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in which p is the pressure, therefore

$$\left\{ \left(\frac{\partial \bar{S}_1}{\partial V_1} \right)_{E_1} - \left(\frac{\partial \bar{S}_2}{\partial V_2} \right)_{E_2} \right\} v = 0. \quad (17)$$

Since in the Bose-Fermi statistics the equation $p = \frac{2}{3}(E_1/V_1)$ is also valid, considering (7) it becomes

$$p = \frac{n_1 k T}{V_1} (1 \mp y). \quad (18)$$

$(\partial^2 \bar{S}_2 / \partial V_2^2)_{E_2} v^2 / 2$ is in the equation of the state probability negligibly small. Furthermore

$$\left(\frac{\partial^2 \bar{S}_1}{\partial V_1^2} \right)_{E_1} = - \frac{k n_1}{V_1^2} (1 \mp 2y). \quad (19)$$

The equation of the state probability: $W = c^{S/k}$ is with the aid of Eqs. (16), (17), (18), (19)

$$W dv = \text{constant} \exp \left(\frac{-n_1 (1 \mp 2y) v^2}{2 V_1^2} \right) dv. \quad (20)$$

Hence the mean, respectively relative mean square of the volume fluctuation of n_1 molecules is given by

$$\langle (V - V_1)^2 \rangle_{av} = \int_{-\infty}^{+\infty} v^2 W dv = \frac{V_1^2}{n_1 (1 \mp 2y)}, \text{ respectively} \quad (21)$$

$$\frac{\langle (V - V_1)^2 \rangle_{av}}{V_1^2} = \frac{1}{n_1 (1 \mp 2y)} = \frac{1 \pm 2y}{n_1}, \quad (22)$$

$$\frac{\langle (V - V_1)^2 \rangle_{av}}{V_1^2} = \frac{\langle (d_1 - d)^2 \rangle_{av}}{d_1^2} = \frac{\langle (n_1 - n)^2 \rangle_{av}}{n_1^2} \quad (23)$$

where d, d_1 and n, n_1 are the suitable density and molecule numbers in the volume V_1 . The relative mean square of the fluctuation of the molecule number is in volume V_1

$$\frac{\langle (n_1 - n)^2 \rangle_{av}}{n_1^2} = \frac{1 \pm 2y}{n_1}. \quad (24)$$

According to F rth⁴ this value is

$$\frac{1 \pm y}{n_1}. \quad (25)$$

In consequence of the interaction of molecules the correction term is again twice smaller than the value on neglecting the actions among the molecules at small degeneration.

⁴ R. F rth, *Zeits. f. Physik* 48, 328-330 (1928), Eqs. (16), (17), (18), (23), and (24).

The Contribution of the Surface of the Specific Heat of Disperse Systems

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A theory of Brager and Schuchowitzky concerning the contribution of the surface of the specific heat is extended to the interfaces of binary systems.

THE determination of the total surface of a highly dispersed substance is of importance for many problems. Usually, only rough estimates could be made from a determination of the size and number of the particles and some assumptions of their geometrical form (e.g., spherical). But lately, Brager and Schuchowitzky¹ have pointed out that there is a measurable property of such systems which is directly proportional to the total area of the surface, namely a certain contribution to the specific heat at very low temperatures. Only, the formulas given by Brager and Schuchowitzky apply to a free surface, whereas in the case of colloidal solutions, which are of main interest, it is rather the interface between two solids (e.g., the colloidal substance and ice), which has to be determined.

¹ A. Brager and A. Schuchowitzky, *Acta Physicochimica (URSS)* 21, 1001 (1946).

It is the aim of this paper to generalize the theory for this case. In doing this, we do not start from the method of Brager and Schuchowitzky, but use the very lucid representation of the problem which has been given by Frenkel.²

The contribution of surface to the specific heat is generally given by the derivative of surface energy with respect to temperature. Customarily, one connects surface energy with the differences of the forces acting on an atom within the bulk of the material and on its surface respectively. This difference may depend on temperature, but it can be easily shown that this contribution to surface energy is proportional to the thermal energy of the substance in bulk and in particular varies with T^4 for low temperatures. But there is

² J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), p. 314.

another somewhat more intricate contribution to surface energy. If the thermal energy of a solid is derived according to Debye's theory, use is made of the eigenfrequencies of a cube with fixed boundaries, with an asymptotical law for the distribution of eigenfrequencies,

$$Z(\nu) = \frac{4\pi}{3} V \left\{ \frac{1}{v_L^3} + \frac{2}{v_T^3} \right\} \nu^3. \quad (1)$$

Here $Z(\nu)$ is the number of eigenfrequencies $\leq \nu$, V the volume of the cube and v_L and v_T the longitudinal and transverse velocities of sound. However, in a cube, whose surface is not fixed, but can move freely, there are no purely longitudinal or transverse waves, but always a mixture of both. This leads to a slight shift of the eigenfrequencies and instead of (1) we have now

$$Z'(\nu) = Z(\nu) + ZA(\nu) = \frac{4\pi}{3} V \left[\frac{1}{v_L^3} + \frac{2}{v_T^3} \right] \nu^3 + \pi A \frac{\nu^2}{v_R^2}, \quad (2)$$

where A is the area of the surface, and v_R is the velocity of the surface waves of Rayleigh.³ These surface waves are a special form of motion of a solid, in which only a thin layer is in motion. For solids satisfying Cauchy's relations, $v_R = 0.92v_T$.

