CONTRIBUTION TO THE THEORY OF LIGHT SCATTERING NEAR THE SECOND-ORDER PHASE-TRANSITION POINTS

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Formulas for the intensity of scattered light near transition points have been derived on the basis of the exact Gibbs expression for fluctuations of the parameter characterizing second-order phase transition. These formulas are employed to estimate the minimum width of the temperature region near the transition point at which the usual macroscopic theory of phase transitions of second order becomes meaningless. The formulas are also used to substantiate the validity of calculations of the scattered light intensity which are presented in reference 1.

In the work of Ginzburg and the author on the calculation of the intensity of fluctuation light scattering in the case of second-order phase transitions, use was made of Boltzmann's principle. In this case the scattering intensity was divided into two parts. One of these, which is connected with fluctuations of second order, gives the principal part of the observed scattering effect. Calculation of this part for the accepted thermodynamic potential leaves no question, since the expression for the fluctuation obtained with the help of Boltzmann's principle coincides with the exact Gibbs expressions (see reference 2). The second part of the scattering in connected with fluctuations of fourth order, and calculation of its intensity requires a foundation which we shall delineate below.

As is well known, the intensity of light scattering from fluctuations of the dielectric constant is given by the formula

$$I = \frac{V^2}{(2\pi)^2} \left| \Delta \epsilon \right|^2 \sin^2 \varphi, \quad q = \frac{4\pi n}{\lambda_0} \sin \varphi. \quad (1)$$

where $V$ is the volume in which the scattering takes place, $\lambda_0$ is the wavelength in a vacuum, $\varphi$ is the angle between the electric vector of the incident wave and the direction of observation, $\theta$ is the scattering angle, and

$$\Delta \epsilon = \frac{1}{V} \int \Delta \epsilon \sin^2 \varphi \, d\varphi. \quad (2)$$

Close to second order phase transition points, the fluctuations of $\epsilon$ are produced by fluctuations of the characteristic parameter $\eta$ (see references 5 and 1), while, neglecting optical anisotropy,

$$\Delta \epsilon = a \Delta \eta^4 = 2a_0 \Delta \eta + a \Delta \eta^2. \quad (3)$$

The dependence (3) is obtained from the same considerations as the dependence on $\eta$ of the thermodynamic potential $F$ (see reference 6). We note that in the complete expression for the quadratic fluctuations of $\epsilon$ terms appear that are connected with fluctuations of other thermodynamic variables, and also with mixed fluctuations of $\eta$ and other variables. However, close to the transition point, where the fluctuations of $\eta$ are anomalously large, one can neglect all other fluctuations and mixing terms in comparison with the fluctuations of $\eta$. This is the more valid in that the smallness of the mixing terms has been shown in reference 1 by direct estimation.

Expanding $\Delta \eta$ in a Fourier series:

$$\Delta \eta = \sum_k A_k e^{ik\cdot r} k = i \frac{2n}{L} n_x + j \frac{2n}{L} n_y + k \frac{2n}{L} n_z \quad (4)$$

$(n_x, n_y, n_z, n_z)$ are integers) and making use of (3), we obtain

$$|\Delta \epsilon|^2 = |\Delta \epsilon| \Delta \epsilon = 4a^2_0 \sum_k A_k A_{-k} + 2a^2_0 \sum_k A_k A_{-k} A_k + a^2 \sum_{k,k'} A_k A_{-k} A_k A_{-k}. \quad (5)$$

Expressions for the mean square of $\Delta \epsilon$ were obtained in reference 1 with the help of Boltzmann's principle. However, as is well known (see reference 2), the Boltzmann principle is not always valid; in particular, at the transition point, the possibility of its application is in considerable doubt. Nonetheless, the expression for the mean square fluctuation is an exact Gibbs expression for which it is impossible to speak of fluctuations of the higher orders. Therefore, additional justification is required for the calculation carried out in reference 1 where, in the calculation of the intensity of
the scattering, use was made of Eqs. (1) and (5), and averaging was carried out on the basis of the Boltzmann principle. This justification will consist in the obtaining of an exact expression for the intensity of scattered light and a comparison of it with the expressions of reference 1 obtained with the help of the Boltzmann principle.

