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Dimerization of ^{3}He in ^{3}He-^{4}He dilute mixtures filling narrow channels

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We consider dimerization of ^{3}He in a dilute solution of ^{3}He in superfluid ^{4}He filling straight narrow channels that can be found in nanoscale porous media. Dimer formation is facilitated by the restricted geometry and occurs despite the fact that in bulk fluid the interparticle interaction is too weak to lead to a bound state. Dimerization results in the effective ''bosonization'' of the system: a Bose quantum fluid of $(^3\mathrm{He})_2$ arises in place of the ^{3}He Fermi component. At high temperatures, when the ^{3}He impurity quasiparticles form a Maxwell-Boltzmann gas, a drastic change in the thermodynamics occurs due to the presence of dimers. The specific heat and magnetic susceptibility of the ^{3}He component, which we calculate at arbitrary degrees of dimerization, show a marked deviation from behavior expected of an undimerized ^{3}He component. We show that the binding energy—which depends on the channel width—is expected to be sufficiently high to make experimental observation feasible. The presence of $(^3\mathrm{He})_2$ dimers gives rise to an extra absorption mechanism for first sound propagating through the superfluid ^{4}He, due to resonant absorption and decay of dimers in the acoustic field. We have calculated the absorption coefficient. Several experiments suggest themselves, utilizing, perhaps, K-L zeolites or carbon nanotubes. If the dimers themselves turn out to be attractive, then quadrumers may appear: it may even be the case that a single ^{3}He polymer will form over the entire length of the channel.

I. INTRODUCTION

The problem of a bound state of two (or more) helium atoms has attracted a great deal of interest over the last few decades, leading to active theoretical and experimental studies throughout the world. To form a molecule, a sufficiently strong attractive interaction potential is required. The van der Waals attraction between two ^{4}He atoms in vacuum results in a weakly-bound state with a binding energy of about 1.7 mK,[1] which makes ^{4}He dimers difficult to observe. Despite the difficulties, experimental observation of ^{4}He dimers in a supersonic expansion beam was reported by Luo *et al.*[2] Experiments with a cooled pulsed beam of ^{4}He atoms carried out by Silvera *et al.*[1,3] revealed the giant cross section consistent with the existence of a dimer state of ^{4}He.

The situation is quite different in the case of ^{3}He. Due to the smaller atomic mass, the kinetic energy of the relative motion of two ^{3}He atoms plays a more important role than in the case of ^{4}He. As a result, the interaction in vacuum proves to be insufficiently strong for a dimer state of ^{3}He atoms to form. In other words, ^{3}He dimers do not exist in vacuum. Experimental data on low-energy ^{3}He-^{3}He scattering[3] did not show any vestige of a bound state.

The interaction between two ^{3}He atoms dissolved in superfluid ^{4}He is, to be sure, affected by the presence of the superfluid background. Nevertheless the basic features of the effective ^{3}He-^{3}He interaction remain the same, and it resembles the interatomic interaction in vacuum. For example, the attraction between two ^{3}He quasiparticles, which exists at large distances, falls off in the same fashion (albeit with a different numerical factor) as in vacuum. It is well established experimentally that on average the overall effective interaction between two ^{3}He impurities in superfluid ^{4}He corresponds to attraction, in the sense that the *s*-wave scattering length a is negative, $a<0$ (for a review see Ref. 4). This attraction is, however, too weak to allow the formation of a dimer state.

Nevertheless, a statement that Mother Nature does not allow ^{3}He dimers to exist would certainly be rash. It was shown[5] that in ^{3}He systems with reduced dimensionality (such as surface impurity states or ^{3}He quasiparticles localized on vortices in superfluid ^{4}He) or in restricted geometries (such as narrow capillaries or porous media) the ^{3}He component will definitely dimerize. The origin of the effect can easily be understood by means of simple arguments. It is well known that in 2D or 1D *any* attraction, no matter how weak it is, leads to a bound state. For that reason, if a ^{3}He-^{4}He solution is placed under these conditions, that is, if the ^{3}He component can effectively be treated as a 2D or 1D system, even the very weak ^{3}He-^{3}He attraction will cause the ^{3}He impurities to form a dimer. An objection may be raised that the ''theorem'' for bound states in 2D and 1D holds only for perturbative potentials, whereas the real ^{3}He-^{3}He interaction has a strong repulsive core and does not satisfy the perturbation theory criterion. However, it will be shown below that this ''theorem'' remains valid even in the ^{3}He-^{3}He case provided the *s*-wave scattering length is negative.

