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Problems Related to Heat Conduction in Solids and Liquids

(Received Sept. 15, 1955)

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Abstract

As a continuation of the investigation on the thermal conductivity of solids and liquids, several problems are discussed in this paper. Mixtures of two pure organic liquids have excess thermal resistance over the mean value of those of the components, as has been shown by Riedel experimentally. This is shown to be primarily due to the mass difference between the component molecules. Secondly, it is pointed out that an isotope effect resulting from the mass difference among isotopic atoms plays a role in the restriction of the heat conduction in crystals at very low temperatures, which has been overlooked until now. Finally, the anharmonicity of vibration in solids which constitutes the fundamental mechanism for the establishment of equilibrium among the lattice phonons as well as for the finiteness of the conductivity contributes to the dissipation of the energy of any forced vibration as heat. This effect is estimated numerically and expressed in terms of the thermal conductivity and other physical properties, but it is found its influence is rather small in technically attainable frequencies.

I. Introduction

Previously¹⁾ I described the results of a theoretical investigation on the thermal conductivity of solids and have given a formula by which the conductivity can be expressed in terms of known physical constants. This calculation was found to be applicable to liquids as well as solids, in coincidence with the current picture of liquids as having a quasi-crystalline structure. In this paper are given discussions on several topics related to the heat conduction phenomenon, the principle of the calculation being based on the idea of the previous paper. They are: 1) thermal conductivity of liquid mixtures, 2) effects of the presence of different isotopic atoms in crystals on the low temperature conductivity and 3) that part of the internal friction of solids which is related to the anharmonicity of the vibrations in solids.

II. Liquid mixtures

The structure of liquids is more similar to that of crystalline solids than to

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that of gases. The thermal conductivity of pure liquids was calculated in the foregoing paper on the approximation which makes use of this similarity and the results were shown to agree with the experimental results fairly accurately. In this chapter the conductivity is calculated on the same basis for mixtures of different liquids. It is shown that there arises some amount of excess resistance beyond the normal resistance calculable theoretically from the apparent properties of each mixture regarded as a pure liquid. The excess resistance owes its origin to the scattering of thermal elastic waves or phonons by the individual molecules with masses and other physical quantities different from one species to another, which does not appear in cases of pure liquids.

In the foregoing paper the conductivity was calculated on the approximation that the phonons contained in some volume element remain at any instant in a certain distribution which is the most probable one among those having a given amount of energy density and a definite momentum density p which is related to the energy flow I as, $I=q^2p$, where q is the sound velocity. This approximation means that the collisions without the change of the total momentum occur far more frequently than the other type, which is accompanied by the momentum change, namely the Umklapp collisions, characterized by the intervention of Bragg reflections by the lattice periodicity and as a result the most probable distribution of the phonon system is attained quickly. By this way of treatment the distribution of the phonon system was uniquely determined at any value of the temperature and the temperature gradient. The expression for the conductivity K is thus,

$$K=3^{-1}C_vq^2\tau, \quad (1)$$

where C_v is the heat content of unit volume (we disregard the contribution from the intramolecular vibrations so that C_v represents the heat content for the intermolecular vibrations only), and τ is the relaxation time for the establishment in the absence of the temperature gradient of the Bose distribution. The calculation of the relaxation time has led to the following formula for the conductivity,

$$K=Cqa(E/V)T^{-1}, \quad (2)$$

where a is the lattice constant of the solid or liquid in question, in the latter case of which molecules are assumed to be located on the sites of a closed-packing lattice, E/V is the cohesive energy per unit volume and T is the temperature. The numerical constant C was calculated to be of the order of about 10^{-1} and the experiments show that it is about 0.05 for ionic crystals having the NaCl type lattice and is about 0.12 for a number of organic liquids. The thermal resistance which is the reciprocal of K in the form of (2) may be called nonlinearity resistance or ordinary resistance since the nonlinearity of the vibration causes the collisions of the phonons in this case.

