nf(N/V,T). \quad (18)$$

The probability of finding M atoms in a cell A of volume v, and $N-M$ atoms in the remainder B of the space, is

$$w(M)=[N!/M!(N-M)!] \times\int^A d^3\mathbf{r}_1\cdots\int^A d^3\mathbf{r}_M\int^B d^3\mathbf{r}_{M+1}\cdots\int^B d^3\mathbf{r}_N\, n_N,$$

or, by (16),

$$w=[\lambda^M/M!][\lambda^{N-M}/(N-M)!] \times\int^A d^3\mathbf{r}_1\cdots\int^B d^3\mathbf{r}_N\exp[(F-\Phi)/\kappa T]. \quad (19)$$

Now, if we have

$$\Phi=\sum_{s<t}\sum\phi(r_{st}),\quad \mathbf{r}_{st}=\mathbf{r}_s-\mathbf{r}_t, \quad (20)$$

and if $\phi(r)$ is effectively zero outside a definite sphere of influence, then it is obvious that the terms

$$\Phi_{AB}=\sum_{s=1}^{M}\sum_{t=M+1}^{N}\phi(r_{st})$$

may be omitted from $\Phi=\Phi_A+\Phi_B+\Phi_{AB}$ in (19) without appreciably affecting the value of the integral, provided M and $N-M$ are large numbers. Then, on dropping Φ_{AB} from Φ in (19), the integrals over A and over B are two independent factors and by (17) and (18)

$$w\simeq\exp\left\{\left[Nf\left(\frac{N}{V},T\right)-Mf\left(\frac{M}{v},T\right) -(N-M)f\left(\frac{N-M}{V-v},T\right)\right]\Big/\kappa T\right\}. \quad (21)$$

This expression (21) has a maximum for $M=vN/V=M_0$. Then for $M-M_0\ll M_0$ we may expand the exponent in powers of $M-M_0$ as far as the square only, and find

$$w\simeq\exp[-\alpha(M-M_0)^2],\quad \alpha=V/2\kappa T\chi_T M_0(N-M_0). \quad (21')$$

Hence, with $M_0\ll N$, we obtain (4). The addition of three-atom, four-atom, etc., terms to the two-atom potential (20) does not affect the above argument, provided the terms Φ_{AB}, consisting of the contribution "acting across the cell boundary" of interactions linking atoms $1\cdots M$ in A to $M+1\cdots N$ in B, may still be neglected in evaluating (19). Obviously, if Φ is composed of various n-atom interactions of type $\sum\phi(\mathbf{r}_1,\cdots,\mathbf{r}_n)$, only up to some definite degree $q\geqslant n$, then this condition may be fulfilled merely by choosing v large enough (with v/V kept small) for the mean number of atoms in the cell, $M_0=\rho v$, to be large compared with q^3.

The classical distribution (16) is of course correct only at high enough temperatures, but the validity of the above argument may be extended to lower temperatures by expressing the distribution given by quantum mechanics as a series in ascending powers of Planck's constant $2\pi\hbar$.[6] Let us do this by replacing Φ

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[6] E. P. Wigner, Phys. Rev. **40**, 749 (1932); M. L. Goldberger and E. N. Adams II, J. Chem. Phys. **20**, 240 (1952).

in (16) by

$$\Phi^*=\Phi+\sum_{n=1}^{\infty}(\hbar^2/2m\kappa T)^n\,\theta_n(\mathbf{r}_1,\cdots\mathbf{r}_N;T),\qquad(22)$$

where θ_n is given by a sum over multiple interactions up to, say, q_n atomic. The first of the θ_n is given[7] by

$$6\theta_1=\sum\nolimits_s[\nabla_s^2\Phi-(1/2\kappa T)|\nabla_s\Phi|^2].\qquad(23)$$