It can be seen at once from (2) that there should be a contribution to the specific heat which is proportional to the surface area and to T^2 for low temperatures.

Now we have to generalize (2) for the case in which there is no free surface, but an interface between two solids. Frenkel obtained (2) by a calculation of the eigenfrequencies of a free sphere.⁴ The appropriate procedure therefore, would be to make the same calculations for a sphere surrounded by a spherical shell of the second material. But these calculations would be very complicated and therefore an attempt is made to get the result by means of a suitable generalization of (1).

The appearance of v_R in (2) indicates that the effect of the surface on the distribution of eigenfrequencies is due to the existence of a peculiar state of motion as described by Rayleigh's theory. It can be supposed that a possible contribution of an interface to the specific heat should depend on the possibility of an analog of Rayleigh surface waves for the interface between two solids. This problem has been investigated in a former paper⁵ and the results will be shortly summarized here. The essential point is, that these interfacial waves can exist only subject to certain conditions, which can be seen in details from Fig. 1. (Roughly, the torsional modulus μ_1 of the solid of the higher acoustical density has to be at least 2.5 times

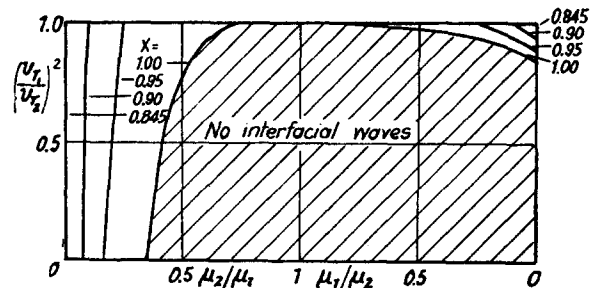


FIG. 1. Diagram for the determination of the velocity v_G of the interfacial waves on the interface of two substances satisfying Cauchy's relations. v_{T1} and v_{T2} are the velocities of transversal waves of sound, μ_1 and μ_2 the respective torsional moduli. (The labeling of the two substances has to be done such that $v_{T1} < v_{T2}$.) The diagram shows the lines $x = \text{const.}$ where x is the ratio v_G^2/v_{T1}^2 . Within the shaded area there are no interfacial waves possible. If Cauchy's relations are not satisfied in both substances, then v_G has to be calculated by the methods indicated in reference 5.

larger than the corresponding μ_2 of the other solid). This means that in a disperse system consisting of two solids a contribution of the area of the interfaces to the specific heat exists only if the two solids differ enough in their constants of elasticity.

There is at the most one interface wave for a given wave vector. The velocity v_G is subject to the condition

$$v_R^{(1)} \leq v_G \leq v_T^{(1)}.$$

$v_T^{(1)}$ is the velocity of transverse waves in the solid of the higher acoustical density (this always being labeled with the suffix 1). It seems therefore that the interface waves correspond to the Rayleigh waves of the solid of higher density, the waves of the other solid being suppressed.

The additional term in (2) which is of importance here is, apart from a numerical factor, fixed by dimensional reasons. That this numerical factor has the value π , is a result of the calculations of Frenkel and Gubanow. It is unlikely that it will change by passing from a free surface to the interface between two solids. On the other hand, it should be expected that v_R has to be replaced by the velocity v_G of the interfacial waves.

The determination of the limiting frequency ν^* remains somewhat problematical. According to Frenkel, ν^* has to be determined so that $Z(\nu^*)$ equals the number of degrees of freedom, i.e., three times the number of atoms. With respect to the behavior of the interfacial waves, these should be treated as surface waves of the acoustically denser solid. For the following calculations, however, this point is of no importance, for they refer to a range of temperatures for which ν^* has no influence on the thermal properties.

We are now prepared to pass on to the calculation of the surface contributions e_ν^A and U^A . The latter quantity is, neglecting the zero-point energy, given by

$$U^0 = \int_0^{\nu^*} \frac{h\nu}{e^{h\nu/kT} - 1} dZA(\nu) = 2\pi A \frac{k^3 T^3}{h^2 v_G^2} \int_0^{\nu^*} \frac{x^2}{e^x - 1} dx. \quad (4)$$

³ Lord Rayleigh, London Math. Soc. **17** (1887), A. E. H. Love, *Elasticity* (Cambridge University Press, London, 1906), second edition, p. 295.

⁴ J. Frenkel and Gubanow, J. Exper. Theor. Phys. **16**, 435 (1946).