1. The method of obtaining the exact Gibbs expression for the fluctuations of any order is given in reference 7. However, the concept of the thermodynamic potential of nonequilibrium states, which is essential in our consideration, was not employed there. Therefore, we shall give a brief derivation of these formulas by the method employed in reference 2, to prove that the Boltzmann expression for the mean-square fluctuation is the exact Gibbs expression. For the derivation it is necessary to introduce the concept of the thermodynamic potential of nonequilibrium states. Let there be a certain parameter characterizing the lack of equilibrium, \( \eta = \hat{\eta}(X) \), where \( X \) is the aggregate of mechanical variables of the system under consideration. The state with \( \eta \neq \eta_0 \) is brought into equilibrium with the inclusion of the external field with potential energy \( U \), so that this state becomes an equilibrium one. Then

\[
\eta = \int \hat{\eta}(X) \exp \left\{ \frac{\Psi - H(X) - U}{kT} \right\} dX. \tag{6}
\]

Here \( H(X) \) is the Hamiltonian of the system, \( \Psi \) is the thermodynamic potential of the system located in the field. The single-valuedness of the thermodynamic potential of the nonequilibrium state is achieved by laying an additional condition on \( U \) (for details see reference 2) which is satisfied for \( U = a\hat{\eta}(X) \), \( a \) is some constant.

\( \Psi(a) \) is the thermodynamic potential of a system located in the external field \( U = a\hat{\eta}(X) \), and is determined by the relation

\[
\Psi(a) = -kT \ln \int \exp \left\{ - \frac{H(X) - a\hat{\eta}(X)}{kT} \right\} dX. \tag{7}
\]

It follows from (7) that

\[
\eta = \partial \Psi / \partial a. \tag{8}
\]

The thermodynamic potential of a nonequilibrium state corresponding to the value \( \eta \) is determined by the relation

\[
F(\eta) = \Psi(a) - U = \Psi(a) - a\partial \Psi / \partial a. \tag{9}
\]

Differentiating (6) after first setting \( U = a\hat{\eta}(X) \), taking (8) into account and then setting \( a = 0 \), we obtain

\[
(\Delta\eta)^2 = kT\Psi'_0 = kT / F_0; \tag{10}
\]

\[
(\Delta\eta)^3 = (kT)^3\Psi''_0 = -(kT)^3F''_0 / (F_0)^3; \tag{11}
\]

Here the primes denote differentiation of \( \Psi \) and \( F \) by \( \alpha \) and \( \eta \), respectively, the index 0 signifies that the derivatives are taken at \( a = 0 \) and \( \eta = \eta_0 \). The derivatives of \( \Psi \) with respect to \( \eta \) are expressed by the derivatives of \( F \) with respect to \( \eta \) by means of (8) and (9).

In a similar way, equations are obtained for the fluctuations of many variables. We now introduce the following necessary expressions:

\[
\Delta\eta = \Delta\eta(a) = kT \langle F_{ik}^{-1} \rangle; \tag{12}
\]

\[
\Delta\eta \Delta\eta \Delta\eta = (kT)^3 \langle \partial F_{ik}^{-1} / \partial \eta \rangle \langle F_{il}^{-1} \rangle; \tag{13}
\]

\[
\Delta\eta \Delta\eta \Delta\eta = (kT)^3 \langle \partial F_{ik}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle + \langle kT \rangle \langle \partial F_{ik}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle + \langle kT \rangle \langle \partial F_{ik}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle \langle \partial F_{im}^{-1} / \partial \eta \rangle. \tag{14}
\]

Here \( F_{ik}^{-1} \) is an element of the matrix inverse to the matrix with elements \( F_{ik} = \partial^2 F / \partial \eta_i \partial \eta_k \); the brackets \( \langle \ldots \rangle \) denote that the derivatives are taken at the equilibrium values of all parameters.

2. In the calculation of the intensity of light scattering in reference 1, the expansion

\[
F(P, T, \eta) = F_0(P, T) + \alpha(P, T) \eta^4 + \frac{\beta(P, T)}{2} \eta^4 + \frac{\gamma(P, T)}{6} \eta^6 + \delta(\text{grad} \eta)^2, \tag{16}
\]

was employed as the thermodynamic potential of the nonequilibrium states. This expression is fundamental to the macroscopic theory of secondary-order phase transitions. In this case, it is assumed that \( \alpha = 0 \) at the transition point, \( \beta = \text{const} \) and \( \gamma = \text{const} \), far from the critical Curie point, and \( \gamma = \text{const} \) close to this point. We shall now exhibit the region close to the transition point in which the expansion (16) becomes invalid if the coefficients \( \alpha, \beta, \gamma \) behave in the manner shown.

