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On the Minimum Entropy of a Large System at Low Temperatures

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This paper examines the general question: How far can one set lower limits on the entropy density $S(T)$ of a large system at low temperatures by using data of a different type, e.g., scattering data or static susceptibilities? It is shown for an arbitrary one-component system that if we make a single unproved but highly plausible assumption about the fluctuations of large subvolumes, we can obtain an inequality relating $S(T)$ to certain integrals over the temperature-dependent correlation functions of the system; and with one further very weak assumption the zero-temperature correlation functions alone determine a lower limit on $S(T)$. It is then shown that the fluctuations of any locally conserved quantity give rise to a contribution to S of at least a constant times T^3; in particular, by considering the density fluctuations we obtain the inequality

$$S(T) \geqslant \tfrac{1}{2} S_D(T),$$

where $S_D(T)$ is the "Debye" entropy which would arise from longitudinal phonons propagating at the hydrodynamic sound velocity determined by the macroscopic compressibility. (This result does *not* assume the existence of such phonons as good elementary excitations of the system.) Some other general results are derived as a by-product: for instance, it is shown that any system obeying a diffusion equation of a certain type must have an entropy at least proportional to T.

1. INTRODUCTION

A great many of the strongly interacting many-particle systems found in nature are characterized by the fact that at sufficiently low temperatures they can be described in terms of elementary excitations, or quasiparticles, with a definite energy-wavevector relationship. The spectrum of the quasiparticles, and the statistics obeyed by them determine most of the thermodynamic properties of the system, and in particular the low-temperature entropy. In most cases, explicit calculation shows that the entropy tends to zero with T as T^n, $n > 0$.

In particular, if the elementary excitations of the system include long-wavelength longitudinal sound waves (phonons), then there is a corresponding contribution to the entropy which we shall call the "Debye" contribution. We consider for simplicity the case of a system which is elastically isotropic; then the "Debye" contribution to the entropy per unit volume has the value

$$S_{\mathrm{D}}(T) = \frac{2\pi^2}{45} \frac{k_B{}^4}{(\hbar c)^3} T^3 \equiv K_{\mathrm{D}} T^3. \tag{1}$$

The constant K_{D} is determined, apart from universal constants, entirely by the quantity c, the speed of longitudinal sound, which in turn is determined by the mass density and a single macroscopic thermodynamic coefficient:

$$c = (K\rho)^{-1/2}, \tag{2}$$

where ρ is the mass density and K an appropriate compressibility; for a system without shear (i.e., a liquid) K is just the inverse of the bulk modulus, while for a system with finite shear modulus it is the inverse of the longitudinal elastic stiffness constant (the quantity usually denoted C_{11}) [1].

If there are other types of quasiparticles present, apart from the phonons, they must contribute a positive term to the entropy. Consequently, it is clear that the expression (1) must be a lower limit on the total entropy per unit volume S of the system

$$S(T) \geqslant S_{\mathrm{D}}(T) = K_{\mathrm{D}} T^3. \tag{3}$$

Thus, in this case, we can deduce a lower limit on the low-temperature entropy of the system from a knowledge of the density and a single macroscopic parameter, the appropriate static compressibility.

The main question we set outselves to consider in this paper is: Does the inequality (3) (or a similar inequality) hold for an arbitrary system? More generally, how far can we establish lower limits on the entropy from a knowledge of data of a different type (e.g., from neutron scattering experiments or spin-susceptibility measurements)? Any result we can obtain, apart from its intrinsic interest, will be useful in establishing the consistency of measurements of the specific heat at low temperatures with other data. In addition, it should give some comfort to those laboring in the field of submillidegree cryogenics, since their efforts will at least not be frustrated by a sudden vanishing of the entropy of their working system!

At first sight it is tempting to argue that the inequality (3) must hold for an arbitrary (elastically isotropic) system, on the following grounds: whatever else is happening to the system, it must be possible to compress it and thus at sufficiently long wavelengths the elementary excitations must include longitudinal sound waves (phonons) whose speed, as determined by ordinary hydrodynamical considerations, must be given by Eq. (2). These phonons must obey Bose statistics and hence their contribution to the entropy will be given by the expression (1). Finally, any other degrees of freedom can only increase the entropy, so (1) will be a lower limit.

However, although the above argument clearly has a certain physical plausibility, there are a number of holes in it. Perhaps the most serious concerns the question of whether the excitations relevant to the low-temperature entropy can be described by hydrodynamics at all. This is certainly not obvious and it is easy to produce a counterexample: the weakly interacting Fermi gas. It is well known [2] that hydrodynamics is valid only for frequencies ω such that $\omega\tau \ll 1$, where τ is of the order of a characteristic quasiparticle lifetime; for the weakly interacting Fermi gas this is proportional to T^{-2}. On the other hand, if a set of excitations obeys a Planck distribution, the dominant contribution to the entropy will come from those with frequency of order $k_B T/\hbar$. It follows that for a Fermi gas at low temperatures, in the region of frequencies important for the entropy, hydrodynamic phonons do not exist.

The argument is also dubious at other points: for instance, even if one grants that the necessary hydrodynamic phonons do exist in the system in question (in the sense that one expects to observe a delta-function type resonance in, say, inelastic neutron scattering experiments), does it necessarily follow that they are distributed according to a Planck law? Or that it is legitimate to add their contribution to the entropy to any other contribution, so that it represents a lower limit on $S(T)$? And so on.

For certain specific systems these difficulties have been circumvented by rigorous microscopic arguments using the techniques of field theory. The prototype of such arguments was the work of Landau and Pitaevskii on the specific heat of a degenerate normal Fermi liquid [3]. Without explicitly introducing the idea of quasiparticles, they made certain assumptions about the structure of the one- and two-particle propagators and then used thermodynamic perturbation theory to show that the entropy for this system is linear in T at low temperatures—a result which is, of course, in accordance with the inequality (3). Similar techniques have been applied by Götze and Wagner [4] to the condensed Bose liquid, and by Götze [5] to the case of a perfect crystal; in both cases the inequality (3) is fulfilled (it becomes an equality for the Bose liquid). It seems very probable that a similar proof could be carried out for the neutral superfluid Fermi liquid [6], although I do not know of any reference where this has been done. However, in any given case these arguments require one to know, or assume, some specific properties of the low-energy excited states of the system, or equivalently of the propagators (at the very least, one must assume that they can be obtained by perturbation theory from some appropriate exactly soluble case, e.g., a noninteracting gas). There is, of course, no guarantee that any many-body system we may meet in the laboratory may be such that we can successfully guess the microscopic structure of its low-lying states[1], so it is of some interest to see whether we can prove some relations which will be quite independent of the specific nature of the system.

This is the task we set ourselves in this paper. We restrict ourselves to an isotropic one-component system. First we show that if we make a single unproved but highly plausible assumption about the behavior of macroscopic subvolumes of the system in the appropriate limit, we can derive an inequality relating the entropy to certain weighted integrals over correlation functions which may be observable in practice (e.g., in scattering experiments). Thus, in cases where we can do the required scattering experiments, we have at least a negative test for consistency between these and the specific-heat data. The result also has some interesting general implications; for instance, we show that if there is any macroscopic variable in the system (e.g., mass or spin density) which obeys a diffusion-type equation in the long-wavelength, low-frequency limit and has a finite "susceptibility" associated with it, then there must be a term in the entropy which tends to zero as $T \to 0$ at least as slowly as T itself (though we are unable to give a rigorous bound on the coefficient). This result is quite independent of the microscopic nature of the system.

We then go on to consider the case where we do not know the form of the correlation functions, but only (say) the macroscopic static compressibility. Then with one further very weak assumption about the temperature dependence of a certain moment of the density correlation function, we are able to prove that the inequality (3) holds in general apart from a constant factor: in fact,

$$S(T) \geqslant \tfrac{1}{2} K_{\mathrm{D}} T^3. \tag{3'}$$

With one further assumption ("normal scaling") we can improve the factor of $\frac{1}{2}$ in the inequality (3′) to 1, thus obtaining our originally conjectured inequality (3). We can also obtain lower limits similar to (3′) for the contribution to the entropy from fluctuation of macroscopic variables other than the density, e.g., the spin density or current density.