If Φ is given by (20) (pair interactions), then (23) becomes

$$6\theta_1=\sum_{s<t}\sum\{\phi''(r_{st})+(2/r_{st})\phi'(r_{rs})-(1/\kappa T)[\phi'(r_{st})]^2\}$$

$$-(1/2\kappa T)\sum_{s<t\neq u}\sum\sum(\mathbf{r}_{ts}\cdot\mathbf{r}_{tu}/r_{ts}r_{tu})\phi'(r_{ts})\phi'(r_{tu}),\qquad(23')$$

where $\mathbf{r}_{ts}\cdot\mathbf{r}_{tu}$ means $x_{ts}x_{tu}+y_{ts}y_{tu}+z_{ts}z_{tu}$. Thus, with pair interactions ($q=2$) for the actual potential Φ, we have $q_1=3$ (and, in fact, $q_2=6$). More generally, q_n increases monotonically with n. If, therefore, the series (22) may in practice be terminated at some point—say at θ_ν, so that Φ^* contains "cluster" functions up to q_ν atomic—then the previous argument leading to (21′) still applies and (4) is still verified. We may expect, however, that as quantum effects become more important (at lower temperatures) the series (22) has to be taken to an increasing number of terms in evaluating (19) with sufficient accuracy, and hence progressively higher cluster-numbers are involved. (Looked at a little differently: if the terms of Φ^* were regrouped in inverse powers of κT, we would expect the coefficient of $(\kappa T)^{-n}$ to contain cluster functions up to $q=n+2$; and thus with decreasing temperature higher clusters should have to be taken into account.) Thus, if at some temperature the series (22) ceases to converge as a functional of Φ [which could happen without the onset of a discontinuity in F, as calculated by (17) in terms of Φ^*] then the above argument for (4), based on restricting Φ^* to clusters of not more than some definite degree q, ceases to be valid at that point. The argument of this section furnishes a proof of (4) under those conditions where the Wigner series, in the form (22), converges.

It might be conjectured that in the case of liquid helium (He^4) the lambda transition, where there are singularities in the second derivatives of F, marks the position of a divergence of the Wigner expansion. (There is some recent experimental evidence,[8] which is of interest in this connection, that the effective range of interaction between atoms through Φ^* increases very considerably from 2.5° to the lambda point.) In this case, the above argument does not exclude the possibility that there is a departure from (4) and (5) between the lambda point and (but not including) absolute zero. On the other hand, if the Wigner series (22) does converge for all temperatures then the above argument shows that (4) and (5) hold for all temperatures.

4. ONE-DIMENSIONAL CRYSTAL

In this section we take the case of a one-dimensional "crystal," a linear chain of atoms with nearest-neighbor harmonic interactions, and show that the analog, for this case, of (4) holds *for all temperatures.* Let the number of atoms in the chain, each of mass m, be N, and let their static equilibrium spacing be a. Let the coordinate of the rth atom in the chain be

$$z_r=ra+x_r,\qquad(24)$$

so that x_r is the displacement from equilibrium. We shall determine, instead of the fluctuation in the linear density of atoms (which does not have a convenient definition for a lattice), the equivalent mean square deviation of the distance between two atoms,

$$\begin{aligned}\Delta_n&=\langle[(z_{n+r}-z_r)-\langle z_{n+r}-z_r\rangle]^2\rangle\\&=\langle(x_{n+r}-x_r)^2\rangle,\end{aligned}\qquad(25)$$

as a function of $\langle(z_{n+r}-z_r)\rangle=na$. It is convenient to adopt cyclic boundary conditions, treating the first atom as the $(N+1)$th. Then the Hamiltonian of the assembly is

$$H=\sum_{r=1}^{N}[p_r^2/2m+\tfrac{1}{2}m\omega_0^2(x_{r+1}-x_r)^2],\qquad(26)$$

where the p_r are the momenta conjugate to the x_r. Taking N as even for convenience, the Hamiltonian is made separable by the transformation to normal coordinates:[9]

$$x_r=(2/N)^{\frac{1}{2}}\sum_{s=1}^{N/2}[u_s\sin(rs\theta)+v_s\cos(rs\theta)],$$

$$p_r=(2/N)^{\frac{1}{2}}\sum_{s=1}^{N/2}[\sigma_s\sin(rs\theta)+\tau_s\cos(rs\theta)],\qquad(27)$$