For a liquid mixture, two mechanisms of collision should be considered which

prevent the free flow of the phonons: the one is the above-mentioned scattering by the mutual collision which is the cause of the ordinary resistance, and the other is the one by the randomly distributed molecules resulting in the excess resistance. In the above approximation that the phonon system remains at any instant in the most probable distribution, these two mechanisms can be considered to act independently, so that the scattering rate as a whole, τ^{-1} , is simply the sum of each rate.

$$\tau^{-1} = \tau^{-1}_{ordinary} + \tau^{-1}_{excess} . \quad (3)$$

Then the excess thermal resistance W_e is

$$W_e = (3/C_v q^2) \tau^{-1}_{excess} , \quad (4)$$

whereas the ordinary resistance retains its original form, the physical constants appearing in (2) changing with composition.

We take up first the ordinary resistance W_o and consider again that the molecules are arranged on the sites of a closed-packing lattice which does not change its structure at any composition though of course the lattice constant should vary. The molecules of the different species are distributed randomly on the lattice sites just as so in substitutional alloys. The realization of this state of affairs necessitates that the molecules of different kinds do not differ much from each other in their sizes and shapes, which means also that the mixtures are nearly ideal solutions. For the sake of comparison with the experimental results, the case of two components will be considered here.

Under these conditions, the sound velocity q and the lattice constant a are nearly linear functions of the molar content of one species in the mixture. Specifically for the former quantity, a number of measurements have shown that this is almost true for many mixtures of organic liquids except those cases where the components differ from each other greatly in the physical properties. Since the cohesive energy per unit volume E/V is also dependent on the composition in the manner analogous to the above quantities, the thermal resistance varies approximately linearly with the molar content between the two values of the conductivity of the components. In that connection it should be noted that the thermal conductivity of organic liquids does not differ much from one to another.

Nextly we have to calculate the scattering rate due to the random local fluctuation of the density and of other properties. Among the several types of local fluctuations, that of the density (molecular mass divided by the molecular volume) seems to exceed that of the compressibility (spring constant between adjacent molecules, which is intimately related to the intermolecular potential) in most cases because the heat of vaporization per mol does not differ greatly among the common organic liquids. The effect of the difference of the molecular size

and of the shape which will result in the disturbance of the lattice structure is not considered here.

We take a bulk liquid of volume V which is held at a uniform temperature T . If there are N molecules contained, the number of vibrational modes is $3N$. Since the distribution of the molecules on the lattice sites is random, the way in which each elastic wave, which is regarded to be progressive, is scattered can be determined by the consideration of the scattering by a single molecule supposed to be immersed in a liquid which has uniform properties throughout.

The collision of a thermal wave against a molecule having different density from the surroundings in which it is embedded may in most cases not be regarded as a perturbation process, since the density differs greatly from that of the surroundings frequently, and sometimes it would be better to treat it as a collision against a rigid obstacle. Here we adopt the well-known scattering formula of Lord Rayleigh which permits the treatment by the differential scattering cross-section $s(\theta, \phi)$.

We take the case in which the momentum of the system is directed towards the positive x -axis. Let there be n_σ phonons in the normal mode which has the wave number vector $\vec{\sigma}$ and is propagating in the direction of that vector at an angle θ against the x -axis. The number of phonons belonging to this mode which pass a unit cross-section per unit time is therefore $n_\sigma q/V$, and that of phonons scattered due to the collision into a small solid angle $d\omega'$ per unit time is $n_\sigma q s d\omega'/V$.

The rate of the momentum decrease in the x -direction due to this process is, since each phonon carries momentum $\hbar\vec{\sigma}$,*

$$V^{-1}n_\sigma \hbar \sigma q s (\cos \theta - \cos \theta') d\omega', \quad (5)$$

where θ' is the angle between the scattering direction and the x -axis.

If the isotropicity of the scattering is assumed for brevity, the integration of the above expression over the whole solid angle gives,

$$(\dot{P})_\sigma = -4\pi V^{-1}n_\sigma \hbar \sigma q s \cos \theta. \quad (6)$$

Here P is the total momentum of the system and is equal to pV . The value of n_σ was calculated in the previous paper and is $(kT/\hbar\omega)(1+3qp \cos \theta/2C_v T)$ at high temperatures.

The summation of (6) over the all modes gives the total rate of the momentum decrease which is replaced by the integral,

$$3V(2\pi)^{-3} \int \sigma^2 2\pi \sin \theta (\text{Integrand}) d\sigma d\theta,$$

*In this paper \hbar stands for the Planck's constant divided by 2π

where the factor 3 means that there are three modes of independent directions of the polarization vector belonging to the same wave vector.