It was shown by M. A. Leontovich that the thermodynamic potential of nonequilibrium states [introduced with the aid of (8) and (9)] is a minimum at equilibrium. However, this is not the only property of \( F(\eta) \), inasmuch as the fluctuations of \( \eta \) of different order are expressed by the derivatives of \( F(\eta) \). The requirement of the positivity of fluctuations of even orders represents certain conditions on the derivatives of \( F(\eta) \). Moreover, it is natural to require that the relation (8), for an arbitrary \( \eta \) in the region of values of interest to us, be satisfied for but a single \( a \). In the case in which we are interested, this latter requirement gives nothing new and we make no use of it.
We now write down the necessary equations for the derivatives:

\[ F'_0 = 2x + 3\beta \gamma^0_0 + 5\gamma^2_0 \]  
(17)

\[ F''_0 = 12\beta \gamma^0_0 + 20\gamma^2_0 \]  
(18)

\[ F'''_0 = 12\beta + 60\gamma^2_0 \]  
(19)

We now consider the region of temperatures \( T > \Theta \), where \( \Theta \) is the transition temperature. Here \( \eta_0 = 0 \), \( F'_0 = 0 \), \( F''_0 = 2\alpha \). The condition of the positiveness of the fluctuations of even order yields

\[ \alpha^2 V / kT > \beta. \]  
(20)

The volume appears in this relation, since it has been taken into consideration that \( F(P, T, \eta) \) is the thermodynamic potential per unit volume.

Similarly, making use of the equation for the fluctuations of sixth order, we can obtain a condition for \( \gamma \):

\[ \alpha^2 V^3 / (kT)^3 > \gamma. \]  
(21)

For \( T < \Theta \), when \( F''_0 \neq 0 \), the condition of positiveness of the fluctuations is satisfied automatically. However, there is another circumstance here which does not allow use to be made of the expansion (16) as close to the transition point as is desired. The fact is that for \( T < \Theta \), Eq. (16) is the nonequilibrium thermodynamic potential of a system with two equilibrium positions \( \eta_0 \) and \( -\eta_0 \), where

\[ \gamma^0_i = (-\beta + V\beta^2 - 2\alpha\gamma) / \gamma. \]  
(22)

To speak of equilibrium positions makes sense, naturally, only when

\[ (\Delta \gamma)^2 < \gamma^2, \]  
(23)

where \( \Delta \gamma \) is the fluctuation about one of the equilibrium positions. In the opposite case, one cannot generally speak of equilibrium, and the possibility of determining the thermodynamic potential is lost, not to speak of the fact that the usual method of calculation of fluctuations loses its meaning when one considers that the fluctuations take place about a mean position.

Setting \( \beta^2 >> 2\alpha\gamma \), which is satisfied in particular for transitions that are far from the critical Curie point, and taking (17) and (10) into account, we get from (23)

\[ 4\alpha^2 V / kT > \beta. \]  
(24)

Thus we can consider that the condition (20) should be satisfied above and below the transition points.

We further note that in (20) and (24) the sign \( > \) should actually appear, and not \( \geq \). For (24), this does not require any explanation. For (20), we see from (10) and (12) that \( (\Delta \gamma)^2 \) initially increases with increasing \( (\Delta \gamma)^4 \) (with decreasing \( F'/T \)), and then decreases. It is natural to assume that an increase in \( (\Delta \gamma)^4 \) corresponds in reality only to an increase in \( (\Delta \gamma)^2 \), which is satisfied for the stronger inequality.

Conditions (20) and (24) refer to the spatially homogeneous case, and do not take correlations into account. If by \( V \) we understand the total volume of the body, then these conditions are satisfied everywhere with the exception of an extremely narrow region in the vicinity of the transition point. But in consideration of fluctuations in small volumes, we must consider correlations, that is we must use not (20) and (24), but conditions obtained by means of successive consideration of spatial inhomogeneity and correlations. In this case, we must take the fluctuations of the Fourier components of \( \eta \) into account and consider the gradient term in (16). Conditions (20) and (24) remain here also, as do conditions on the fluctuations of the zero Fourier components, while \( V \) denotes the total volume of the body. However, in this case, there are additional positive definite quantities, for example the intensity of the scattered light \( I \), the condition of positiveness of which represents certain conditions on \( F(\eta) \), in particular on the quantity \( \delta \). We shall give further details on this matter below after obtaining exact formulas for \( I \).