The paper is set out as follows. For simplicity of presentation we first derive our results for a one-component liquid (system without shear). In Section 2 we describe the limit in which we shall be interested and make plausible our fundamental assumption about the behavior of macroscopic subvolumes. In Section 3 we show that this assumption leads rigorously to a lower limit on the low-temperature entropy in terms of various correlation functions; with one further very weak assumption the result can be expressed in the relatively simple form of Eq. (42), which involves only the zero-temperature correlation functions. In Section 4 we test this result for various systems for which results are already known,

[1] As an example of a system of current interest whose microscopic structure is still controversial, one might mention the (quasi-two-dimensional) system formed by helium atoms adsorbed on a solid substrate.

and furthermore show that the existence of a diffusion-type equation for any macroscopic quantity implies an entropy which is at least linear in temperature. In Section 5 we consider the case where the correlation functions are completely unknown, and show that the fluctuations of any locally conserved quantity must give rise to a term in the entropy at least as large as const. T^3, where the constant may in certain cases be found from macroscopic thermodynamic data; the inequality (3′) then follows as a particular case of this. We also briefly examine the conditions under which the original conjecture (3) holds. In Section 6 we treat the more complicated case of a system with finite shear modulus. In Section 7 we briefly summarize the results and discuss their significance.

2. Postulate on the Fluctuations of Macroscopic Subvolumes

We shall consider for the present a system of N identical particles of mass m, enclosed in a volume Ω; as usual we shall be interested in the "thermodynamic limit" $N \to \infty$, $\Omega \to \infty$, $mN/\Omega = \text{const} \equiv \rho$. Throughout this work we shall assume that the system behaves normally in this limit, in the sense that for a given value of ρ and T quantities like the average energy are proportional to Ω, that is

$$\lim_{\Omega \to \infty} (\bar{E}/\Omega) = f(\rho, T). \tag{4}$$

We shall further assume, for the present, that if we slowly alter the shape of the system without changing the total volume Ω, then the energy is unchanged to relative order Ω^{-n}, $n > 0$; i.e., that the system has zero shear modulus. (This assumption is made only to simplify the presentation and will be relaxed in Section 6.) Under these conditions we can define the zero-temperature compressibility K uniquely by the relation

$$K \equiv \lim_{\Omega \to \infty} \left(\Omega \frac{\partial^2 E_0}{\partial \Omega^2} \right)_N^{-1}, \tag{5}$$

where E_0 is the ground-state energy. Furthermore, we can formally define a "speed of hydrodynamic sound" c_s by the usual expression

$$c_s \equiv (K\rho)^{-1/2} \tag{6}$$

[cf. Eq. (2) above]. It must be emphasized that Eq. (6) is simply a definition of the quantity c_s and does not imply that hydrodynamic sound waves can actually propagate in the system. Finally we define a characteristic length λ_T by the relation

$$\lambda_T \equiv \hbar c_s / k_B T. \tag{7}$$

For simplicity we take our total volume Ω in the shape of a cube of side l. Now we divide this total volume into a large number n of equal subvolumes

V_i ($i = 1,2,..., n$) which we take to be cubes of side d. Eventually we shall want to take the limits $V_i \to \infty$ and $T \to 0$ as well as $\Omega \to \infty$, and we have to specify rather carefully how this is to be done. For reasons which will become clear subsequently we choose to work in the following limit:

$$\begin{gathered} N \to \infty, \Omega \to \infty, V_i \to \infty, T \to 0, \\ mN/\Omega \to \text{const} \equiv \rho, \\ \lambda_T/l \to 0, d/\lambda_T \to 0, \qquad \text{but} \quad (a\lambda_T{}^3/d^4)\ln(\lambda_T/b) \to 0, \end{gathered} \tag{8}$$

where a, b are any fixed lengths. We shall refer to the limiting process described by (8) as "the appropriate limit" and indicate it by the shorthand notation $\lim_{\epsilon\to 0}$. It is to be emphasized that the quantity d here is a construct and has no physical significance.

For the total system there will generally exist a set of operators with the following properties: (a) they commute with the total Hamiltonian[2], (b) they commute with one another, (c) they can be expressed in the form of integrals over the total volume Ω of some locally defined operator. Examples of members of such a set are the total particle number $\hat{N}$, the total particle current $\hat{\mathbf{J}}$ (for a translationally invariant system) and the total spin $\hat{\mathbf{S}}$ (for systems in which the Hamiltonian is invariant against rotation of the spins alone). We write the members of such a set in the general form

$$\hat{\mathscr{A}}_\nu = \int^\Omega \hat{A}_\nu(\mathbf{r})\, d\mathbf{r}, \tag{9}$$

where ν labels the particular operator we are considering. The eigenvalues of the operator $\hat{\mathscr{A}}_\nu$ will be labelled α_ν : in general we find that as Ω tends to infinity, their spacing is of order 1 or less (not of order Ω). The energy is then a function of the α_ν's, among other things; we denote the minimum energy compatible with a given set of values $\{\alpha_\nu\}$ by $E_m\{\alpha_\nu\}$. Suppose that the system of interest to us is characterized by the fact that at $T = 0$ the α_ν's take a certain set of values $\{\alpha_\nu^{(0)}\}$; these values may be determined either (as in the case of the total number of particles) by the conscious choice of the experimenter or (as in the case of the total spin) by the condition of energy minimization plus, possibly, weak residual interactions with the walls. Given this set of values, the ground-state energy E_0 is uniquely determined:

$$E_0 \equiv E_m\{\alpha_\nu^{(0)}\}. \tag{10}$$

Consider now states in which the α_ν differ from their original values $\alpha_\nu^{(0)}$ by an amount of order Ω^k, $0 < k < 1$. We can then regard the α_ν as continuous variables;

[2] Excluding the interaction with the enclosing walls. More precisely, we require that they are locally conserved, in the sense that $[\hat{A}_\nu(\mathbf{r}), \hat{H}]$ is the divergence of some current.

since they are eigenvalues of extensive operators, we have $\partial^n E_m\{\alpha_\nu\}/\partial \alpha_\nu{}^n \sim \Omega^{-n+1}$ and hence successive terms in a Taylor expansion of the energy around $\alpha_\nu^{(0)}$ are smaller by a power of Ω. Thus, defining

$$\Delta E_m \equiv E_m\{\alpha_\nu\} - E_0\,, \qquad a_\nu \equiv \alpha_\nu - \alpha_\nu^{(0)}, \tag{11}$$

we have

$$\Delta E_m = \sum_\nu \left(\frac{\partial E_m}{\partial \alpha_\nu}\right) a_\nu + \frac{1}{2} \sum_{\nu,\nu'} \left(\frac{\partial^2 E_m}{\partial \alpha_\nu\, \partial \alpha_{\nu'}}\right) a_\nu a_{\nu'} + \cdots, \tag{12}$$

where the derivatives are evaluated at $\{a_\nu\} = 0$.

For simplicity of notation we shall assume from now on that we have chosen the operators $\hat{\mathscr{A}}_\nu$ in such a way that the cross terms ($\nu \neq \nu'$) in (12) vanish; this is clearly always possible. We define now

$$\mu_\nu \equiv \left(\frac{\partial E_m}{\partial \alpha_\nu}\right), \qquad \chi_\nu^{-1} \equiv \Omega \left(\frac{\partial^2 E_m}{\partial \alpha_\nu{}^2}\right), \tag{13}$$

the derivatives being evaluated at $a_\nu = 0$, i.e., in the original state. According to our hypotheses μ_ν and χ_ν are independent of Ω in the limit $\Omega \to \infty$. Moreover we define the quantum-mechanical expectation value of any operator $\hat{C}$ as $\langle C \rangle$:

$$\langle C \rangle \equiv \mathrm{Tr}\{\hat{\rho}\hat{C}\}, \tag{14}$$

where $\hat{\rho}$ is the density matrix. Also we define the deviation of $\hat{C}$ from its value in the ground state $\langle C \rangle_0$ as $\Delta\langle C \rangle$:

$$\Delta\langle C \rangle \equiv \langle C \rangle - \langle C \rangle_0\,. \tag{15}$$

Finally we define an operator representing the fluctuations of $\hat{\mathscr{A}}_\nu$ from its ground-state value

$$\hat{A}_\nu \equiv \hat{\mathscr{A}}_\nu - \alpha_\nu^{(0)}. \tag{16}$$

Clearly the eigenvalues of $\hat{A}_\nu$ are just the quantities a_ν.

Consider now a state of the system which is arbitrary subject only to the restrictions (for all ν)

$$|\langle (\hat{A}_\nu)^n \rangle| \lesssim \Omega^{bn}, \qquad b < 1, \qquad \text{for all} \quad n. \tag{17}$$

It then follows from Eqs. (12)–(17) and the definition of $E_m\{\alpha_\nu\}$ that for such a state, to within terms of relative order Ω^{-1+b}, we have

$$\Delta\langle E \rangle - \sum_\nu \mu_\nu \Delta\langle A_\nu \rangle \geqslant \tfrac{1}{2}\Omega^{-1} \sum_\nu{}' \chi_\nu^{-1} \langle (\hat{A}_\nu)^2 \rangle, \tag{18}$$

where the prime indicates that the sum runs over any subset of the total set of A_ν's.