Then,

$$\dot{P} = -(3kqP/\pi VC_v) \int_0^{\sigma_0} \sigma^2 s d\sigma, \quad (7)$$

The functional relationship of the differential cross-section with σ is not clear at the shorter wavelengths or at large value of σ whereas that at longer wavelengths or at small values of σ should be represented by $s = Z\sigma^4$, where Z is a constant. For convenience we assume the latter relation to hold up to the shortest wavelengths or the largest value of σ , designated by σ_0 . This assumption may result in the too high values of the thermal resistance.

When there are m such targets being distributed randomly, m being taken to be small compared to the total number of molecules in the first stage, the relaxation time for the dissipation of the momentum is given by

$$\tau^{-1} = 3kqZ\sigma_0^7 m / 7\pi VC_v. \quad (8)$$

The momentum deprived from the phonon system is changed to the force upon the targets which in turn acts upon the whole lattice, since we have considered these targets being fixed on their respective lattice sites.

From (4) and (8) the excess resistance is expressed as

$$W_e = (3^2/7\pi)kZ\sigma_0^7 m / C_v^2 qV.$$

As the heat content at high temperatures is $3Nk/V$, we get,

$$W_e \simeq 600(N/V)^{1/3} Zm/kqV. \quad (9)$$

Here we have taken σ_0 to be equal to $2\pi(3N/4\pi V)^{1/3}$.

Now according to the calculation on the scattering of sound waves by a gaseous obstacle the differential cross-section is

$$s = (\pi v / \lambda^2)^2 \{ (\kappa' - \kappa) / \kappa + 3 \cos \theta (\rho' - \rho) / (\rho + 2\rho') \}, \quad (10)$$

where v is the volume of the obstacle, λ the wavelength, ρ and ρ' are the densities, κ and κ' the volume elasticities, of the medium and the obstacle respectively. Since the first term in the curly bracket on the right side of (10) is small as said before and the scattering in the crystalline lattice is very complicated because of the existence of three different polarization directions of the thermal wave and so forth, we approximate the differential cross-section in the present case by,

$$s = (\pi v / \lambda^2)^2 U^2, \quad U = \frac{3(\rho' - \rho)}{\rho + 2\rho'} \simeq \frac{M' - M}{M_0}, \quad (11)$$

which is angle-independent. M and M' are the average molecular weights of the mixture and that of the obstacle. M_0 is the mean of the molecular weights of the two components. Z in (9) is given then by, $Z = v^2 U^2 / 16 \pi^2$ and the thermal resistance becomes,

$$W_e \simeq 4 v^2 U^2 (N/V)^{1/3} (m/V) / kq.$$

If we introduce the molar fraction x instead of m and consider that $N/V = 4a^{-3}$, then the above expression changes to

$$W_e \simeq U^2 a^2 x / kq. \quad (12)$$

When the concentration of one component is not low, $U^2 x$ in (12) has to be replaced by, since both kinds of molecules contribute to the scattering,

$$U^2 x \rightarrow U_1^2 x + U_2^2 (1-x);$$

$$U_1 = (M_1 - M) / M_0, \quad U_2 = (M_2 - M) / M_0, \quad (13)$$

where M_1 and M_2 are the molecular weight of the components respectively. Since $M = xM_1 + (1-x)M_2$, (13) becomes $(\Delta M / M_0)^2 x(1-x)$; $\Delta M = M_1 - M_2$, and finally,

$$W_e \simeq (a^2 / kq) (\Delta M / M_0)^2 x(1-x). \quad (14)$$

Experiments on the conductivity of several mixtures have been carried out by Riedel²⁾ and the results seem to be reliable. As had been noticed by Riedel himself, the observed resistances vary with composition almost in a parabolic form when plotted against the molar fraction, confirming the above calculation. These excess resistances are calculated from his data and shown in Fig. 1.