3. We now set about to obtain exact expressions for \( I \). We denote the intensity of scattering associated with the first term of the right hand side of (5) by \( I_1 \), that associated with the second and third terms by \( I_2 \), and that associated with the fourth term by \( I_4 \). As has already been shown, the value of \( I_2 \) computed with the aid of Boltzmann's principle coincides with the exact value; therefore it is necessary to compute only \( I_3 \) and \( I_4 \). Making use of (4) and (16), we obtain

\[ \langle F_{1,2} \rangle = V(F'_0 + 2\delta q)\delta q, -q; \]  
(28)

\[ \langle F_{1,2,3} \rangle = V^3\delta q, -q, -q; \]  
(29)

\[ \langle F_{1,2,3,4} \rangle = V^2\delta q, -q, -q, -q. \]  
(30)

Here \( F_1,...,n \) denotes the derivative of \( F \) with respect to \( A_{q_1} \cdots A_{q_n} \), \( \delta q_1, q_2 \) is the Kronecker symbol. To express the right hand side of (14) and (15) in terms of (28) — (30), we renumber the variables \( A_{q_1} \) that is, we renumber the vector \( q \). We carry out the numbering on both sides of zero in such a fashion that if \( q_1 \) and \( q_2 \) have the corresponding numbers \( n_1 \) and \( n_2 \), and \( q_1 = -q_2 \), then \( n_1 = -n_2 \), and conversely. If we denote by \( n \) the total number of vectors with integral coordinates, smaller
in modulus than a certain \( k_{\text{max}} \), then the indices of the matrix \( F_{ik} \) will take on the values from \(-(n - 1)/2\) to \((n - 1)/2\). We can arrive at a matrix with such indices from the ordinary matrix by means of a transformation of the indices \( i' = i - (n + 1)/2, \ k' = k - (n + 1)/2 \). This transformation is possible since \( n + 1 \) is an integer.

It is seen from (28) that the elements in the matrix \(<F_{ik}>\) that are different from zero lie only on the diagonal which is orthogonal to the principle diagonal.

\[
D(<F>) = \prod_{a=-\frac{n-1}{2}}^{\frac{n-1}{2}} <F_{a,-a}>, \quad (31)
\]

\( D(<F>) \) is the determinant of the matrix \(<F_{ik}>>\). As is well known, we have for an element of the inverse matrix

\[
\frac{\partial F_{ik}}{\partial \eta_p} = \frac{\partial F_{ik}^{\text{adj}}}{\partial \eta_p} / D(F), \quad (32)
\]

where \( F_{ik}^{\text{adj}} \) is the adjoint of the matrix \( F_{ik} \) relative to the element \( F_{ki} \). Furthermore,

\[
\langle F_{ik}^{\text{adj}} \rangle = \delta_{i,-k} \prod_{b=-\frac{n-1}{2}}^{\frac{n-1}{2}} \langle F_{b,-b} \rangle, \quad (33)
\]

Here \( \Pi^i \) denotes that \(<F_{b,-b}>\) as a factor runs over all \( b \) except \( b = i \).

Let us first calculate \( I_3 \). In what follows we shall write \( \eta_p \) in place of \( A_q \), where \( p \) is the number of the vector \( q \). We now calculate \(<\partial F_{ik}\rangle / \partial \eta_p>\). Taking (32) into account,

\[
\frac{\partial F_{ik}^{\text{adj}}}{\partial \eta_p} = \frac{1}{D(F)} \frac{\partial F_{ik}^{\text{adj}}}{\partial \eta_p} = \frac{\partial F_{ik}^{\text{adj}}}{\partial \eta_p} / D(F). \quad (35)
\]

Further,

\[
F_{ik}^{\text{adj}} = (-1)^{i+k} \sum_{(i-k+1)\cdots n} (-1)^{i-k+1} \prod_{r=1}^{i-k} (p_r+1) \cdots (n-1), \quad (36)
\]

\([p_1 \cdots p_{i-k-1} p_{i+k+1} \cdots p_n] \) denotes the number of disorders in the permutation of \( p_1 \cdots p_{i-k-1} p_{i+k+1} \cdots p_n \) from the numbers \(- (n + 1)/2 \ldots 1, \ i+1, \ldots (n - 1)/2 \). Summation is carried out over all permutations. We differentiate (36) with respect to \( \eta_p \). On the right hand side there are \( n - 1 \) sums over the permutations. We consider one of such sums:

\[
(-1)^{i+k} \sum_{(i-k+1)\cdots n} (-1)^{i-k+1} \prod_{r=1}^{i-k} (p_r+1) \cdots (n-1), \quad (37)
\]