⁵ H. Koppe, Zeits. f. angew. Math. Mech. **28**, 355 (1948).

If T is small enough, the upper limit of the integral can be replaced by ∞ . The integral is then equal to $\zeta(3) = 1.202$. Differentiation with regard to T yields

$$e_{\nu}^0 = 6\pi\zeta(3) \frac{k^3 T^2 A}{h^2 v_G^2} = 3.243 \cdot 10^{-2} \frac{\text{cal. } T^2 A}{\text{sec.}^2 v_G^2}.$$

Since ν^* has been neglected, the range of temperatures for which this formula is valid, has an upper limit which may be somewhere about 30°K , but which is not of importance, since experiments must be done at considerably lower temperatures, in order that e_{ν}^A is sufficiently large compared to the rest of the specific heat. But there is also a lower bound for the validity of (5) which we shall presently establish. It has been mentioned already that interfacial waves, and with them the surface component of the specific heat, exist only if the two substances are different enough. Since both the differences in the elastical constants as well as in the densities, which determine whether interfacial waves are possible or not, vary with temperature, it could be possible that for certain combinations of solids interfacial waves cease to be possible, if the temperature rises above (or drops below) a critical value. This would result in a discontinuity of the specific heat, resembling a phase-transition of second order. Actually, this cannot happen for the following reason: It has been mentioned already that interfacial waves take place only in a thin layer which should be small compared with the diameter of the colloidal particles. But the theory of these waves⁵ shows that the penetration depth approaches infinity at least within the acoustically denser substance if the representative point of the binary system approaches the shaded area in Fig. 1. If, therefore, the penetration depth is not small compared with the size of the particles, the present theory is no longer valid, and the specific heat depends not only on the area of the surface of the particles, but also on their geometrical form.

This is essential in another respect: even for fixed elastical constants and densities the penetration depth of the interfacial waves depends on the frequency:

$$\delta = \frac{v_T}{2\pi\nu} \left(\frac{x}{1-x} \right)^{\frac{1}{2}}. \quad (6)$$

The parameter x can be taken from Fig. 1. In any case, δ becomes infinite if ν approaches zero. In order that (5) is valid, it must be postulated that δ is small compared with the mean diameter D of the particles at least for these frequencies ν_M which contribute most to e_{ν}^A . ν_M can be found from the derivative of the integrand of (4),

$$\nu_M = 1.6(kT/h)$$

and therefore we get as a necessary condition for the validity of (5)

$$\frac{1.6k}{h} \frac{TD}{v_T} \left(\frac{1-x}{x} \right)^{\frac{1}{2}} > 1 \quad (7)$$

or, if we disregard extremely small values of the square root

$$(T \cdot D)/v_T \geq 10^{-11} \text{ sec.} \quad (8)$$

To give a numerical example, we may assume that $v_T \sim 10^5 \text{ cm sec.}^{-1}$. $D \sim 10^{-6} \text{ cm}$, then T must be $> 1^\circ\text{K}$. The question then arises whether the whole effect is large enough to make an application feasible. This splits at once into two subquestions: whether it is possible to obtain reasonably good experimental values of e_{ν}^A , and whether it is possible to calculate A from these values. We answer the second question first. In order to obtain A , v_G must be known, and it has to be calculated from the constants of elasticity. It is advisable then, first to calculate or to obtain experimentally the value of v_T , then $v_G^2 = x v_T^2$ where x can be obtained from the diagram of Fig. 1. It is really not very critical, for x can only vary within rather narrow limits: $0.845 \leq x \leq 1$. e_{ν}^A itself according to definition, is the difference between the specific heat of the sample and that of the same amount of bulk material. It is necessary to consider, for which temperatures this difference would be sufficiently large. Now the specific heat of the sample consists of two (or three) parts: the specific heat of the lattice vibrations, the contribution of the surface, and the specific heat of the electrons if metallic phases are present. But these three contributions vary as T^3 , T^2 , and T , respectively. Therefore T should not be too high, for then the large specific heat of the lattice vibrations would screen the whole effect. On the other hand, the temperature should not be too low, for then the specific heat of the electrons would become predominant. (This refers of course, only to cases where metals are present, which are therefore less favorable.) A short calculation shows then that in most cases a compromise is possible, and for particles of a size of about 10^{-6} cm , e_{ν}^A can amount to about 10 percent of the specific heat at temperatures of about 1°K . If one assumes an accuracy of about 1 percent for the total specific heat, then the surface could be calculated with an accuracy of about 10 percent at most.

Summarizing the results, we can state that the contribution of the interface between two solids is, if one excludes some limiting cases, very nearly the same as the contribution which would arise from an equal free surface of the acoustically denser substance. The calculations have been based on the simple Debye-model, and it is known that this model is not too accurate. However, it might be assumed that the qualitative result stated above is independent of the special model.

In conclusion, it should be stated that surface effects of this kind could be expected also in eutectical alloys and even in polycrystalline samples of substances with a high elastical anisotropy.