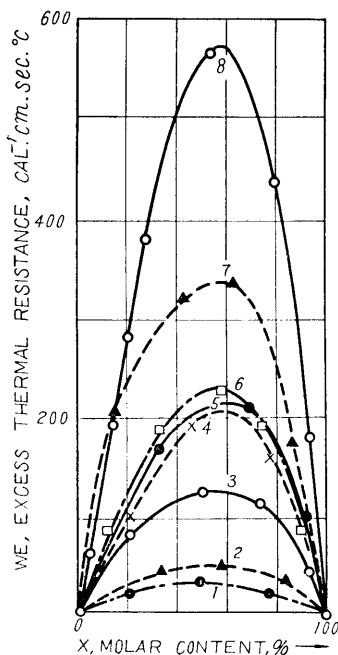


Fig. 1. Excess thermal resistance for various kinds of liquid mixtures determined by experiment.

- 1 Benzene - Nitrobenzene
- 2 Benzene - Acetone
- 3 Benzene - Cyclohexane
- 4 Benzene - Chloroform
- 5 Benzene - Methanol
- 6 Acetone - Carbon disulfide
- 7 Benzene - Carbon tetrachloride
- 8 Benzene - Bromoform

As seen in the figure the maximum of W_e occurs at the 50-50 composition in mols, i. e., at which $x = 0.5$.

To compare the results of the calculation with the experiment, the maximum values of the excess resistances observed and calculated are plotted in Fig. 2. Here a in (14) was taken to be equal to the mean of those of the component liquids which

were calculated by $N/V=4a^{-3}$ and q equal to the mean of the sound velocities of the components which were calculated by the approximate formula $q=(\chi\rho)^{-1/2}$ where χ is the compressibility. The straight line in the figure corresponds to the expression $W_e=0.1(a^2/kq)(\Delta M/M_0)^2$.

The calculated values exceed thus the observed values by a factor of about ten, which seems to be caused by the too large values of the scattering crosssection, as mentioned before. But the general tendency is an expected one and a reasonable proportionality between the observed and the calculated values can be seen to exist.

Mixtures showing anomalously higher resistance than expected are benzene-cyclohexane and acetone-carbon disulfide. This will primarily be due to the inaccuracy of the assumption that the ordinary resistance varies linearly with composition.

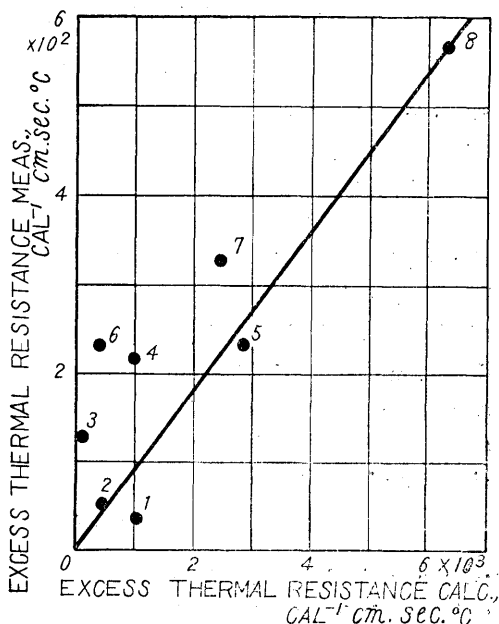


Fig. 2. Maximum values of excess resistance for liquid mixtures

Note : Numerals in the figure mean the same thing as in Fig. 1.

III. Isotope effect in crystals

The free flow of lattice phonons in a solid is prevented by the existence of various kinds of irregularities and also by the Umklapp collisions among themselves, from which the finite value of the thermal conductivity results.

Several types of these irregularities may be tabulated. Usually, the following types are taken into account for the calculation of the conductivity: foreign atoms, lattice vacancies, mosaic boundaries (or dislocations), grain boundaries and the boundary of the specimen.

It is the aim of this chapter to point out that there exists another type of the lattice imperfection which may not be neglected for the cases of the analysis of the conductivity of a nearly perfect single crystal at low temperatures on which a certain number of experiments have been performed from the point of view of theoretical interest.

Nearly all crystals are composed of elements which are not single in the isotopic composition. Because of the mass difference among these isotopic atoms and the random distribution in the crystal lattice, even a perfect crystal may be regarded as a kind of substitutional alloys. In the following the effect of this fact is estimated.