The inequality (18) is of no great intrinsic interest; it serves merely to motivate our fundamental physical postulate, which we now introduce. We turn our attention to the subvolumes V_i and define operators in analogy with (9)

$$\hat{\mathscr{A}}_\nu^i = \int^{V_i} \hat{A}_\nu(\mathbf{r})\, d\mathbf{r}, \tag{19}$$

so that obviously

$$\hat{\mathscr{A}}_\nu \equiv \sum_i \hat{\mathscr{A}}_\nu^i. \tag{20}$$

Since the subvolumes are completely equivalent, we have

$$\langle \mathscr{A}_\nu^i \rangle_0 = n^{-1} \alpha_\nu^{(0)}. \tag{21}$$

We therefore define "fluctuation" operators analogous to the $\hat{A}_\nu$ [Eq. (16)]

$$\hat{A}_\nu^i \equiv \hat{\mathscr{A}}_\nu^i - n^{-1} \alpha_\nu^{(0)}. \tag{22}$$

Note that in general the $\hat{A}_\nu^i$ do *not* commute with the total Hamiltonian, and therefore the mean-square value of $\hat{A}_\nu^i$ is not zero even in the ground state.

Now we consider the system in a thermal equilibrium state in the appropriate limit. From general thermodynamic considerations we should expect that

$$|\langle (\hat{A}_\nu^i)^n \rangle| \lesssim V_i^{kn}, \qquad 0 < k < 1;$$

so that for the subvolumes V_i the condition analogous to (17) is fulfilled. (For the case $n = 2$, this can be verified directly from the formulas of the next section.) We therefore postulate for any thermal equilibrium state in the appropriate limit, an inequality analogous to (18)

$$\Delta\langle E \rangle - \sum_\nu \mu_\nu \Delta \langle A_\nu \rangle \geqslant \tfrac{1}{2} \sum_i {\sum_\nu}' V_i^{-1} \chi_\nu^{-1} \Delta \langle (\hat{A}_\nu^i)^2 \rangle \equiv \mathscr{E}_m(T) \tag{23}$$

(the primed sum is taken over any subset of the A_ν).

More precisely, we make the following postulate:

$$\Delta\langle E \rangle - \sum_\nu \mu_\nu \Delta\langle A_\nu \rangle \geqslant (1 - \delta)\, \mathscr{E}_m(T), \qquad \lim_{\epsilon \to 0} \delta = 0. \tag{24}$$

The inequality (24) is the keystone of all our subsequent results. Although we have perhaps succeeded in making it plausible from an intuitive point of view, it is not a rigorous consequence of any theorems of quantum mechanics or statistical mechanics known to the author. In particular, it is important to realize that it cannot be obtained simply by comparing the subvolume V_i with the total volume Ω and invoking the extensive property of the mean energy. This would be equivalent to breaking up the volume Ω into subvolumes V_i and treating them as isolated volumes completely equivalent to Ω apart from a scale factor, thus ignoring (among other things) the finite value of $\langle(\hat{A}_\nu^i)^2\rangle_0$. To see why this will not work, we have to remember that the first corrections to Eq. (4) for finite Ω are of order Ω^{-l}, $l > 0$ (usually $l = 1/3$). Thus, if we imagine that we impose the same boundary conditions on the subvolumes V_i as on the volume Ω and then compare the relevant ground-state energies $E_0{}^i$ and E_0,

$$(E_0 - nE_0{}^i)/E_0 \sim nV_i^{-l} \sim \Omega d^{-3(l+1)}. \tag{25}$$

On the other hand, as we shall see in the next section, the quantity $E_m(T)$ may be as small as of order $\Omega\lambda_T^{-4}$. In other words, we have neglected an effect which in the appropriate limit tends to zero slower than the one we are looking for. Physically speaking, we are trying to calculate the effect of the thermal long-wavelength fluctuations, and it is not *a priori* obvious that it is legitimate simply to superimpose this on the much larger effect of the corresponding zero-point fluctuations, which is assumed to be constant.

We cannot therefore claim to have demonstrated the inequality (24) in any meaningful sense. Rather, we treat it as a general statement which we conjecture will be obeyed by all systems likely actually to occur in nature. To this extent we may hope it might have a status analogous to the third law of thermodynamics which has not (to the author's knowledge) ever been proved in general either. In our case as well, the conjecture (24) must eventually be disproved, or tentatively established, by comparison with experiment for a wide range of systems. In Section 4 we shall show that the conclusions drawn from it are consistent with the experimental evidence for a number of different types of system; we have not found any counterexample.

We can simplify the formula (23) slightly if we include all interactions with external fields, etc., in the Hamiltonian. In that case for any given ν we have either $\mu_\nu = 0$ (for quantities A_ν which are not rigorously conserved) or $\Delta\langle A_\nu\rangle = 0$ (for quantities such as the total particle number which are). Thus we can write (24) in the simpler form

$$\Delta\langle E\rangle \geqslant (1 - \delta)\, \mathscr{E}_m(T), \qquad \lim_{\epsilon\to 0} \delta = 0, \tag{25'}$$

where E includes interactions with any external fields (which are assumed held constant as we vary T). It is precisely this energy which is related directly to the entropy, which is what we calculate in the next section.

3. Inequality for the Entropy

In this section we shall show that the assumption (25′) leads rigorously to a lower limit on the entropy of an arbitrary many-body system in the limit $T \to 0$ in terms of the correlation functions. We start by expressing the quantity $\sum_i \langle \hat{A}_\nu{}^i)^2\rangle$ in terms of the response functions [7] of the system. We first introduce Fourier transforms of the operators $\hat{A}_\nu(\mathbf{r})$

$$\hat{A}_\nu(\mathbf{r}) \equiv \alpha_\nu^{(0)}/\Omega + \Omega^{-1} \sum_{\mathbf{k}} \hat{A}_{\mathbf{k}\nu} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{26}$$

$$\hat{A}_{\mathbf{k}\nu} = \int^{\Omega} d\mathbf{r}[\hat{A}_\nu(\mathbf{r}) - \alpha_\nu^{(0)}]\, e^{-i\mathbf{k}\cdot\mathbf{r}}, \tag{27}$$

where the sum over $\mathbf{k}$ goes over values allowed by the usual periodic boundary conditions. Then we have [cf. Eq. (22)]

$$\hat{A}_\nu{}^i \equiv \int^{V_i} d\mathbf{r}[\hat{A}_\nu(\mathbf{r}) - \alpha_\nu^{(0)}/\Omega] = \Omega^{-1} \sum_{\mathbf{k}} A_{\mathbf{k}\nu} \int^{V_i} d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{28}$$

Let $\mathbf{R}_i$ denote the center of the subvolume V_i. Then (28) reduces to

$$\hat{A}_\nu{}^i = \Omega^{-1} V_i \sum_{\mathbf{k}} \varphi(\mathbf{k})\, \hat{A}_{\mathbf{k}\nu} e^{i\mathbf{k}\cdot\mathbf{R}_i}, \tag{29}$$

where

$$\varphi(\mathbf{k}) \equiv \prod_{i=x,y,z} \frac{\sin(k_i d/2)}{(k_i d/2)}\,. \tag{30}$$

Note that in the limit $|\,k\,|\,d \to 0$, we have $\varphi(\mathbf{k}) \to 1$ independently of the direction of $\mathbf{k}$. From (29) we have

$$\begin{aligned}\sum_i \langle(\hat{A}_\nu{}^i)^2\rangle &= \sum_i \Omega^{-2} V_i{}^2 \sum_{\mathbf{k}\mathbf{k}'} \varphi(\mathbf{k})\, \varphi(\mathbf{k}')\, e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{R}_i} \langle \hat{A}_{\mathbf{k}\nu} \hat{A}_{\mathbf{k}'\nu}\rangle \\ &= (V_i/\Omega) \sum_{\mathbf{k}} |\,\varphi(\mathbf{k})|^2 \langle \hat{A}_{\mathbf{k}\nu} \hat{A}_{-\mathbf{k}\nu}\rangle.\end{aligned} \tag{31}$$

Notice that since $\hat{A}(r)$ is a Hermitian operator, $\hat{A}_{k\nu}$ and $\hat{A}_{-k\nu}$ are Hermitian conjugates. Substituting (31) in the definition of $E_m(T)$ [eq. (23)] for a given choice of the subset of A_ν over which the summation is taken, we find

$$\mathscr{E}_m(T) = \tfrac{1}{2} \sum_\nu{}' \chi_\nu^{-1} \Omega^{-1} \sum_{\mathbf{k}} |\,\varphi(\mathbf{k})|^2\, \Delta\langle \hat{A}_{\mathbf{k}\nu} \hat{A}_{-\mathbf{k}\nu}\rangle. \tag{32}$$