We now set \( \eta_p = 0 \), that is, we consider the equilibrium values for the derivatives. We shall show that for \( a = -i \), the expression (37) at equilibrium values of \( \eta_p \) differs from zero only for \( i = -k \). In fact, if \( i = -k \), for equilibrium values of its derivatives, the product (37) contains a term of the form \(<F_{-i-,p-i}>\) which differs from zero only for \( p_{-i} = i \), but this equality is not possible. It is easy to see that in such a case \( p_{-i} = -a \). It follows from (29) that in this case \( p = 0 \). If \( a = -i \) (this is possible only for \( i = -k \)) then, by an argument similar to the foregoing, \( \eta_p = -k \). By virtue of (29) \( q_l + q_k = q_p \), where \( q_l \) is the vector corresponding to the number \( l \).

For \( a = -i \) in the sum (37), considered at equilibrium, only one component is different from zero with \( p_{-i} = -a \).

Carrying out similar considerations for

\[
D(F) = \sum (-1)^{\frac{j-j-1}{2}} F_{-\frac{(n-1)}{2}, p_1} \cdots F_{\frac{(n-1)}{2}, p_n}, \quad (39)
\]

we obtain

\[
\frac{\partial D(F)}{\partial \eta_p} = \sum_{a=-\frac{n-1}{2}}^{\frac{n-1}{2}} \frac{1}{D(F)} <\partial F_{ik}^{\text{adj}} / \partial \eta_p > D(F) / <\partial F_{ik}^{\text{adj}} / \partial \eta_p >, \quad (40)
\]

From (35) and from (38) - (40) we obtain

\[
\langle \partial F_{ik}^{\text{adj}} / \partial \eta_p > = -VF_{a,-a}^{\text{adj}} <F_{ik}^{\text{adj}} / \partial \eta_p > D(F) / <\partial F_{ik}^{\text{adj}} / \partial \eta_p >, \quad (41)
\]

For \( I_3 \) we have

\[
I_3 = C 2a^3 \sum_k A_{q_k, q_{-q-k}} A_{q_{-q-k} A_{q_{-q-k}}}, \quad (42)
\]

where

\[
C = (V / 4 \pi)^2 (2 \pi / \lambda_0)^4 \sin^4 \varphi. \quad (43)
\]

We now substitute (41) in (14) and (42) and obtain
\[ I_3 = -C_4 a^2 \sum_k \langle F_{q,-q} \rangle \langle F_{k,-k} \rangle \langle F_{q-k,k-q} \rangle \]
\[ = -\frac{C_4 a^2 \delta_{k0}}{\sqrt{k}} \sum_k \langle F_{q,-q} \rangle \langle F_{k,-k} \rangle \langle F_{q-k,k-q} \rangle \]
\[ \times \langle F_{q+k} + 2k^2 \rangle. \] (43)

Here we assume \( \gamma = 0 \), i.e., we consider a transition that is far from the critical Curie point. Changing now from summation to integration, we have
\[ I_4 \]

\[ = \frac{V}{(4\pi)^n} \sum_{k,k'} A_{q-k} A_{q-k'} \cdot \]
\[ \times \langle F_{q-k,-k} \rangle \langle F_{k',k} \rangle \langle F_{-q-k',k+q} \rangle \]
\[ \times \langle F_{q-k',k-q} \rangle \langle F_{k',k-q} \rangle \langle F_{q-k',k+q} \rangle \]
\[ \times 2 \sum_{k,k'} \langle F_{q-k,-k} \rangle \langle F_{k',k-q} \rangle \]. (46)

On the right hand side of (46) we omit terms that vanish upon subsequent integration over \( k \).

We denote the scattering connected with the first term on the right hand side of (46) by \( I_{41} \), with the second, by \( I_{42} \). The scattering connected with the latter term is \( I_4 \), computed with the aid of Boltzmann's principle. We denote it by \( I_4 \). It was obtained in reference 1, whence
\[ I_4 = \frac{V}{(4\pi)^n} \sum_{k,k'} A_{q-k} A_{q-k'} \langle F_{q-k,-k} \rangle \langle F_{k',k} \rangle \langle F_{-q-k',k+q} \rangle \]
\[ \times \langle F_{q-k',k-q} \rangle \langle F_{k',k-q} \rangle \langle F_{q-k',k+q} \rangle \]
\[ \times 2 \sum_{k,k'} \langle F_{q-k,-k} \rangle \langle F_{k',k-q} \rangle \]. (47)