First the case of a dilute isotopic composition is considered. Due to the randomness of the distribution of the minor atoms in the lattice, estimation of this effect can be done by the consideration of the case of a single minor atom in the lattice.

Then the perturbation hamiltonian is,

$$H' = (\delta m/2) |\dot{D}|^2, \quad (15)$$

where δm is the mass difference, $\delta m = m_{minor} - m_{major}$, and D is the displacement of that atom.

As has been shown in the preceding paper, and also as proved by Klemens³⁾, the thermal resistance can be obtained by the calculation of the relaxation time for the attainment of the equilibrium among the lattice phonons in a definite volume kept at a determined temperature throughout. Now the perturbation causes the attainment of the equilibrium distribution of the lattice phonons. The excess or deficit number of phonons belonging to each vibrational mode $\vec{\sigma}$ decreases with a certain rate characterized by a relaxation time. The calculation of the relaxation time τ is rather straightforward, as in this case only two phonon collisions are in problem, if temporarily a monatomic crystal is assumed. The result is

$$\tau^{-1} = 3(\delta m/m)^2 q \sigma^4 V / 2^4 \pi N^2, \quad (16)$$

where m is the mean of the atoms, q the sound velocity, σ the wave number, V the volume of the crystal and N the number of atoms in V .

When there are x of minor atoms present in mole fraction, where $x < 1$, (2) becomes

$$\tau^{-1} = 3x(\delta m/m)^2 q \sigma^4 / 2^4 \pi (N/V). \quad (17)$$

The corresponding mean free path l is then,

$$l = 2^4 \pi (N/V) / 3x(\delta m/m)^2 \sigma^4. \quad (18)$$

According to Klemens, the thermal resistance due to the lattice defects in general, W_D , can be added to the total resistance arithmetically at extremely low temperatures.

$$W_D = (2\pi)^3 a^3 \varepsilon T / 4\pi h q^3 F \times 0.90, \quad (19)$$

where a is the lattice constant, ε the concentration of the defects and F a constant depending on the mechanism of scattering,

After expressing F in terms of l in (18),* combination of (18) and (19) gives

$$W_D \approx 10x(\delta m/m)^2 a^3 T / 2\pi h q^2. \quad (20)$$

In order to get the order of magnitude of this effect, we take the following typical case.

$$\delta m/m = 1/30, \quad a = 4 \times 10^{-8} \text{ cm}, \quad x = 10^{-1}, \quad T = 10^0 \text{ K}, \quad q = 2 \times 10^5 \text{ cm/sec.}$$

3) P. G. Klemens, Proc. Roy. Soc. (London), 208, 108 (1951).

* See reference 3)

The corresponding resistance is $W_0 = 0.03 \text{ watt}^{-1}$. Since the conductivity of a crystal of KCl at very low temperatures was measured to be $K \approx 0.04 T (\text{watt})$, the isotope effect can not be neglected if the component element is rich in minor isotopic species such as,

$\text{Cl}^{35}:\text{Cl}^{37} = 75.4:24.6$, $\text{Br}^{79}:\text{Br}^{81} = 50.6:49.4$, $\text{Rb}^{85}:\text{Rb}^{87} = 72.8:27.2$, $\text{Sb}^{121}:\text{Sb}^{123} = 56:44$, and also Cd, Gd, Ge, Pb, Hg, and many others.

Now let there be several isotopic species of atoms, with masses m_1, m_2, \dots , in the crystal and their fractions be x_1, x_2, \dots , respectively. Then, $\sum x_i = 1$ and the mean mass of the atoms m is $\sum x_i m_i$. If we denote the deviations of the masses of these isotopic atoms from the mean value by $\delta m_1, \delta m_2, \dots$ respectively, $x(\delta m/m)^2$ in (5) should be changed to

$$(1/m)^2 \sum_i x_i (\delta m_i)^2. \quad (21)$$

For the case of two isotopic component systems, this may be written as

$$(\delta m/m)^2 x(1-x), \quad (22)$$

which takes its maximum value at the 50-50 composition just as in the case of the electrical resistance of two component alloys.

As for the experimental verification of the above calculation, it is unfortunate that the lack of the experimental data prevents the comparison.