Consider now a general thermal average of the form

$$\Delta\langle C^\dagger C\rangle \equiv \mathrm{Tr}(\hat{\rho}_T \hat{C}^\dagger \hat{C}) - \mathrm{Tr}(\hat{\rho}_0 \hat{C}^\dagger \hat{C}), \tag{33}$$

where $\hat{\rho}_T$ is the density matrix corresponding to thermal equilibrium at temperature T. Let us introduce the spectral density

$$\chi_T''^{(c)}(\omega) \equiv \pi Z^{-1} \sum_m e^{-\beta E_m} \sum_n |\langle n \mid C \mid m \rangle|^2 \{\delta(E_n - E_m - \hbar\omega) - \delta(E_n - E_m + \hbar\omega)\},$$
$$\Big(Z \equiv \sum_m e^{-\beta E_m},\ \beta \equiv 1/k_B T\Big). \quad (34)$$

$\chi_T''^{(c)}(\omega)$ is just[3] the imaginary part of the time Fourier transform of the retarded response function [7]. We notice for future reference that it obeys the sum rules

$$\frac{2}{\pi} \int_0^\infty \omega \chi_T''^{(c)}(\omega)\, d\omega = -\frac{1}{\hbar^2} \langle [C, [C^\dagger, H]] \rangle, \quad (35)$$

$$\frac{2}{\pi} \int_0^\infty \frac{\chi_T''^{(c)}(\omega)}{\omega}\, d\omega = \chi_T^{(c)}, \quad (36)$$

where $\chi_T^{(c)}$ is the temperature-dependent static "susceptibility" corresponding to the quantity C, i.e., the (adiabatic) change in $\langle C \rangle$ induced by a perturbation $\lambda C^\dagger$, divided by λ, in the limit $\lambda \to 0$. With the above definitions it follows from the fluctuation-dissipation theorem that

$$\Delta \langle C^\dagger C \rangle = |\Delta \langle C \rangle|^2 + \frac{\hbar}{\pi} \int_0^\infty (\coth(\beta\hbar\omega/2)\, \chi_T''^{(c)}(\omega) - \chi_0''^{(c)}(\omega))\, d\omega. \quad (37)$$

We now apply this equality to the quantity $E_m(T)$ [eq. (32)], taking $\hat{C}$ to be the operator $\Omega^{-1/2} A_{\mathbf{k}\nu}$. We denote the corresponding spectral density by $\chi_\nu''(k, \omega : T)$. To avoid complications we shall omit the term $\mathbf{k} = 0$ from the sum; this is legitimate since we are interested in obtaining a lower limit on the quantity $E_m(T)$ and the contribution of the $\mathbf{k} = 0$ term is clearly nonnegative. For all other values of $\mathbf{k}$ we have $\Delta\langle A_{\mathbf{k}\nu}\rangle = 0$. Then replacing the sum by an integral in the usual way, we find

$$\mathscr{E}_m(T) \geqslant \tilde{\mathscr{E}}_m(T) \equiv \frac{\Omega}{(2\pi)^3} \sum_\nu{}' \int d^3\mathbf{k}\, |\varphi(\mathbf{k})|^2\, \Lambda_\nu(\mathbf{k}, T), \quad (38)$$

where

$$\Lambda_\nu(\mathbf{k}, T) \equiv \frac{1}{2} \chi_\nu^{-1} \frac{\hbar}{\pi} \int_0^\infty [\coth(\beta\hbar\omega/2)\, \chi_\nu''(\mathbf{k}, \omega : T) - \chi_\nu''(\mathbf{k}, \omega : 0)]\, d\omega. \quad (39)$$

Finally, combining the inequalities (25′) and (38) and recalling that according to

[3] Apart possibly from a numerical factor depending on the convention used for the definition of the response function. We follow the conventions of Ref. (7).

our definition of $\langle E\rangle$ we have $d\langle E\rangle = \Omega T dS$, we obtain* the required lower limit on the entropy per unit volume $S(T)$

$$S(T) \geqslant S_m(T) = \frac{1}{(2\pi)^3} \sum_\nu{}' \int_0^T \int d^3\mathbf{k} \mid \varphi(\mathbf{k})|^2 \frac{1}{T'} \frac{d\Lambda_\nu(\mathbf{k}, T')}{dT'} dT', \tag{40}$$

or more strictly,

$$S(T) \geqslant (1 - \eta) S_m(T), \qquad \lim_{\epsilon \to 0} \eta = 0. \tag{41}$$

This may be regarded as the first major result of this paper. It takes a simpler form if we can neglect the temperature dependence of $\chi_\nu''(\mathbf{k}, \omega : T)$: in that case we find

$$S(T) \geqslant S_m(T) = \frac{1}{(2\pi)^3} \sum_\nu{}' \int d^3\mathbf{k} \mid \varphi(\mathbf{k})|^2 Q_\nu(\mathbf{k}, T), \tag{42}$$

$$Q_\nu(\mathbf{k}, T) \equiv k_B \frac{\beta\hbar}{\pi\chi_\nu} \int_0^\infty \left\{ \frac{1}{e^{\beta\hbar\omega} - 1} - \frac{1}{\beta\hbar\omega} \ln(1 - e^{-\beta\hbar\omega}) \right\} \chi_\nu''(\mathbf{k}, \omega : 0)\, d\omega. \tag{43}$$

This then is a lower limit on the total entropy in terms of the zero-temperature correlation functions of the system.

That it is legitimate to neglect the temperature dependence of $\chi_\nu''(\mathbf{k}, \omega : T)$ is in fact a very weak assumption. The additional term contributed to $\tilde{E}_m(T)$ by this temperature dependence is proportional to $L_\beta(T) - L_\beta(0)$, where

$$L_\beta(T') \equiv \int d^3\mathbf{k} \int_0^\infty d\omega \mid \varphi(\mathbf{k})|^2 \coth(\beta\hbar\omega/2)\, \chi_\nu''(\mathbf{k}, \omega : T') \tag{44}$$

(where T' is in general *not* equal to $T \equiv 1/k_B\beta$). [This follows from (39).] All that we need to suppose is that for sufficiently small T and $T' \leqslant T$ we can write

$$L_\beta(T') \geqslant L_\beta(0)(1 - \alpha T'), \tag{45}$$

where α is some constant independent of β, and also of the subvolume dimension d which enters L_β through its appearance in $\varphi(\mathbf{k})$ [Eq. (30)]. Now we can show that in the appropriate limit $L_\beta(0)$ is at most of order Ad^{-4} where A is a constant independent of β [4]; consequently, if the inequality (45) holds, the quantity $L_\beta(T) - L_\beta(0)$ is either positive or, if negative, at most of order $Td^{-4} \sim \lambda_T^{-1} d^{-4}$. Hence it can subtract from the quantity $S_m(T)$ at most a term of order $d^{-4} \ln(\lambda_T/b)$, where b is a constant. But we shall see that the terms kept in (42) are at least of order λ_T^{-3}, and hence from the last condition involved in the definition of the appro-

* That the inequalities (25′) and (38) do in fact imply (40) is possibly not quite obvious at first sight, the result is most easily obtained by integrating the expression for $S(T)$ by parts, using (25′) and (38) and then reversing the integration by parts.

[4] This follows by arguments analogous to those used in the Appendix.

priate limit [Eq. (8)], we can drop the terms arising from the temperature dependence of χ''. Thus the validity of (42) requires only the very weak condition (45) in addition to our fundamental postulate. We shall, however, be able to prove some useful results without involving the assumption (45); in particular, we do not need to invoke it as an assumption in the next section, since for the cases discussed we know that χ'' is temperature independent to a sufficient approximation.

4. Illustrations for Simple Systems

In this section we shall apply the inequality (40) to some simple systems where some of the low-temperature correlation functions are known explicitly. We include both real systems (e.g., liquid helium II) where both the correlation functions and the entropy are known experimentally, and model systems (e.g., the weakly interacting Fermi gas) for which both can be rigorously calculated. We shall show that in all cases considered the known results are in agreement with the inequality (40). In addition, we demonstrate the interesting result that any system which has a macroscopic variable which at low temperatures obeys a temperature independent diffusion equation, must have an entropy which tends to zero no faster than T, irrespective of the microscopic nature of the diffusion process.

Except where explicitly otherwise stated, the correlation functions for the systems considered in this section are temperature independent to a sufficient approximation, and we can therefore rigorously replace (40) by (42).

