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Comment on the pressure dependence of the interactions between isotopic impurities in solid helium

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This comment discusses the pressure dependence of the interaction between isotopic impurities in solid helium and its implications for (i) the phase separation of ^{3}He-^{4}He solid mixtures and (ii) the tunneling of impurities in ^{4}*He*-^{3}He as studied by NMR.

The recently published data by Arnold and Pipes[1] exhibit a marked decrease of the phase separation temperature for dilute mixtures of ^{4}He in bcc ^{3}*He*-^{4}He with increasing pressure. The study of this phase separation and related properties of isotopic impurities in solid helium probe the interactions between impurities and so provide a severe test of our current understanding of the physics of quantum crystals. In this Comment we relate the interpretation of the results of Arnold and Pipes to those that have been obtained from some NMR experiments.

I. PHYSICAL ORIGIN OF THE INTERACTION BETWEEN ISOTOPIC INTERSTITIAL IMPURITIES

Some knowledge concerning the basic mechanisms leading to these interactions is first necessary: these mechanisms depend on the distance between impurities, which is not a situation unique to helium mixtures. Just as in the very different case of solutions of atomic hydrogen in metals,[2] we have to distinguish between short-ranged and long-ranged interactions. Elasticity theory can only be applied to the latter. Generally speaking both types of interaction in the case of helium are believed to result from the difference between the amplitude of zero-point motion of an impurity atom and that of a host atom, which leads to a local dilation δ.

This local dilation is related to the large difference in mass of ^{3}He and ^{4}He, and it is intimately related to the quantum character of solid helium. By this we mean that the average kinetic energy of helium is a substantial fraction f of the total ground-state energy and we argue that the smaller this fraction, the more "classical" the crystal; on increasing the density of the crystal, the atoms feel more and more of the hard-core repulsive potential between them, the fraction f and the amplitude of zero-point motion are reduced, so that the crystal tends to behave less "quantum mechanically." At a given density, the kinetic energy is larger for ^{3}He than for ^{4}He and this is related to the fact that at a given pressure P and for a given crystallographic structure, the molar volume V_3 of ^{3}He is larger than the molar volume V_4 of ^{4}He. This difference occurs for only a limited pressure range for bcc structures because of the limited existence of this structure for ^{4}He, but it is well established for hcp structures, where our analysis of thermodynamic data[3] leads to the results

$$\frac{V_3(P)-V_4(P)}{V_4(P)} \propto V_3^{2.2}(P) \quad . \tag{1}$$

Going to mixtures, we believe that the smaller the difference $V_3(P)-V_4(P)$, the smaller the local dilation δ around one isolated isotopic impurity.[4] Consequently, one should have

$$\frac{\partial \ln|\delta|}{\partial \ln V} > 0 \quad . \tag{2}$$

1. In addition to this local dilation the zero-point motion also plays an important role in the phase separation of isotopic mixtures. This phase transition has been treated microscopically by Mullin.[5] He stresses the fact that unlike classical solids, the ground-state energies $\Delta e_3, \Delta e_4$ $[\Delta e_a(X,P) = e_a(X,P) - e_a^0(P)]$ of the two components are very different as a result of the different zero-point motions of a ^{3}He (or ^{4}He) atom in the mixtures. These energies $e_a(X,P) = t_a + \omega_{aa}$ (where in Mullin's notation t_a and ω_{aa} are, respectively, the quantum-mechanical kinetic energies and interaction energies) are related self-consistently to the "effective" short-range interactions between impurities (e.g., ^{3}He-^{3}He) and the local dilation around an impurity. All quantum-mechanical calculations[5–7] for the case of bcc ^{3}*He*-^{4}He lead to local volume dilations δ less than 2%.