The dimerization of the ^{3}He component leads to the effective ''bosonization'' of the impurity system: as the temperature is lowered, instead of a Fermi fluid of ^{3}He impurity atoms, one ends up with a Bose quantum fluid of $(^3\mathrm{He})_2$ dimers. In other words, as a result of dimer formation, the Fermi-Bose liquid of ^{3}He-^{4}He is replaced with a quantum liquid that contains two Bose components, ^{4}He and $(^3\mathrm{He})_2$. Needless to say, the thermodynamics and transport of a dimerized ^{3}He-^{4}He dilute mixture differ drastically from those given by the conventional description. Of course, any significant changes in the macroscopic properties of the mixture due to dimerization can occur only if the temperature T is lower than or at least comparable to the binding energy Δ of a ^{3}He dimer, $T \lesssim \Delta$. For this reason, the binding energy is the most important scale in the dimerization problem.

So far research has concentrated primarily on dilute ^{3}He-^{4}He solutions in various 2D geometries and on the Andreev states of ^{3}He at the free surface of ^{4}He.[7–9] A number of encouraging results for thin ^{3}He-^{4}He films on various substrates, which yield reasonable values for the binding energies, have been obtained with the help of the density functional method.[10] It should be emphasized, however, that the binding energy of a dimer state in two dimensions is exponentially small, so irrespective of the substrate or experimental conditions it is difficult to hold a dimer long enough for it to be observed.[10] Also, computations in the 2D case are limited because the pre-exponential factor in the expression for the binding energy Δ cannot be calculated exactly.

The one dimensional problem is free of these drawbacks. First, the binding energy of the dimer state can be calculated rigorously. Second, in contrast to the 2D case, the magnitude of Δ has a power law, rather than exponential, dependence on the interaction strength and pore radius. This means that the binding energy in one dimension is generically higher than in two dimensions. Observing the phenomenon experimentally in traditional 1D ^{3}He systems is, unfortunately, not straightforward. Vortex filaments in superfluid ^{4}He with captured ^{3}He atoms are difficult to work with. Moreover, the density of vortices is usually very low, necessitating an apparatus with high sensitivity. Conventional porous media (like Vycor glass) are far from ideal because they cannot provide a suitable network of sufficiently straight capillaries, as the geometry of pores in such systems tends to be random and chaotic. In typical conventional porous media the average diameter of a pore is about 100 Å which is simply too big to allow a sizable binding energy.

To achieve a significant binding energy one has to turn to porous nanomaterials such as aluminosilicate, aluminophosphate, and zincophosphate zeolites. Recently, zeolitic materials have found application in chemistry, materials science and advanced technology. Zeolites are inorganic crystalline compounds comprised of networks of nanoscale pores typically less than 15 Å in diameter.[11] Of most interest to the dimerization problem are those materials (such as mordenite, K-L zeolite and carbon nanotubes) that exhibit a good network of narrow, straight pores. The behavior of ^{3}He and ^{4}He in three-, two-, and one-dimensional geometries of zeolitic pores has been actively studied experimentally.[12–17] In all cases it was demonstrated that helium can flow (as a gas or liquid depending on the amount of helium adsorbed) through the pores. Motional states of ^{3}He and ^{4}He in one-dimensional channels of K-L zeolite at relatively high temperatures $T \sim 0.1–10$ K were studied experimentally[12,13] by measuring the heat of sorption and heat capacity. One should keep in mind that the effective diameter of the pore may be even smaller due to solidification of helium on the walls and the formation of 1–3 solid atomic layers. Under these circumstances the ''healing'' (correlation) length in superfluid helium could become comparable to or greater than the effective diameter of the pore, which would mean that the liquid helium is no longer a superfluid. (Moreover, in two-dimensional geometries an unconventional type of superfluidity, the Kosterlitz-Thouless phase transition, can come into effect). Recent experimental data[18,19] provide evidence for superfluidity of ^{4}He in nanoporous media with pores of diameter 17–25 Å, and the suppression of superfluidity in zeolite of 10 Å pore diameter has also been reported.[19] But even a diameter of 17 Å is small enough to give rise to a binding energy of high magnitude, and this is what makes zeolites suitable for the experimental search for ^{3}He dimers.