1. *System with Hydrodynamic Sound Waves*

Our first example is a more or less trivial one: a system for which the density response function for small $\mathbf{k}$ and T is adequately derived from hydrodynamics, (so that weakly damped sound waves are good elementary excitations of the system). The explicit form of the spectral density for the density response function (that corresponding to $\hat{\mathscr{A}}_\nu = \hat{N}$, the total particle number) for small $\mathbf{k}$ and $\omega(\omega \geqslant 0)$ is then [8]

$$\chi_N''(\mathbf{k}, \omega) = \frac{\pi}{2} \frac{\rho}{m^2 c_s^2} \cdot c_s k \delta(\omega - c_s k), \tag{46}$$

where c_s is given by Eq. (2) and in this case is, of course, indeed the speed of longitudinal sound. The experimental evidence from neutron scattering [9] for He II indicates that this form of $\chi_N''(k, \omega)$ is applicable there to a good approximation. The corresponding static "susceptibility" χ_N is given from Eqs. (13), (5) and (6) by

$$\chi_N \equiv \lim_{\Omega\to\infty} \left(\Omega \frac{\partial^2 E}{\partial N^2}\right)^{-1} = \left(\frac{\rho}{m}\right)^2 K \equiv \frac{\rho}{m^2 c_s^2} \,. \tag{47}$$

We also consider among the set $\hat{\mathscr{A}}_\nu$ the three components of particle current $\hat{J}_\alpha$. In this case the susceptibility corresponding to each is

$$\chi_{J_\alpha} = \lim_{\Omega\to\infty} \left(\Omega \frac{\partial^2 E}{\partial J_\alpha{}^2}\right) = \frac{\rho}{m^2}. \tag{48}$$

Since the system is isotropic, the (imaginary part of the) current–current correlation function has the general form

$$\chi''_{J_\alpha}(\mathbf{k}, \omega) = k_\alpha{}^2 \chi''_{Jl}(\mathbf{k}\omega) + (k^2 - k_\alpha{}^2)\, \chi''_{Jt}(\mathbf{k}\omega), \tag{49}$$

where the "longitudinal" and "transverse" contributions χ''_{Jl}, χ''_{Jt} are both nonnegative, It follows from the continuity equation that $\chi''_{Jl}(\mathbf{k}, \omega)$ is related to the density correlation function χ''_N by

$$\chi''_{Jl}(\mathbf{k}, \omega) = (\omega^2/k^2)\, \chi''_N(\mathbf{k}, \omega). \tag{50}$$

Substituting Eqs. (46)–(50) and (43) into the inequality (42), taking the sum over ν to include the contributions from density and current fluctuations and dropping the (nonnegative) contribution of χ''_{Jt}, we finally obtain

$$S(T) \geqslant \frac{k_B}{(2\pi)^3} \int d^3\mathbf{k} \mid \varphi(\mathbf{k})|^2\, \beta\hbar c_s k \left[\frac{1}{e^{\beta\hbar c_s k} - 1} - \frac{1}{\beta\hbar c_s k} \ln(1 - e^{-\beta\hbar c_s k})\right]. \tag{51}$$

The term in square brackets vanishes exponentially for $\beta\hbar c_s k \equiv k\lambda_T \gg 1$; since our limit involves that $\lambda_T/d \to \infty$, we can put the cut-off factor

$$\varphi(\mathbf{k}) \equiv \prod_{i=x,y,z} \sin(k_i d/2)/(k_i d/2)$$

equal to 1 everywhere.
Then we find

$$\begin{aligned} S(T) &\geqslant \frac{k_B}{(2\pi)^3} (\beta\hbar c_s)^{-3} \cdot 4\pi \int_0^\infty \left\{\frac{x^3}{e^x - 1} - x^2 \ln(1 - e^{-x})\right\} dx \\ &= \frac{2k_B}{3\pi^2} (\beta\hbar c_s)^{-3} \int_0^\infty \frac{x^3\, dx}{e^x - 1} \\ &= \frac{2\pi^2}{45} \frac{k_B{}^4}{(\hbar c_s)^3} T^3 \equiv S_{\mathrm{D}}(T). \end{aligned} \tag{52}$$

Thus we have reached the unsurprising result that a system whose density correlation function shows temperature-independent hydrodynamic behavior must have at least the "Debye" entropy. This result can actually be slightly strengthened:

it can be shown that it follows if the behavior at zero temperature is hydrodynamic, irrespective of the form at finite temperature (see the end of Section 5).

2. *The Ideal Fermi Gas*

In this case $\chi_N''(\mathbf{k}, \omega)$ is given for small $\mathbf{k}$ and ω by the expression

$$\chi_N''(\mathbf{k}, \omega) = \frac{\pi}{2}\left(\frac{dn}{d\epsilon}\right)\left(\frac{\omega}{v_F k}\right)\theta(v_F k - \omega), \tag{53}$$

where $(dn/d\epsilon)$ is the density of states (of both spins) per unit volume at the Fermi surface, v_F is the Fermi velocity and $\theta(x)$ the usual step function. The static susceptibility is simply

$$\chi_N = (dn/d\epsilon). \tag{54}$$

We substitute this in the inequality (42) and take the sum over the density fluctuations only. After some simple transformations we obtain

$$S_m(T) = \frac{k_B}{2(2\pi)^3}\frac{1}{d^3\xi}\int d^3\mathbf{u}\,|\,u\,|^{-1}\prod_{i=x,y,z}\left(\frac{\sin(u_i/2)}{u_i/2}\right)\int_0^{\xi|u|} f(x)\,dx, \tag{55}$$

$$f(x) \equiv \frac{x}{e^x - 1} - \ln(1 - e^{-x}), \tag{56}$$

where

$$\xi \equiv (\hbar v_F/dk_B T) = \sqrt{3}\,(\lambda_T/d) \tag{57}$$

[cf. Eq. (7); for a free Fermi gas, $c_s = 3^{-1/2}v_F$]. The appropriate limit involves that $\xi \to \infty$; in this limit the double integral in (55) is independent of ξ and we therefore get

$$S_m(T) = Ak_B d^{-3}\xi^{-1} = \left(\frac{A}{\hbar v_F d^2}\right)k_B{}^2 T, \tag{58}$$

where A is a numerical constant of order unity. This result is slightly curious in that it depends on d, the dimension of our subvolumes, which is an arbitrary construct and has no physical significance. To interpret the result, we note that our basic inequality (41) implies that for any given large but finite value of d the quantity $\eta(d, \lambda_T, l)$ is less than some constant η_0 as λ_T and l tend to infinity; moreover, by choosing d large enough we can obviously ensure that $\eta_0 < 1$. Thus, Eq. (58) means that there exists a term in the entropy of an ideal Fermi gas which is (at least) linear in T, although we cannot in this case put an explicit lower bound on the coefficient. If we were to assume that η_0 does not become of order 1 until d becomes comparable with the characteristic length of the system (the interparticle spacing) we should get a coefficient which agrees with the exact result within a numerical factor [that is, it is proportional to $(dn/d\epsilon)$]. We note, by the way, that the inequality following from (58) for $S(T)$ could be strengthened by a factor of 4 by considering the spin fluctuations as well as the density fluctuations.

Having examined the case of the ideal Fermi gas, it would be natural to go on to the ideal Maxwell–Boltzmann and Bose gases. However, in both these cases the static compressibility is singular at $T = 0(\chi_N^{-1} = 0)$ and hence the inequality (3′) is trivially fulfilled.

3. *Normal Neutral Fermi Liquid*

For this model (which is generally believed to give a good description of liquid He^3 at low temperatures) $\chi_N''(\mathbf{k}, \omega)$ is given by the general form [2] (for small $\mathbf{k}$ and ω)

$$\chi_N''(\mathbf{k}, \omega) = \frac{\pi}{2}\left(\frac{dn}{d\epsilon}\right) f(s), \qquad s \equiv \omega/kv_{\mathrm{F}} . \tag{59}$$

The function $f(s)$ depends on the Landau parameters F_l and in general cannot be written down in a closed form. However, it has the property that for any finite set of values of F_l we can write

$$f(s) \geqslant Cs \qquad \text{for} \quad 0 \leqslant s \leqslant s_0 , \tag{60}$$

where C and s_0 are some dimensionless constants. Proceeding as above, we obtain the result

$$S_m(T) \geqslant \left(\frac{A'}{\hbar v_{\mathrm{F}} d^2}\right) k_B{}^2 T, \tag{61}$$

where A' is a numerical constant. Thus, we predict a linear term in the entropy, in agreement with experiment.

It should be emphasized that in this case (as in the case of the ideal Fermi gas) we can obtain other linear terms in the entropy by including other values of $\hat{\mathscr{A}}_\nu$ (e.g., the components of spin $\mathbf{S}$ and particle current $\mathbf{J}$ (in the latter case, it is the "transverse" current fluctuations which give a linear term). Thus we can obtain a linear term by this technique even for the case of a *charged* Fermi liquid, where the density correlation function χ_N'' has no low-lying spectral weight at all [7].