2. The asymptotic limit for the long-ranged interactions is estimated using the continuum theory of elasticity[8,9]; for two impurities separated by a vector $\vec{R}_{jk}$ we have for the bcc lattice

$$E(\vec{R}_{jk}) = V_0(a/R_{jk})^3[1-\tfrac{5}{3}(l^4+m^4+n^4)] \quad , \tag{3}$$

$$V_0 = -\frac{2a^3\delta^2}{27\pi}(C_{11}-C_{12}-2C_{44})\left(1+2\frac{C_{12}}{C_{11}}\right)^{-2} \quad . \tag{4}$$

a is the distance between nearest neighbors, l,m,n are the direction cosines of the vector $\vec{R}_{jk}$ with respect to the edges of the cubic cell, and C_{11},C_{12},C_{44} are the elastic constants for bcc helium. Note that the radial dependence is governed by a monotonic R_{jk}^{-3} decrease but that the interaction (3) is anisotropic with respect to the crystal axes. In order to discuss the volume dependence of V_0, we define a quantity

$$\Gamma_V = -\frac{\partial \ln |V_0|}{\partial \ln V} \quad . \tag{5}$$

If we assume that all the elastic constants remain proportional to one another for all molar volumes, their volume dependence is entirely described by the Grüneisen constant

$$\Gamma = -\frac{\partial \ln \Theta_D}{\partial \ln V}$$

Θ_D being the Debye temperature; in that case

$$\Gamma_V = 2\left[\Gamma - \frac{1}{3} - \frac{\partial \ln |\delta|}{\partial \ln V}\right] \quad . \tag{6}$$

3. For intermediate interatomic distances, one should somehow interpolate between the elastic asymptotic limit and the short-ranged attraction. Presumably the radial dependence is more rapid than R_{jk}^{-3}; when one takes into account the fact that the elastic constants themselves are functions of the atomic concentration of impurities, an anisotropic term varying as R_{jk}^{-6} shows up in the interaction.[8]

II. PHASE SEPARATION IN ISOTOPIC MIXTURES

As stated above this phase separation depends crucially on zero-point effects—and especially on the fact that a ^{3}He atom finds itself in a smaller molar volume in the mixture than it would in pure ^{4}He. This effect associated with the reduced zero-point motion has another important aspect. The ^{3}He atom in the "wrong" environment will also result in a local stress on the surrounding lattice (determined by the local dilation δ) and the subsequent lattice deformation will determine the "effective" short-range interaction between two impurity atoms. The phase separation temperature and the short-range interactions between impurities are therefore related but no formal unified treatment of these two aspects seems to be available. The phase separation temperature T_{ps} for a given ^{3}He concentration x_3 decreases with increasing pressure as illustrated by the work of Arnold and Pipes and of previous workers[10,11] and as predicted theoretically.[5] We consider this trend as a confirmation of the statement.[2]

If one is interested in the volume dependence of the short-ranged interactions (identified with the energy of mixing ΔE of Arnold and Pipes) one writes

$$-\frac{\partial \ln \Delta E}{\partial \ln V} \simeq \frac{1}{T_{\text{ps}}} \frac{dT_{\text{ps}}}{dP} \frac{1}{K} = -5.7 \pm 0.9 \quad , \tag{7}$$

where we have used the data of Arnold and Pipes for the phase-separation ps temperature (for $x_3 = 0.987$ and $P = 40$ atm) and an average value $K \simeq 3 \times 10^{-3}$ atm^{-1} for the compressibility of pure bcc ^{3}He.[12]

III. NUCLEAR MAGNETIC RESONANCE IN ISOTOPIC MIXTURES

The long-ranged elastic contribution to the interaction between impurities is responsible for various aspects of magnetic resonance experiments on the motion of isotopic impurities, for instance the collision of impuritons.[13] The system which has been most studied by NMR is hcp ^4He-^{3}He and not the bcc mixture studies by Arnold and Pipes. For an hcp structure one can write equations analogous to Eqs. (3) and (4) (see Ref. 9): obviously the R_{jk}^{-3} dependence and the proportionality of V_0 to δ^2 remain for any structure.

NMR provides a powerful tool for studying the dynamics of atoms (through the transverse relaxation time T_2 or the diffusion constant D for instance). NMR can then be used to study the influence of the interaction (3) on the motion of a ^{3}He impurity which can tunnel from one lattice site to a neighboring one with some frequency J_{34}.[14–16] As discussed for instance by Andreev[13] the resulting motion of a ^{3}He impurity depends on the impurity concentration and several rather different regimes are to be considered.