This paper has a two-fold goal. First, it elucidates a complete description of the dimerized state of a ^{3}He-^{4}He dilute mixture in a 1D geometry. We focus mainly on calculating the binding energy and thermodynamic properties. The high-temperature range where the ^{3}He dimers behave as a Maxwell-Boltzmann gas of quasiparticles, as well as the low-temperature regime in which collective phenomena come into effect and interaction between dimers may become important, will be discussed. As an example of a qualitatively new phenomenon that pertains to a gas of $(^3\mathrm{He})_2$ dimers in a superfluid ^{4}He background, we discuss an extra mechanism of sound absorption caused by the decay of the dimer state in the field of an acoustic wave propagating through the ^{4}He component. Second, for concreteness, we make clear predictions and recommendations for experimental study of a ^{3}He-^{4}He mixture in a particular type of nanoporous medium. The magnitude of the effect suggests that zeolites provide the most favorable conditions under which ^{3}He dimer states could be observed conclusively.

We restrict ourselves to considering dimers in a rarefied system of Fermi particles. Clearly, the mechanism that leads to formation of dimers in restricted geometries can also manifest itself in Bose fluids, as well as, in principle, in systems of higher density. We discuss briefly some of these possibilities in the last section of the paper.

II. BINDING ENERGY

Let us consider a narrow pore (capillary) filled with a dilute ^{3}He-^{4}He mixture. The radius of the pore R is assumed to be large enough, $R \gg d$ where d is the atomic size, for the superfluid ^{4}He component to be considered a bulk continuous medium. From here on we also assume that the temperature is low enough so that the effect of rotons and phonons can be neglected. An isolated ^{3}He quasiparticle can travel freely and perform infinite motion along the pore (the z axis) whereas its motion in the xy–plane is finite and quantized. A bound state (if any) of two ^{3}He impurities should be sought as a solution to the appropriate Schrödinger equation with the exact ^{3}He-^{3}He interaction potential. Because the latter has a strong repulsive core, one could not *a priori* be absolutely sure that in the pure 1D case where $R \sim d$ a bound state of two ^{3}He atoms exists. On the other hand, in the quasi-1D circumstances we are considering, in which the characteristic length describing the delocalization of a single-particle ^{3}He excitation in the xy direction (perpendicular to the capillary axis) is much larger than the interaction range, the situation is entirely different. (We are considering a hybrid bulk-1D system, whose existence is strongly suggested by the results of recent experiments by Wada and others.[12–17] The ^{3}He atoms form an *ideal* 1D gas of impurities moving *unhindered* along the axis of zeolite pores, *even when the initial pore* *width is close to* 5 Å. This is the experimental justification for our approach. The actual effective mass and scattering length in such a system in general will approach the bulk values when the radius is ''large enough,'' but when the most important quantities (such as interaction range) fall off exponentially quickly, then ''large enough'' can be taken to mean ''not much larger than the quantity itself.'' This appears to be the case with zeolites. Moreover, the error bars in experimental values for M and a are not inconsiderable—we choose two conservative values—and to this level of accuracy it is permissible to consider a tight radius to be within the hybrid bulk-1D superfluid regime, especially given the experimental facts for zeolites. This is why we use bulk experimental values in our estimates.) As will be proved below, for this case, whether or not a bound $(^3\mathrm{He})_2$ state forms depends only on the sign of the effective interaction (the 3D s-wave scattering length a) in bulk. [The overall strategy may be viewed as follows. We shall find the first term in an expansion for the binding energy. Other terms—due to attractive or repulsive effects mediated by phonons in the superfluid background, fourth sound, etc.—must be added to this. When the radius is large enough, these will be negligible. As the radius of the pore is decreased, these will become stronger, but in the case of zeolites, experiments suggest that they are unlikely to overwhelm the van der Waals attraction (or change the sign of the scattering length) before the lower limit for the radius is reached at which ^{4}He ceases to be superfluid. As already noted above, this hybrid 1D system is free of the drawbacks of 2D films (such as the KT transition).] If a is negative, which corresponds to an effective attraction, two ^{3}He impurities do form a spinless bound state. As was indicated above, all theoretical calculations and experimental data demonstrate that $a<0$.[4,20,21] That is why the $(^3\mathrm{He})_2$ dimer exists. Hence a dimerized phase of ^{3}He is expected to manifest itself at sufficiently low temperatures. The magnitude of the binding energy Δ can be expressed in terms of the 3D s-wave scattering length a and an integral of the wave function of a bare ^{3}He quasiparticle in the xy plane.