4. *System Obeying a Diffusion Equation*

As our final example we consider a system in which some macroscopic variable $C(\mathbf{r}, t)$ obeys a diffusion-type equation

$$\frac{\partial C}{\partial t}(\mathbf{r}, t) = D\nabla^2 C(\mathbf{r}, t). \tag{62}$$

We assume that both the diffusion coefficient D and the associated static susceptibility χ_c tend to a finite limit as $T \to 0$. Such a situation is characteristic of, for instance, spin diffusion in a metal. For notational simplicity, however, we shall assume that it is the particle density which obeys Eq. (62) (as in a hypothetical neutral gas scattered by static impurities); the generalization to the case of diffusion of spin or other locally conserved quantities is obvious.

In this case the form of χ_N'' is (cf. Ref. [8])

$$\chi_N''(\mathbf{k}, \omega) = \frac{\pi}{2} \chi_N \frac{\omega \cdot Dk^2}{\omega^2 + (Dk^2)^2} \cdot \tag{63}$$

In this case, it is natural to define, instead of λ_T, a different "characteristic thermal wavelength" λ_T' by

$$\lambda_T' \equiv (D\hbar/k_B T)^{1/2} \tag{64}$$

and replace λ_T by λ_T' in the definition of the "appropriate limit", Eq. (8). (Since d is an arbitrary construct, this does not amount to making any new physical assumption.) Then after some changes of variables we find from (42)

$$\frac{S_m(T)}{\Omega} = \frac{\beta\hbar k_B D}{2(2\pi)^3 d^5} \int_0^\infty \frac{z\, dz}{1 + z^2} \int d^3\mathbf{u}\, u^2 \mid \varphi'(u)|^2 g(\alpha z u^2), \tag{65}$$

where

$$\varphi'(u) \equiv \prod_{i=x,y,z} \frac{\sin(u_i/2)}{(u_i/2)}, \tag{66}$$

$$g(x) \equiv \frac{1}{e^x - 1} - \frac{1}{x} \ln(1 - e^{-x}), \tag{67}$$

$$\alpha \equiv \beta\hbar D d^{-2} \equiv (\lambda_T'/d)^2. \tag{68}$$

In the appropriate limit, $\alpha \to \infty$, we easily see that the main contribution to the double integral comes from the region $|\mathbf{u}| \sim 1$, $z \lesssim \alpha^{-1}$, and is proportional to α^{-2}. Hence we get finally

$$\frac{S(T)}{\Omega} \geqslant \left(\frac{A''}{\hbar d D}\right) k_B{}^2 T, \tag{69}$$

where A'' is a numerical constant.

Thus, for any system possessing a conserved macroscopic variable which obeys a temperature-independent diffusion equation at low temperatures, we expect an entropy which is at least linear in temperature. This is interesting, since at first sight one would think that scaling arguments would lead to a contribution from the diffusion modes which would vary as $T^{3/2}$. Equation (69) is of course consistent with the result of exact calculations for a free Fermi gas scattered elastically by impurities (in this case the entropy depends only on the density of single-particle states at the Fermi surface, which is not qualitatively affected by a dilute concentration of elastic scatterers). The result is also consistent with the experimental specific heat of dirty metals [in this case, it is the spin rather than the particle (charge) density which obeys a diffusion equation]. However, it should be noticed that in the general case, if we are trying to use (69) to put a lower limit on the coefficient of the linear term, it is illegitimate to take d shorter than the longest characteristic length of the system, which in this case is the mean-free path l; this is because, for $k > l^{-1}$, the form of χ'' certainly differs substantially from Eq. (63). Thus, in general, we can only say that a system obeying a diffusion equation will have an entropy of at least γT, where the constant γ is at least of order

$$(\hbar l D)^{-1} \sim (\hbar l^2 \bar{v})^{-1},$$

where $\bar{v}$ is some characteristic particle velocity.

5. Minimum Entropy for an Arbitrary System

In this section we turn to the question of the constraints imposed on the low-temperature entropy of an arbitrary many-body system by the static susceptibilities. We shall show that every independent locally conserved quantity must give rise to (at least) a T^3 term in the entropy, with a minimum coefficient which for quantities such as the particle and spin density may be determined from the static susceptibility.

We consider a general operator $\hat{\mathscr{A}}_\nu$ of the type considered in Section 2. Then, according to (42) and (43), this contributes to the entropy a term at least equal to

$$S_{m\nu}(T) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \mid \varphi(\mathbf{k})|^2 \, Q_\nu(\mathbf{k}, T), \tag{70}$$

$$Q_\nu(\mathbf{k}, T) \equiv \frac{\beta\hbar k_B}{\pi\chi_\nu} \int_0^\infty \left\{ \frac{1}{e^{\beta\hbar\omega} - 1} - \frac{1}{\beta\hbar\omega} \ln(1 - e^{-\beta\hbar\omega}) \right\} \chi_\nu''(\mathbf{k}, \omega : 0) \, d\omega. \tag{71}$$

According to Eqs. (35) and (36), the nonnegative function $\chi_\nu''(\mathbf{k}, \omega : 0)$ obeys the sum rules

$$\frac{2}{\pi} \int_0^\infty \omega \chi_\nu''(\mathbf{k}, \omega : 0) \, d\omega = -\hbar^{-2} \langle [\hat{A}_{k\nu}, [\hat{A}_{-k\nu}, \hat{H}]] \rangle, \tag{72}$$

$$\frac{2}{\pi} \int_0^\infty \omega^{-1} \chi_\nu''(\mathbf{k}, \omega : 0) \, d\omega = \chi_{\mathbf{k}\nu}, \tag{73}$$

where $\chi_{\mathbf{k}\nu}$ is the static susceptibility. We shall assume that as $\mathbf{k} \to 0$ the quantity $\chi_{\mathbf{k}\nu}$ tends to χ_ν defined by Eq. (13)[5], and in fact that

$$\chi_{\mathbf{k}\nu} = \chi_\nu[1 + \mathcal{O}(k^n)], \qquad n \geqslant 1. \tag{74}$$

We further notice that since $\hat{A}_\nu(r)$ is a locally conserved quantity, the right-hand side of Eq. (72) must be proportional to k^2 for small k. We therefore define

$$\lim_{\mathbf{k}\to 0} \left\{ -\frac{1}{\hbar^2 k^2} \langle [\hat{A}_{\mathbf{k}\nu}, [\hat{A}_{-\mathbf{k}\nu}, \hat{H}]] \rangle \right\} \equiv \xi_\nu \geqslant 0 \tag{75}$$

and a quantity with the dimensions of a velocity

$$c_\nu \equiv (\xi_\nu/\chi_\nu)^{1/2}. \tag{76}$$

Now we introduce the dimensionless quantities

$$s \equiv \omega/c_\nu k, \tag{77}$$

$$\zeta_\nu(\mathbf{k}, s) \equiv \frac{2}{\pi\chi_\nu} \chi_\nu''(\mathbf{k}, \omega : 0). \tag{78}$$

In terms of these we have

$$Q_\nu(\mathbf{k}, T) = \frac{1}{2} k_B \alpha \int_0^\infty ds \left\{ \frac{1}{e^{\alpha s} - 1} - \frac{1}{\alpha s} \ln(1 - e^{-\alpha s}) \right\} \zeta_\nu(\mathbf{k}, s)\, ds, \tag{79}$$

where

$$\alpha \equiv \beta\hbar c_\nu k. \tag{80}$$

The sum rules (72) and (73) take the simple form

$$\int_0^\infty s\zeta_\nu(s)\, ds = \int_0^\infty s^{-1}\zeta_\nu(s)\, ds = 1. \tag{81}$$

It is shown in the Appendix that Eqs. (79) and (81) imply the result

$$Q_\nu(\mathbf{k}, T) \geqslant \frac{1}{2} k_B \left\{ \frac{\alpha}{e^\alpha - 1} - \ln(1 - e^{-\alpha}) \right\}. \tag{82}$$

The right-hand side of (82) falls off exponentially in the limit $k \to \infty$; hence after substituting it into (70) we can take $\varphi(\mathbf{k})$ [Eq. (30)] equal to 1 for all $\mathbf{k}$.

[5] In the case of superfluid systems we must be careful if ν indicates a Cartesian component of the particle current: for a given component $\chi_{\mathbf{k}\nu}$ depends on the direction of $\mathbf{k}$, and the "transverse" part does *not* tend to χ_ν as $\mathbf{k} \to 0$. However, with a little care this case is easily included.

Then we have finally [cf. Eqs. (51), (52)]

$$S_{m\nu}(T) \geqslant \frac{1}{2} \cdot \frac{2\pi^2}{45} \frac{k_B{}^4}{(\hbar c_\nu)^3} T^3. \tag{83}$$

Thus, each independent[6] locally conserved quantity gives rise to a term in the entropy with the minimum value (83) determined uniquely by the quantity c_ν; in fact, the total entropy per unit volume $S(T)$ obeys the inequality

$$S(T) \geqslant \frac{1}{2} \cdot \frac{2\pi^2}{45} k_B \sum_\nu{}' \left(\frac{k_B T}{\hbar c_\nu}\right)^3. \tag{84}$$

This is the second principal result of this paper.