IV. Damping of vibration in solids

Factors which cause the damping of vibration or the attenuation of sound in solids may be divided into two groups. In the one group there are the movable irregularities in the lattice, such as the dislocations, the grain boundaries, solute atoms and so forth which, while being moved by the applied stress, dissipate the vibrational energy as heat. It should be noted in this connection that the static irregularities, such as the lattice vacancies and fixed solute atoms can contribute likewise to the scattering of the progressive sound waves, but they are inactive for the consumption of energy of the periodic vibrations of the specimen. In contrast to the first group that is related to the imperfectness of the crystal lattice, the second group comprises those factors which exist inevitably in all solids. Thermal diffusion current across the specimen or the grains due to the thermoelastic effect is the typical one.

Now we wish to estimate the effect of the anharmonicity of vibration upon the internal friction, which seems to have been overlooked heretofore and should be classified into the second group. Anharmonicity or nonlinearity of vibration is fundamental in crystal since the interatomic potential is not at all quadratic in the relative displacements. As a result, when the specimen is expanded, for instance, the frequencies of the normal modes of vibration decrease, and vice versa. Therefore these normal modes undergo some kind of frequency modulation if the specimen is set into periodic vibration, accelerating the transitions of

energy among the numerous modes. This process is accompanied with the taking up of energy from the periodic vibration and giving it to the other normal modes or the lattice phonon system, until the energy of that vibration becomes equal to the value given by thermodynamics.

The general procedure of calculation follows that of the preceding paper. For convenience we suppose the normal modes as well as the periodic vibration to be progressive rather than stationary in a crystal of volume V having periodic boundary conditions. The problem is to study how the vibration in question reacts with each normal modes. In the calculation this is treated as a consequence of three phonon collisions caused by a perturbation. The nonlinearity of vibration is expressed by the following perturbing hamiltonian that is third order in the amplitudes.

$$H' = \lambda N^{-3/2} \sum_{\sigma_1, \sigma_2} \sigma \sigma_1 \sigma_2 (aa_1 a_2 \exp i(\vec{\sigma} + \vec{\sigma}_1 + \vec{\sigma}_2) \mathbf{r} - \bar{a} a_1 \bar{a}_2 \exp i(\vec{\sigma} + \vec{\sigma}_1 - \vec{\sigma}_2) \mathbf{r} + \dots), \quad (23)$$

where $\vec{\sigma}$ represents the wave propagation vector of the vibration in question, and $\vec{\sigma}_1$ and $\vec{\sigma}_2$ the representatives of the other normal modes. N is the total number of atoms, a is the amplitude operator which is time-dependent, \bar{a} its complex conjugate and the sum over $\vec{\sigma}_1$ and $\vec{\sigma}_2$ means also the sum over the modes with different polarizations. λ is the nonlinearity constant. (23) causes the transition

$$\Psi_0(\dots n \dots n_1 \dots n_2 \dots) \rightarrow \Psi(\dots n-1 \dots n_1-1 \dots n_2+1 \dots), \quad (24)$$

with the reaction theme

$$\vec{\sigma} + \vec{\sigma}_1 \rightarrow \vec{\sigma}_2,$$

where n , n_1 and n_2 are the number of phonons belonging to each mode. In this reaction the vibration $\vec{\sigma}$ and the mode $\vec{\sigma}_1$ lose one phonon respectively while a new one is created in the mode $\vec{\sigma}_2$. Here the total momentum has to be conserved during the reaction.

$$\hbar \vec{\sigma} + \hbar \vec{\sigma}_1 = \hbar \vec{\sigma}_2.$$

The rate R_1 of the above transition is,

$$R_1 = L \sigma \sigma_1 \sigma_2 n n_1 (n_2 + 1) \Omega(E_f - E_i); L = \lambda^2 V^2 \hbar^2 / N^3 (2m)^3 q^3, \\ \Omega(x) = 4 \sin^2(xt/2\hbar) / x^2, \quad E_f = \hbar \omega_2, \quad E_i = \hbar(\omega + \omega_1), \quad (25)$$

where m is the mass of an atom, q the propagation velocity and ω is the frequency.

