Phonon contribution to melting of thin films. NMR study of diphenyl

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A thin film of melt on a crystal surface, $\Delta T = 0.1$–40 K below the melting point T_0 of its bulk (see Refs. 1–6), has been recorded for diphenyl. The thickness of the film turned out to be $\alpha \Delta T^{-1}$. This effect is explained by the discreteness of the phonon spectrum of the thin film.

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We studied the formation of films of a diphenyl melt ($T_0 = 343$ K) on the interface between diphenyl crystals and amorphous SiO_2 (Aerosil) using NMR.[6] The specimens consisted of a mixture of diphenyl with different amounts of Aerosil beads with a diameter of 200 Å. The mixture was prepared by mechanical rubbing of diphenyl with Aerosil (because of their poor mutual wetting). A count of the number of separate Aerosil particles from electron microscope pictures showed that in specimens with a 3:1 diphenyl-to-Aerosil weight ratio the specific surface is 1.5–2 times larger than in specimens with a 9:1 ratio. The control specimen consisted of polycrystalline diphenyl without Aerosil. The mixture was packed into a glass test tube, and then placed into a NMR spectrometer. The temperature was maintained constant to within ± 02 and ± 1 K in a high and low resolution spectrometer, respectively. Figure 1 shows the derivatives of the absorption signal with low resolution from the pure diphenyl control (curve 1) and diphenyl with Aerosil (3:1, $T = 338$ K) (curve 2). The broad peaks in curves 1 and 2 are due mainly to the low-mobility protons in diphenyl crystals, while the narrower peak in curve 2 is due to protons in liquid diphenyl. The intensity of the narrow signal increases as T approaches T_0 (Fig. 2). The narrow peak is already observed at $T > 240$ K, but its intensity does not change down to $T = 300$ K, and the peak must be associated with protons in the hydrate shell of the Aerosil. Subtracting this background from the high-resolution spectra and measuring the area under the broad and narrow peaks, we obtain the ratio η of the number of molecules in the liquid phase to their total number ($1.5 \lesssim \eta \lesssim 70\%$) at different temperatures $T = T_0 - \Delta T$. The ratio $\eta_{3:1}(\Delta T)/\eta_{9:1}(\Delta T) = 2$ to within 20% for all temperatures used (squares in

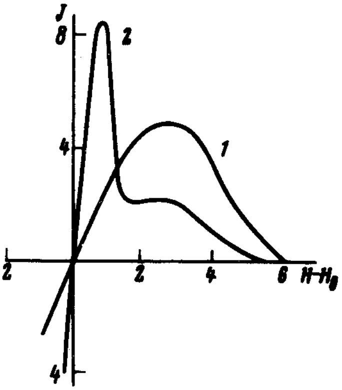

FIG. 1. The NMR signal J as a function of the magnetic field intensity $h - h_0$ in the low-resolution instrument. The antisymmetric part with $h - h_0 < 0$ is not shown. 1) Polycrystalline diphenyl without Aerosil; 2) diphenyl-Aerosil mixture (3:1), $T = 338$ K. The narrow peak is related to mobile protons in liquid diphenyl.

Fig. 3), which agrees with estimates of the diphenyl Aerosil contact area determined by electron microscopy.

At $\eta \simeq 1$, the regions of the liquid phase must overlap strongly, which is reflected in the nature of the dependence $\eta(\Delta T)$. For this reason, this dependence is represented in Fig. 3 up to $\eta \leqslant 0.4$. Aside from diphenyl, data on $\eta(\Delta T)$, obtained by the same method for mixtures of ice with Aerosil and fluoro-plastic, as well as for finely dispersed ice, are shown in Fig. 3.[6] From all of the coordinates tested, the best straight line is obtained for those used in constructing Fig. 3 $\eta - \Delta T^{-1}$. Rescaling the liquid fraction η to the average thickness H of the film surrounding each small sphere of Aerosil, in an approximation that does not include overlapping of these liquid shells, gives for diphenyl $H = 106$ Å at $T = 340.5$ K, 75 Å at 338 K, 39 Å at 333 K, 24 Å at 328 K, and 14 Å at 323 K.