Now, we may if we wish restrict the sum over ν to a single quantity, the particle density. In this case Eq. (72) is just the well-known longitudinal sum rule and so in Eq. (75) we have $\xi_\nu = \rho/m^2$. Further, χ_N is related to the bulk modulus K defined in Eq. (5) by Eq. (47), and so c_ν for this case is identical to the "speed of hydrodynamic sound" c_s defined by Eq. (6). Then comparing the inequality (84) with the "Debye" entropy $S_D(T)$ [Eq. (1)], we finally find

$$S(T) \geqslant \tfrac{1}{2} S_D(T). \tag{85}$$

Thus, we have found a lower limit on the entropy of an arbitrary many-body system which is *half* the "Debye" entropy as defined in terms of the macroscopic compressibility by Eqs. (1) and (2). For a translationally invariant system at least one would expect intuitively that it should be possible to improve the factor $\frac{1}{2}$ to 1. However, this more difficult than it looks at first sight. Suppose that, as in Section 4, Part 1, we sum over the current fluctuations as well as the density fluctuations. Using Eqs. (49) and (50) and dropping, as above, the "transverse" current fluctuations, we find

$$S(T) \geqslant \frac{1}{2} k_B \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \mid \varphi(\mathbf{k})|^2 \beta\hbar c_s k \int_0^\infty \left\{\frac{1}{e^{\alpha s} - 1} - \frac{1}{\alpha s} \ln(1 - e^{-\alpha s})\right\}$$
$$\times (1 + s^2)\, \zeta_N(\mathbf{k}, s)\, ds \qquad (\alpha \equiv \beta\hbar c_s k), \tag{86}$$

where ζ_N is the normalized density correlation function, which obeys the sum rules (81). We have found no way of proving that the right-hand side of (86) is at least equal to $S_D(T)$ without involving some extra assumption about ζ_N. The most general such assumption which will allow a proof that $S(T) \geqslant S_D(T)$ seems to be that $\zeta_N(\mathbf{k}, s)$ is a function only of s, i.e., that $\chi_N''(\mathbf{k}, \omega)$ is a function only of the ratio ω/k in the limit $\mathbf{k}, \omega \to 0$. ("normal scaling"). If this is so, we can do the integral over $\mathbf{k}$ first and using the formulas of the Appendix, get the required

[6] "Independent" have means such that the cross terms in the second of Eqs. (12) vanish (see discussion of that equation).

result. Although the assumption of normal scaling seems to hold for all known translationally invariant models which have a finite compressibility at $T = 0$, we have not found a proof that it must be so for an arbitrary system.

To conclude this section, we notice that if the system is translationally invariant and the density fluctuation spectrum at zero temperature is hydrodynamic, then we can prove the result $S(T) \geqslant S_D(T)$ even without assuming the inequality (45). In fact, when summed over the density and "longitudinal" current fluctuations, this inequality follows from formula (A12) of the Appendix;[7] we do, of course, have to make the extremely weak assumption that the "transverse" contribution to $\Lambda_J(k, T)$ does not actually decrease with increasing T. This is trivially true for superfluid systems with vanishing normal density at $T = 0$.

6. Systems with Shear

It is clear that the inequality (85) cannot be valid in general for a solid, if S_D is defined from (1) and (2) by taking K^{-1} in (2) to be the bulk modulus (i.e., the modulus for *isotropic* compression). To see this, recall that for an ordinary harmonic solid whose elastic constants are restricted only by the requirements of symmetry and stability we can always choose the constants so that the bulk modulus is arbitrarily small, while the velocities of sound remain greater than some fixed finite value. Then an elementary calculation shows that the bulk modulus cannot place a lower limit on the entropy. We shall now show that for an isotropic solid the inequality (85) remains valid provided that we interpret K^{-1} in Eq. (2) as the longitudinal elastic modulus C_{11}.

For simplicity of presentation we first consider the ordinary classical theory of an elastic solid. In this case the elastic strain is described by a vector field $\mathbf{u}'(r)$; we can separate $\mathbf{u}'$ into an irrotational part $\mathbf{u}$ and a residual part, which contributes nothing to the elastic energy since it corresponds to a local rotational displacement. For a general solid with cubic symmetry the energy is specified by three elastic constants C_{11}, C_{12} and C_{44} according to the formula

$$E = \int U(\mathbf{r})\, d\mathbf{r}, \tag{87}$$

$$\begin{aligned} U(\mathbf{r}) = \frac{1}{2} C_{11} &\left[\left(\frac{\partial u_x}{\partial x}\right)^2 + \left(\frac{\partial u_y}{\partial y}\right)^2 + \left(\frac{\partial u_z}{\partial z}\right)^2\right] \\ &+ 2C_{44}\left[\left(\frac{\partial u_y}{\partial z}\right)^2 + \left(\frac{\partial u_z}{\partial x}\right)^2 + \left(\frac{\partial u_x}{\partial y}\right)^2\right] \\ &+ C_{12}\left[\left(\frac{\partial u_y}{\partial y}\right)\left(\frac{\partial u_z}{\partial z}\right) + \left(\frac{\partial u_z}{\partial z}\right)\left(\frac{\partial u_x}{\partial x}\right) + \left(\frac{\partial u_x}{\partial x}\right)\left(\frac{\partial u_y}{\partial y}\right)\right], \end{aligned} \tag{88}$$

[7] It is simplest in this case to work directly from Eq. (38).

or, in other words,

$$U(\mathbf{r}) = \frac{1}{2}\sum_{\mu\nu}(C_{11}\delta_{\mu\nu} + C_{12}(1 - \delta_{\mu\nu}) - 2C_{44}\delta_{\mu\nu})\left(\frac{\partial u_\mu}{\partial x_\mu}\right)\left(\frac{\partial u_\nu}{\partial x_\nu}\right) + \sum_{\mu\nu} C_{44}\left(\frac{\partial u_\mu}{\partial x_\nu}\right)^2. \tag{89}$$

We shall impose the condition that the solid is isotropic; since the only quantities invariant under rotation are

$$\sum_{\mu\nu}\left(\frac{\partial u_\mu}{\partial x_\nu}\right)^2, \qquad \sum_{\mu\nu}\left(\frac{\partial u_\mu}{\partial x_\mu}\right)\left(\frac{\partial u_\nu}{\partial x_\nu}\right) \equiv (\nabla \cdot \mathbf{u})^2 \tag{90}$$

the condition of isotropy implies

$$C_{11} - C_{12} - 2C_{44} = 0 \tag{91}$$

—a condition which can also be found from the isotropy of the phonon spectrum. Hence (89) takes the form

$$U(\mathbf{r}) = (\tfrac{1}{2}C_{11} - C_{44})(\nabla \cdot \mathbf{u})^2 + \sum_{\mu\nu} C_{44}\left(\frac{\partial u_\mu}{\partial x_\nu}\right)^2. \tag{92}$$

Now it follows from the irrotationality condition on **u** and the fact that the displacement at the boundaries is zero[8] that

$$\int d\mathbf{r} \sum_{\mu\nu}\left(\frac{\partial u_\mu}{\partial x_\nu}\right)^2 = \int d\mathbf{r}(\nabla \cdot \mathbf{u})^2. \tag{93}$$

Consequently, the total energy takes the simple form

$$E = \tfrac{1}{2}C_{11}\int (\nabla \cdot \mathbf{u})^2\, d\mathbf{r}. \tag{94}$$

Furthermore, the change in the particle density from its equilibrium value $\delta\rho(\mathbf{r})$ is related to **u** by

$$\delta\rho(\mathbf{r}) = -\nabla \cdot \mathbf{u}(\mathbf{r}) \tag{95}$$

and hence we finally get

$$E = \tfrac{1}{2}C_{11}\int [\delta\rho(\mathbf{r})]^2\, d\mathbf{r}. \tag{96}$$

[8] This may not strictly be true, but the correction term is proportional to the surface area rather than the volume and may therefore be dropped.