Combining (25) with that of the reverse process $\vec{\sigma} + \vec{\sigma}_1 \leftarrow \vec{\sigma}_2$, we get the rate of the decrease of the number of phonons in the vibration under discussion.

$$R_2 = L \sigma \sigma_1 \sigma_2 \{n n_1 (n_2 + 1) - (n + 1)(n_1 + 1) n_2\} \Omega. \quad (26)$$

n_1 and n_2 are given by thermodynamics as,

$$n_{1,2} = (e^{h\omega_{1,2}/kT} - 1)^{-1},$$

while n is decomposed into two terms as

$$n = \Delta n + (e^{h\omega/kT} - 1)^{-1}, \quad (27)$$

where Δn is the number of excess phonons compared with that given by the equilibrium distribution law. The term in the curly bracket of (26) becomes then

$$n n_1 (n_2 + 1) (n_1 + 1) - (n + 1) (n_1 + 1) n_2 = (kT/h) (\omega/\omega_1 \omega_2) \Delta n, \quad (28)$$

at temperatures higher than the characteristic temperature.

Now we have to sum up all the reaction rates of the type of (26) to get the rate of the decrease of Δn at various sets of $\vec{\sigma}_1$ and $\vec{\sigma}_2$.

As is well known well, the simultaneous conservation of energy and momentum during the three phonon collision is not allowed in the continuum approximation of the lattice such as adopted here. The periodic structure of the lattice makes the collision possible, the details of which can not be determined.

The sets of $\vec{\sigma}_1$ and $\vec{\sigma}_2$ become fixed if one of these is given. The sum over the sets is therefore replaced by the sum over $\vec{\sigma}_1$, which in turn is replaced by the integral in the wave vector space, as,

$$\sum_{\sigma_1, \sigma_2} = \frac{3^2 V}{(2\pi)^3} \int \sigma_1^2 d\sigma_1 d\theta d\varphi. \quad (29)$$

It can easily be shown that the $\vec{\sigma}_1$'s satisfying the conservation laws, if present, should lie on planes in the wave vector space. We denote the mean value of the distance between the origin and these planes by σ_0 and replace the integral in (29) by $4\pi C \int \sigma_1^2 d\sigma_1$, where C is a constant of the order of unity.

The calculation yields,

$$\sum_{\sigma_1, \sigma_2} R_2 = (3^2 \lambda^2 C \sigma_0^2 k T / 2^3 \pi \rho^3 q^5) \sigma^2 \Delta n. \quad (30)$$

The nonlinearity constant λ can be expressed by the thermal conductivity K as given previously

$$\lambda^2 = 0.01 \rho^3 q^7 a / K T,$$

where a is the lattice constant.

We get finally the rate of the decrease of Δn , which is expressed by the relaxation time τ .

$$1/\tau = \Delta \dot{n} / \Delta n = (3^2 \cdot 10^{-2} C \sigma_0^2 q^2 a k / 2^3 \pi K) \sigma^2. \quad (31)$$

Now we wish to replace σ_0 in the above equation by the characteristic temperature Θ , both being related by the equation

$$\sigma_0 = \omega_0 / q = C' k \Theta / h q, \quad (32)$$

where C' is a constant of the order of unity. Then (31) changes to

$$1/\tau \simeq 4 \times 10^5 (a\Theta^2/Kq^2) \nu^2 C C', \quad (33)$$

where ν is the frequency and equal to $q\sigma/2\pi$. In (33) all quantities are expressed in c. g. s. units.

As an example we take the case of NaCl, for which $a=5.63 \times 10^{-8}$ cm, $\Theta=220^\circ K$ (Einstein), $q=3 \times 10^5$ cm/sec, $K=0.0087$ cal/cm.sec. $^\circ C$ and assume CC' to be unity.

The followings are the result.

ν (cycles/sec)	10^6	10^{12}	0.46×10^{13}
τ (sec)	29.4	0.294×10^{-10}	1.4×10^{-12}

Here the frequency in the last row is that corresponding to the characteristic temperature and the corresponding relaxation time is seen to be reasonable.

As can be seen in the above list, the attenuation at the artificially attainable frequencies is rather small for observation, the Q being of the order of a hundred million at megacycle regions. But at higher frequencies it is clear that this mechanism predominates the others for the attenuation of vibrations in solids.

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