In reference 1, \( I_4 \) was written as \( I_2 \). Transforming (46) from summation to integration over \( k \), we obtain for \( I_{41} \) and \( I_{42} \):
\[ I_{41} = \frac{V}{(4\pi)^n} \sum_{k,k'} A_{q-k} A_{q-k'} \langle F_{q-k,-k} \rangle \langle F_{k',k} \rangle \langle F_{-q-k',k+q} \rangle \]
\[ \times \langle F_{q-k',k-q} \rangle \langle F_{k',k-q} \rangle \langle F_{q-k',k+q} \rangle \]
\[ \times 2 \sum_{k,k'} \langle F_{q-k,-k} \rangle \langle F_{k',k-q} \rangle \]. (48)

We also cite an expression for \( I_2 \) obtained in reference 1:
\[ I_2 = \frac{V}{(4\pi)^n} \sum_{k,k'} A_{q-k} A_{q-k'} \langle F_{q-k,-k} \rangle \langle F_{k',k} \rangle \langle F_{-q-k',k+q} \rangle \]
\[ \times \langle F_{q-k',k-q} \rangle \langle F_{k',k-q} \rangle \langle F_{q-k',k+q} \rangle \]
\[ \times 2 \sum_{k,k'} \langle F_{q-k,-k} \rangle \langle F_{k',k-q} \rangle \]. (49)

Here and throughout we consider only regions far from the critical Curie point.

We now compare the exact expression for the total intensity of scattered light
\[ I = I_2 + I_4 + I_3 + I_{41} + I_{42} \]

with the intensity \( I^0 = I_0 + I_1 \), computed by Boltzmann's principle. For \( T > \Theta \), we obtain
\[ I = I_2 = I_4 = 0, \quad I / I^0 \]
\[ = 1 + I_{41} / I_0 = 1 - \frac{3\beta kTS}{2}. \] (51)

The condition for the validity of the calculation carried out in reference 1, as also the condition for the validity of the expansion (16), takes the form
\[ 3\beta kTS \ll 1. \] (52)

For each given substance, \( S \) is a function of \( T \) and \( q \). For fixed \( T \), the inequality (52) must be satisfied for any \( q \), since we are discussing the positiveness of \( I \) or, irrespective of the physical meaning of \( I \), the positiveness of some positive definite combination of Fourier components of \( \Delta n \). Thus, fixing \( T \), we must prove whether (52) is satisfied for a \( q \) which brings about a maximum for \( S \). It is easy to see that for fixed \( T \), \( S \) is maximum for \( q = 0 \). In this case
\[ S = 1 / 16\pi^2 \frac{V}{F_{q} / 2}. \] (53)

Further, taking it into account that \( \delta = \alpha_\Theta \alpha / 2 \) (the discontinuity in the heat capacity at the transition \( \Delta c = \alpha_\Theta / \beta \) and \( F_\Theta = 2\alpha_\Theta (T - \Theta) \) for \( T > \Theta \)), we write (52) in the form
\[ T - \Theta > 3(16 \pi)^2 \theta (k / \Delta c)^3. \] (54)

For the \( \lambda \)-transition in quartz we have \( \Delta c = 4 \times 10^7 \) erg/deg-cm\(^3\) (reference 8), \( \Theta \sim 10^3 \). Setting \( d \sim 10^{-7} \), we obtain from (54)
\[ T - \Theta > 10^{-4} \rightarrow 10^{-3}. \] (55)

In this region of temperatures above the transition point the expansion (16) does not lead to a contradiction and the exact expressions are insignificantly different from the expressions obtained with the help of Boltzmann's principle.

For the \( \lambda \)-transition in liquid helium, \( \Delta c \sim 10^7 \) erg/deg-cm\(^3\), \( d \sim 2 \times 10^{-9} \) (see references 9, 1), \( \Theta \sim 1 \). Substituting these values in (54) we obtain
\[ T - \Theta > 10^{-2}. \] (56)

For \( T < \Theta \) such estimates do not present any fundamental difficulty, although there are rather tedious. As can be shown, the condition (54) holds with accuracy up to an insignificant numerical factor.

We see in total that the conditions for applica-
bility of the calculations reduce to the inequality (52). If it is not satisfied, use of the expansion (16) is not valid. If the inequality (54) is satisfied, then the results obtained in reference 1 remain valid both for scattering on fluctuations of second order and also for scattering of fluctuations of fourth order.

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