The observed "premelting" could be due to accumulations of impurities, which lower the melting point, and due to local stresses, for example, surrounding the dislo-

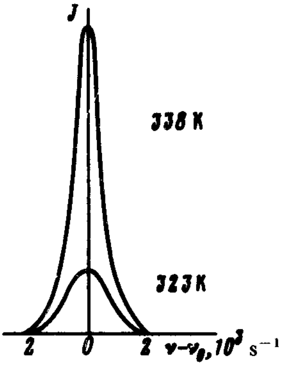

FIG. 2. High-resolution peaks from liquid diphenyl at $T = 323$ K (a) and $T = 338$ K (b).

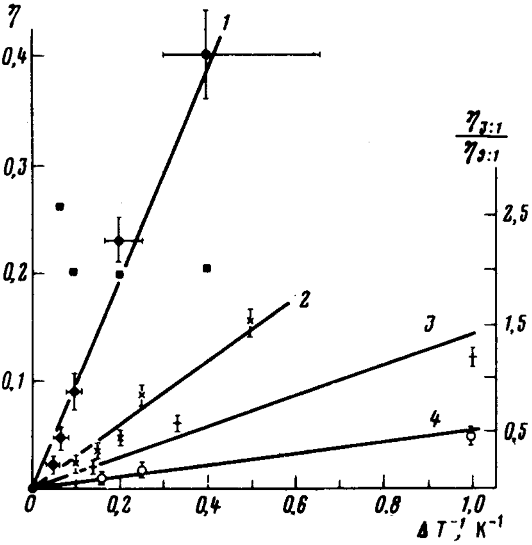

FIG. 3. The liquid-phase fraction η in the spectrum as a function of the inverse distance ΔT^{-1} to the melting temperature. The scale on the right and the squares refer to the ratio of the relative liquid-phase fractions in the specimen with 3:1 and 9:1 diphenyl-Aerosil ratios. Scale on the left: 1) diphenyl-Aerosil; 2) ice-Aerosil; 3) dispersed ice; 4) ice-fluoroplastic.

cations. A luminescence-spectral analysis of diphenyl showed that impurities in it are $<0.02\%$ and the liquid fraction does not exceed $\sim 0.06\%$, if for the estimate we use the depression in T_0 in the diphenyl-anthracene phase diagram (the latter is the more typical impurity in diphenyl). An even smaller amount of liquid phase is expected, according to our estimate, due to the formation of liquid channels around dislocations, even if the density of the latter is 10^6 cm^{-2}. We emphasize, furthermore, that in contrast to specimens with Aerosil, the control specimens do not give a liquid-phase signal.

The dependence $\eta \propto \Delta T^{-1}$ established is much stronger than $\eta \propto \Delta T^{-1/3}$, which follows from the usual assumption of the action of molecular forces ignoring retardation[7] and a number of measurements of the thickness dependence of the disjoining pressure.[8] These forces displace the chemical potential of the film by $\delta\mu = A\Omega / H^3$, where $A \simeq 10^{-14}$–10^{-15} erg,[9] and Ω is the specific molecular volume. Thus the dependence $\eta \propto H \propto \Delta T^{-1}$ is due to other reasons. We shall consider the vibrational energy, which has not been examined previously in this context.

The absorption coefficient of shear hypersonic waves in liquids $\simeq 10^4$ cm^{-1},[10] i.e., sound waves in films with thickness $\lesssim 1$ μm undergo many reflections before damping and viscous transverse modes can be viewed as being undamped, especially for small longitudinal dimensions L of the films (in our case, the circle of the little sphere $L < 10^{-5}$ cm). For this reason, we shall examine the Debye model of an isotropic solid film with dimensions $L \times L \times H$. In such a film, the characteristic oscillations are longitudinal-transverse symmetrical s and antisymmetrical a Lamb waves and horizontally polarized transverse waves t. Their discrete spectra consist of branches