(a) An impuriton regime where ^{3}He impurities form a band of coherently propagating states which scatter from one another by pairwise collisions, the scattering potential being given by Eq. (3). For this regime the kinetic energy of an impuriton is on the average larger than the interaction between impurities and one should have

$$\begin{gathered} x_3 \lesssim J_{34}/V_0 \quad , \\ D \propto x_3^{-1} V^{2/3} J_{34}^{5/3} V_0^{-2/3} \quad . \end{gathered} \tag{8}$$

(b) A strong interaction regime,[13,15] which can also be described as a "dense fluid regime" where a given ^{3}He impurity tunnels in the *mean* elastic field due to many other impurities and where Eq. (3) is still a good approximation to the elastic field. For this regime one should have[17]

$$x_3 \gtrsim J_{34}/V_0 \quad ,$$

$$D \propto x_3^{-4/3} V^{2/3} J_{34}^{2} V_0^{-1} \quad , \tag{9}$$

$$1/T_2 \propto x_3^{4/3} V^{-2} J_{34}^{-2} V_0^{-1} \quad . \tag{10}$$

(c) A high concentration regime when the asymptotic limit (3) of the interaction is no longer valid; the average distance between impurities being such that the interaction really varies as $R_{jk}^{-n}(n=6)$ the diffusion constant should then have a stronger concentration dependence than given by Eq. (9):

$$D \propto x_3^{-(n+1/3)} \quad .$$

Whether the impuriton regime has actually been observed is a matter of controversy, but it may well have been seen by the Sussex group.[15] The point is that it is very difficult to observe experimentally the difference between the concentration dependences of Eqs. (8) and (9). On the other hand the dense fluid regime has definitely been studied. Let us concentrate here on the T_2 data of the Kyoto group,[16] which agree reasonably well with those of the Cornell group[14] and the Sussex group.[15] The result for the volume dependence of T_2 in hcp ^4He-^{3}He is[16]

$$\frac{\partial \ln T_2}{\partial \ln V} = 54 \pm 6 \qquad (11)$$

for $7\times10^{-3} < x_3 < 7\times10^{-2}$. From Eq. (10) one easily predicts a volume dependence

$$\frac{\partial \ln T_2}{\partial \ln V} = 2\frac{\partial \ln J_{34}}{\partial \ln V} + \Gamma_V + 2 \quad . \qquad (12)$$

If we want to use the experimental result (11) to find Γ_V we need the volume dependence of J_{34}. The only guess we can make is that it is identical to the molar volume dependence of the exchange in pure hcp ^{3}He (Refs. 16 and 18):

$$\frac{\partial \ln J_{34}}{\partial \ln V} \simeq 23 \pm 2 \quad . \qquad (13)$$

In such a guess we of course ignore the details of various tunneling processes[19] which could invalidate estimate (13). Combination of Eqs. (11), (12), and (13) leads to the rather inaccurate predictions

$$\Gamma_V = 6 \pm 10 \qquad (14)$$

but note that the volume dependence of this long-ranged elastic interaction does not have necessarily the same sign as for the short-ranged one [see Eq. (7)]. If one uses the value $\Gamma = 2.6$ of Ref. 20 for the Grüneisen constant in Eq. (6) and inequality (2) one finds

$$\Gamma_V < 4.6$$

which is compatible with statement (14). Obviously the local dilation should decrease rapidly with increasing pressure, to reconcile the trends of the long-ranged and the short-ranged interactions.

We end by a comment on the magnitude of the constant V_0 of Eq. (4). It can be shown[9,13] that V_0 should be of the order of 10 mK to account for NMR data. The local dilation necessary to obtain such a value by using elasticity theories[8,9] is of the order of 18%[9]; this figure is much larger than the theoretical predictions previously mentioned.[5-7] On the other hand it is comparable either to the values obtained by Klemens, De Bruyn Ouboter, and Le Pair[4] in a phenomenological isotropic elastic medium model or to the volume misfits necessary to account for the large cross section for Rayleigh scattering of phonons by impurities, deduced from thermal conductivity measurements in bcc ^3He-^{4}He.[21]

The problems discussed here have some resemblance to that of quantum tunneling of *HD* impurities in solid hcp para H_2, analyzed by one of the authors (N.S.).[22]

To conclude we would point out that the details of elastic interactions between impurities in quantum crystals (order of magnitude, volume dependence, mechanism) still seem to be an open question, and new contributions both theoretical and experimental are needed.

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