where $\theta=2\pi/N$. σ_s and τ_s are the momenta conjugate to the normal coordinates u_s, v_s, and fulfill with them the standard commutation relations. Then H transforms to

$$\begin{aligned}H=\sum\nolimits_s[(\sigma_s^2/2m+\tfrac{1}{2}m\omega_s^2u_s^2)+(\tau_s^2/2m+\tfrac{1}{2}m\omega_s^2v_s^2)]\\=\sum\nolimits_s[H_s^{(1)}+H_s^{(2)}],\end{aligned}\qquad(28)$$

where

$$\omega_s=2\omega_0\sin(\tfrac{1}{2}s\theta).\qquad(29)$$

From (29) the velocity of long waves, under the conditions of classical mechanics, is $c_0=a\omega_0$. Each of the normal coordinates thus represents an harmonic oscillator; and hence, for a stationary state of the ensemble,

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[7] Equation (23) refers to the series for classical (Boltzmann) statistics; but similar series may be established for the Bose and Fermi cases [see H. S. Green, J. Chem. Phys. **19**, 955 (1951)], and the argument which follows covers all three.

[8] D. F. Brewer and K. Mendelssohn, Phil. Mag. **44**, 559 (1953).

[9] The center-of-gravity coordinate corresponding to $s=0$ is of no interest in this analysis and may be ignored.

or for any equilibrium state,

$$\begin{aligned}\langle u_s v_t\rangle &= 0,\\ \langle u_s u_t\rangle &= \langle H_s^{(1)}\rangle \delta_{st}/m\omega_s^2, \qquad (30)\\ \langle v_s v_t\rangle &= \langle H_s^{(2)}\rangle \delta_{st}/m\omega_s^2.\end{aligned}$$

From (27) and (30),

$$\begin{aligned}\langle x_r x_{n+r}\rangle &= (2/N)\textstyle\sum_s \frac{1}{2}(\langle u_s^2\rangle+\langle v_s^2\rangle)\cos(ns\theta),\\ \langle (x_{n+r}-x_r)^2\rangle &= (2/N)\textstyle\sum_s 4\sin^2(\frac{1}{2}ns\theta)\frac{1}{2}(\langle u_s^2\rangle+\langle v_s^2\rangle),\\ \Delta_n &= (2/N)\textstyle\sum_s[\sin^2(\frac{1}{2}ns\theta)/m^2\omega_0^2\sin^2(\frac{1}{2}s\theta)]\\ &\qquad \times\frac{1}{2}(\langle H_s^{(1)}\rangle+\langle H_s^{(2)}\rangle). \qquad (31)\end{aligned}$$

For the ground state of the assembly,

$$\langle H_s^{(1)}\rangle=\langle H_s^{(2)}\rangle=\tfrac{1}{2}\hbar\omega_s=\hbar\omega_0\sin(\tfrac{1}{2}s\theta),$$

and hence

$$\Delta_n=(\hbar/m\omega_0)(2/N)\sum_{s=1}^{N/2}[\sin^2(\tfrac{1}{2}ns\theta)/\sin(\tfrac{1}{2}s\theta)]. \qquad (32)$$

If N is large, and $n\ll N$, we may replace the sum (32) by an integral over $\phi=\frac{1}{2}s\theta$:

$$\Delta_n=\left(\frac{\hbar}{m\omega_0}\right)\frac{2}{\pi}\int_0^{\pi/2}\frac{\sin^2(n\phi)d\phi}{\sin\phi}. \qquad (32')$$

The integral in (32′) is

$$\sum_{p=1}^{n}(2p-1)^{-1}\simeq \text{const.}+\tfrac{1}{2}\log n+O(1/n).$$

Hence $\Delta_n/an\rightarrow 0$ as $n\rightarrow\infty$, and *the fluctuation is infranormal.* Although Δ_n tends to infinity when an does, it does not increase "as fast as n" but only "as fast as $\log n$."