$\omega_m^i = \omega_m^{(i)}(\kappa)$, where $i = s, a, t$ and the number of the branches $m = 1, 2, \ldots$, while κ is the modulus of the wave vector in the plane of the film (x, y). The distance along the ω axis between branches $\simeq 2\pi c/H$, where c is the velocity of sound, increases with decreasing H. In this case, the total number of allowed modes $M_i = \omega_D H/\pi c_i \simeq a/H$ decreases. Here $\omega_D \simeq 2\pi c/a$ is the Debye frequency and $a = \Omega^{1/3}$ is the average intermolecular distance. The discreteness of the spectrum decreases the free energy of the film and its chemical potential by $\delta\mu \propto a/H$. The partition function summed over all acoustical oscillators can be replaced by an integral along each of the branches $\omega_m^{(i)}(\kappa)$, since the neighboring characteristic values of the vectors k_x and k_y differ by $2\pi/L \ll 2\pi/H$. On the other hand, the sum along the branches with different m, i.e., different k_z, which are distinguished from each other at least by $2\pi/H$, must be found to within terms $\propto a/H$. For this reason, the free energy F of an isolated plate is

$$-F/T = (L^2/2\pi) \sum_{i=s,a,t} \sum_{m=0}^{M_i} \int_0^{\kappa_{Dm}^{(i)}} f(\hbar\omega_m^{(i)}(\kappa)/T)\,\kappa\,d\kappa\ , \tag{1}$$

$$f(x) = \ln[\exp(-x/2)/(1-\exp(-x))], \quad M_i = \omega_D H/\pi c_i .$$

The waves s_m and a_m at $m \geqslant 1$ can be put into one-to-one correspondence with uncoupled volume transverse (t) and longitudinal (l) waves, for which

$$\kappa^2 + (\pi m/H)^2 = \omega^2/c_{t,l} . \tag{2}$$

The waves s_0 and a_0 in the limit $\kappa H \to \infty$ go over into the Rayleigh waves, propagating at a velocity c_R along both surfaces of the plate with the dispersion law $\omega = c_R \kappa$. Thus, in (1), it is important to go over from s and a waves to t, l, and R waves. In this approximation, $i = t$, l and

$$\int_0^{\kappa_{Dm}^{(i)}} f(\hbar\omega_m^{(i)}(\kappa)/T)\,\kappa\,d\kappa = (1/2)(T/\hbar c_i)^2[\psi(x_D) - \psi(x_m^{(i)})] \tag{3}$$

$$\psi(x) = x^2/2 - x^2\ln x - x^3/3, \quad x_D = \hbar\omega_D/T, \quad x_m^{(i)} = \pi\hbar c_i m/TH .$$

Substituting (3) into (1) and using the Gaussian summation formula, after the substitution $s,a \to t,l,R$, we obtain for $T > \hbar\omega_D \equiv \theta$:

$$\delta\mu = -(3\Omega/8\pi H)(T/\hbar c_2)^2\psi(\theta/T), \quad 3c_2^{-2} \equiv 4c_R^{-2} - c_l^{-2} . \tag{4}$$

The Debye frequency also depends on H,

$$\omega_D \simeq (6\pi^2/\Omega)^{1/3}c_3 - \pi c_3^3/4Hc_2^2 , \quad 3c_3^{-3} = 2c_t^{-3} + c_l^{-3} . \tag{5}$$

If we make the substitution $s_0 + a_0 \to 2R$, then $3c_2^{-2} = 2c_t^{-2} + c_l^{-2}$.

Substituting (5) into (4), we finally obtain

$$\delta\mu = -(9\pi\hbar c_3^3/8Hc_2^2)(T/\theta + 1/3). \tag{6}$$

In the film on a substrate or between two solid bodies, the vibrational spectrum of the film narrows: part of the characteristic waves is collectivized with the substrate (in general, undamped waves along the film are possible only if $c_{t,l}$ is less than the velocity of sound in the substrate). For this reason, $|\delta\mu|$ will be slightly less than (6). Taking this situation into account in the factor χ, which depends on the velocity of sound, we obtain from the equality of the chemical potentials of the film and of the substrate

$$H = (9\pi\chi\hbar c_3^3 / 8c_2^2 \Delta s\Delta T)(T/\theta + 1/3). \tag{7}$$

If the entropy of melting $\Delta s = 3\times10^{-16}$ erg/K, $c_3^3/c_2^2 = 1.5\times10^5$ cm/s, $\theta = 100$ K, $T = 333$ K, $\Delta T = 10$, then (7) gives $H = 60$ Å, i.e., $\chi = 0.7$, since experimentally $H = 40$ Å.

In conclusion, we recall that both (7) and our estimate give only the form of the dependence $H(\Delta T)$ and its order of magnitude.

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