Now for the static properties of the total system we need not of course invoke the idea of an elastic continuum; all we need to suppose is that we can define the displacement $\mathbf{u}$ of a given point on the surface of the solid. Then if we consider a homogeneous deformation and write $\Delta_\mu u_\nu$ for the difference in displacement along the ν axis of the faces perpendicular to the μ axis, we have in analogy to (18)

$$\Delta\langle E\rangle \geqslant \tfrac{1}{2}\Omega^{-1}\left\{(C_{11}-2C_{44})\left(\sum_\mu B_{\mu\mu}\right)^2 + 2C_{44}\sum_{\mu\nu} B_{\mu\nu}^2\right\}, \tag{97}$$

where

$$B_{\mu\nu} \equiv \Omega\left(\frac{\Delta_\mu u_\nu}{l}\right). \tag{98}$$

The $B_{\mu\nu}$'s therefore have the right properties to be counted among our set of operators $\hat{\mathscr{A}}_\nu$ in Section 2, and we therefore define them for our subvolumes V_i (taking, where necessary, u_μ to be an average over the appropriate surface) and postulate in analogy to (23)

$$\Delta\langle E\rangle \geqslant \tfrac{1}{2}\sum_i V_i^{-1}\left\{(C_{11}-2C_{44})\left(\sum_\mu B_{\mu\mu}^i\right)^2 + 2C_{44}\sum_{\mu\nu}(B_{\mu\nu}^i)^2\right\}. \tag{99}$$

We could of course add terms involving other independent variables A_ν such as the spin if required.

Now, however, we can follow through an argument exactly analogous to the one developed above for the continuum model, and show that provided the displacement at the walls is neglected we can rewrite (99) as simply

$$\Delta\langle E\rangle \geqslant \tfrac{1}{2}\sum_i V_i^{-1}C_{11}\left(\sum_\mu B_{\mu\mu}^i\right)^2 = \tfrac{1}{2}\sum_i V_i^{-1}C_{11}(\delta N_i)^2, \tag{100}$$

where δN_i is the fluctuation of the number of particles in the i-th subvolume. From here on all the argument of Sections 2–5 goes through provided only that the "susceptibility" χ_N is everywhere replaced by C_{11}^{-1}. [We notice that for $\mathbf{k} \neq 0$ it is indeed C_{11} which appears in the sum rule (73).]

Thus, we finally obtain the result that the inequality (85) is valid also for a system with finite shear modulus, provided that the quantity S_D is defined from (1) and (2) with $K = C_{11}^{-1}$. In summary, we have proved (given our basic assumptions about the fluctuations of large subvolumes) that the entropy of an arbitrary one-component many-body system, solid or liquid, is at least half what we would calculate by assuming the existence in it of longitudinal phonons whose speed is determined by the appropriate macroscopic compressibility.

As an aside, it is worth mentioning that we have so far been unable to generalize the above results to the case of a multicomponent system. The difficulty here is that the usual bulk modulus is defined in terms of the change in energy with volume at constant relative concentration of the components; however, if large subvolumes are subjected to rarefaction and compression it may be energetically advantageous to them to change the relative concentration too. If therefore we wish to obtain an inequality in terms of the usual bulk modulus, it is essential to consider the effect of concentration fluctuations as well as those of the total density, and when this is done it is not at all clear whether we can prove Eq. (85).

7. Conclusion

In this paper we have demonstrated the following results for an arbitrary isotropic one-component system in the limit $V \to \infty$ then $T \to 0$, whether or not it has a finite shear modulus:

(1) Given our fundamental assumption (23) about the fluctuations of large subvolumes, the entropy is related to the correlation functions of locally conserved quantities A_ν by the inequality (40).

(2) With the additional very weak assumption (45), a lower limit (42) can be found for the entropy in terms of the zero-temperature correlation functions alone.

(3) Provided only that the relevant static susceptibility tends to a finite limit as $\mathbf{k} \to 0$, each independent locally conserved variable gives rise to a contribution to the entropy which is at least a constant times T^3. In particular

(4) The entropy of an arbitrary large system must be at least one-half of the entropy which it would have if it could sustain longitudinal phonons whose velocity is determined by the usual hydrodynamic formula. If the system is translation invariant and the correlation functions obey "normal scaling" the factor of one half in this statement can be canceled.

At first sight these results may seem somewhat unsurprising. However, to the best of the author's knowledge they are the first *lower* limits on the entropy (and hance on the specific heat) which have been derived independently of a microscopic model. They may therefore be used to check the consistency of specific-heat measurements with other types of experimental data. As a practical example, it should be possible to test whether data on the low-temperature specific heat of a given amorphous antiferromagnetic is compatible with susceptibility measurements, even though no very good microscopic model is yet available for such a system.

Finally, we notice that the result (42) with (43) may be put in a rather intuitively appealing form. For, if we define a weighted normalized spectral density $\psi_\nu''(\mathbf{k}, \omega)$ by [cf. Eq. (36)]

$$\begin{aligned}\psi_\nu''(\mathbf{k}, \omega) &\equiv \frac{\chi_\nu''(\mathbf{k}, \omega : 0)}{\omega} \times \left(\int_0^\infty \frac{\chi_\nu''(\mathbf{k}, \omega : 0)\, d\omega}{\omega} \right)^{-1} \\ &= \frac{2}{\pi \chi_\nu} \chi_\nu''(\mathbf{k}, \omega : 0)/\omega, \end{aligned} \tag{101}$$

then the expression $Q_\nu(\mathbf{k}, T)$, which is the contribution to the entropy from a fluctuation of wave vector $\mathbf{k}$, takes the simple form

$$Q_\nu(\mathbf{k}, T) = \tfrac{1}{2} k_B \int_0^\infty [(n(\omega) + 1) \ln(n(\omega) + 1) - n(\omega) \ln n(\omega)]\, \psi_\nu''(\mathbf{k}, \omega)\, d\omega, \tag{102}$$

where $n(\omega)$ is the usual Bose distribution function.

Appendix

We shall demonstrate some inequalities needed in Section 5. We consider a function $\zeta(s) \geqslant 0$ defined for $0 \leqslant s < \infty$ and obeying the sum rules

$$\int_0^\infty s\zeta(s)\, ds = \int_0^\infty s^{-1}\zeta(s)\, ds = 1. \tag{A.1}$$

If we define those moments which are finite by

$$K_n \equiv \int_0^\infty s^n \zeta(s)\, ds, \tag{A.2}$$

then it obviously follows that

$$K_{n+1} + K_{n-1} - 2K_n \geqslant 0, \tag{A.3}$$

and so in view of (A.1) we get by iteration of (A.3)

$$K_0 \leqslant 1 \leqslant K_2 \leqslant K_3, \ldots, \tag{A.4}$$

$$K_0 \leqslant 1 \leqslant K_{-2} \leqslant K_{-3}, \ldots . \tag{A.5}$$

Consider now the quantity[9]

$$I(\alpha) \equiv \int_0^\infty \left\{ \frac{1}{e^{\alpha s} - 1} - \frac{1}{\alpha s} \ln(1 - e^{-\alpha s}) \right\} \zeta(s)\, ds. \tag{A.6}$$

[9] The essentials of this proof are due to Dr. J. Plaskett.

We write this in the form

$$I(\alpha) = \int_0^\infty s^{-1}\zeta(s) f_\alpha(s)\, ds, \tag{A.7}$$

$$f_\alpha(s) \equiv \frac{s}{e^{\alpha s} - 1} - \frac{1}{\alpha} \ln(1 - e^{-\alpha s}). \tag{A.8}$$

Now $f(s)$ is concave upwards, and hence

$$f_\alpha(s) \geqslant f_\alpha(1) + (s - 1) f_\alpha'(1). \tag{A.9}$$

Therefore

$$\begin{aligned} I(\alpha) &\geqslant f_\alpha(1) \int_0^\infty s^{-1}\zeta(s)\, ds + f_\alpha'(1) \int_0^\infty (1 - s^{-1})\, \zeta(s)\, ds \\ &= f_\alpha(1) + f_\alpha'(1)(K_0 - 1). \end{aligned} \tag{A.10}$$

But $f_\alpha'(1)$ is always negative, and so using (A.4) we conclude

$$I(\alpha) \geqslant f_\alpha(1) \equiv \frac{1}{e^\alpha - 1} - \frac{1}{\alpha} \ln(1 - e^{-\alpha}) \tag{A.11}$$

which is the result needed for the proof of (82) in the text.

We can also demonstrate the inequality

$$J(\alpha) \equiv \int_0^\infty \coth(\alpha s/2)\, \zeta(s)(1 + s^2)\, ds \geqslant 2 \coth(\alpha/2). \tag{A.12}$$

The proof is similar to the above one: we write J in the form

$$J(\alpha) = \int_0^\infty s^{-1}(1 + s^2)\, g_\alpha(s)\, ds, \tag{A.13}$$

$$g_\alpha(s) \equiv s \coth(\alpha s/2). \tag{A.14}$$

The function $g_\alpha(s)$ is concave upwards, but now $g_\alpha'(s) > 0$. On the other hand, we have from (A.2)–(A.5)

$$\int_0^\infty s^{-1}(1 + s^2)(s - 1)\, \zeta(s)\, ds \geqslant 0, \tag{A.15}$$

so that the result (A.12) follows.

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