For thermal equilibrium at a temperature T, we have for the time average of the expectation energy of an oscillator:

$$\langle H_s^{(1)}\rangle=\langle H_s^{(2)}\rangle=\kappa T\epsilon\coth\epsilon \qquad (33)$$

where $\epsilon=\hbar\omega_s/2\kappa T=(\hbar\omega_0/\kappa T)\sin(\frac{1}{2}s\theta)$. Making the same transformation as from (32) to (32′),

$$\Delta_n=\left(\frac{\kappa T}{m\omega_0^2}\right)\frac{2}{\pi}\int_0^{\pi/2}G(\phi)\left[\frac{\sin(n\phi)}{\sin\phi}\right]^2 d\phi, \qquad (34)$$

where

$$G(\phi)=[\hbar\omega_0\sin\phi/\kappa T]\coth[\hbar\omega_0\sin\phi/\kappa T].$$

The form of the integral in (34),

$$I_n(F)=\int_0^{\pi/2}F(x)[\sin(nx)/\sin x]^2dx,$$

is essentially Fejér's integral,[10] and has the property

$$\operatorname*{Lim}_{n\rightarrow\infty}(I/n)=(\pi/2)\operatorname*{Lim}_{x\rightarrow+0}F(x),$$

provided $F(x)$ is integrable in $(0,\pi/2)$. In the present case $F(+0)=G(0)=1$, and hence

$$\operatorname*{Lim}_{n\rightarrow\infty}(\Delta_n/an)=\kappa T/am\omega_0^2 \qquad (35)$$

for all T. To relate (35) to the one-dimensional compressibility, we have to regard a as a variable. The expectation of H (26) is a function of ω_0, T and N, and does not depend on a; but we should add to the potential energy in (26) a term

$$V_0=\tfrac{1}{2}m\omega_0^2a^2N \qquad (36)$$

to take account of the change in the total energy, E, on compression of the lattice. Then $(\partial^2E/\partial a^2)_{N,T}=m\omega_0^2N$. The isothermal compressibility is thus

$$\chi_T=aN/[a^2(\partial^2E/\partial a^2)_{N,T}]=1/am\omega_0^2; \qquad (37)$$

and (35) may be written

$$\Delta_n\simeq(a^2n)\rho\kappa T\chi_T, \quad 1\ll n\ll N, \qquad (38)$$

where $\rho=1/a$ is the linear density of atoms. Formula (38) is the precise analog of (4), in terms of the *inverse* of a mean linear density $n/(z_{n+r}-z_r)$, and has been found here to be correct for all temperatures.

APPENDIX

For the ground state of a quantum liquid, we may justify (11) and (12) by assuming

(a) the energy of the unperturbed state is given by an expression of the form $N[\epsilon(\rho)/\rho]$, being otherwise independent of the shape and surface area of the boundary enclosing the assembly provided the ratio of volume to surface is large enough compared with a characteristic length $l(\rho)$;[11]

(b) the internal energy of the ground state when it is perturbed by an external field (such as gravity) tends to that of the unperturbed state as the gradient of the field tends to zero; and

(c) the energy of the perturbed ground state is not appreciably affected when the volume is bisected by a thin solid boundary wall, provided the two subvolumes are each large compared with l times the area of the new surface.

Then, choosing k small enough, by (c) we may, without appreciably changing the energy of the assembly perturbed by the potential $\Omega\phi$, partition the volume by thin walls into cells each with linear dimensions small compared with $1/k$. After this move, the perturbed system is replaced by a large number of subsystems, each with a fraction of the original N atoms, with the same total internal energy. On removing the perturbing potential, by (b) the internal energies of the subsystems are not appreciably changed. Hence by (a) the internal energy of the original perturbed system is given by a sum over the cells which may be replaced by the integral $\int\epsilon(\rho)d^3\mathbf{r}$ taken over the whole volume of the assembly; from which (11) follows.

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[10] See Whittaker and Watson, *A Course of Modern Analysis* (Cambridge University Press, London, England and Macmillan Publishing Company, New York, 1947), p. 170.

[11] For liquid helium (He^4), l may be as large as $\sim 10^{-3}$ cm (see reference 8).