To calculate the binding energy Δ we will apply the Fermi renormalization method,[22] according to which a two particle pseudopotential $V(\vec{r},\vec{r}\,')$ is introduced which is assumed to meet the perturbation theory criterion. Let us emphasize that such a pseudopotential has nothing to do with the real interaction between particles, which indeed cannot be treated in terms of a perturbation theory at all. However, the pseudopotential $V(\vec{r},\vec{r}\,')$ is postulated to give rise to the true scattering amplitude when calculated within the Born approximation,

$$a=\frac{M}{4\pi\hbar^2}\int V(r)d^3r,\quad |\vec{r}-\vec{r}\,'|=r, \tag{1}$$

where M is the effective mass of a bare ^{3}He excitation. The idea of the method is to carry out all calculations in the framework of a perturbation theory for the pseudopotential and then to express the final formulas through the true s-wave scattering length a by means of the renormalization relation (1). All expressions thus obtained contain the pseudopotential $V(\vec{r})$ only in the integral form (1).

The starting point of the calculation is the fact that the interaction between ^{3}He atoms just slightly disturbs the motion of particles in the xy plane but entirely changes their relative motion along the z axis, which leads to a bound state. In other words, a perturbation theory for the weak pseudopotential can be applied to describe the perpendicular motion in the xy plane only but the dynamics of both particles along the pore axis should be found as an exact solution to the two-particle Schrödinger equation. Quantitatively it means that one has to solve the 1D Schrödinger equation rigorously with the pseudopotential averaged over the unperturbed wave functions of the bare ^{3}He quasiparticles in the xy plane.

The two-particle Hamiltonian can be represented as follows:

$$\hat{H}=\hat{H}_0+\hat{V}(\vec{\rho}_1,z_1;\vec{\rho}_2,z_2),$$

$$\hat{H}_0=\hat{H}_1^{(0)}(\vec{\rho}_1)+\hat{h}_1^{(0)}(z_1)+\hat{H}_2^{(0)}(\vec{\rho}_2)+\hat{h}_2^{(0)}(z_2), \tag{2}$$

where $\vec{\rho}_i=(x_i,y_i)$ and the index $i=1,2$ designates different particles. Equations (2), indeed, imply some extra requirements for an external potential acting on the ^{3}He particle. For instance, in the case of a narrow channel the potential of the walls of the capillary is assumed to depend only on the $\vec{\rho}$ coordinate. [It is reasonable to ask at this point whether channel walls can ever be smooth enough for this condition to hold. We believe that the zeolites investigated by Wada and others[12–19] are smooth enough. Wada's group[13] find a stable situation in which ^{4}He atoms are adsorbed into the phosphorous ''valleys'' in the zeolite wall, making the wall smooth and the motion one dimensional (translations in the x-y direction are reduced to vibrations). Channels with an initial radius of 5 Å were used in Wada's experiments, and the ^{4}He was reportedly superfluid even after adsorption of the first layer. The heat capacity of the ^{3}He impurities at high temperature was found experimentally to be 1/2, indicating free motion in 1D and vibration in the other two dimensions of the bulk system. So it is reasonable to assume in a first approximation that the external potential of the wall does not depend on z, and that the motion in the x-y plane can be averaged. The fact that a second solid layer forms later is irrelevent to the question of the existence of suitable conditions for dimerization (just choose a bigger channel to start with; or a sample with many channels of various widths).]

As was explained above, we assume that the influence of the interparticle interaction V on the motion in the (xy) plane can be taken into account through perturbation theory, whereas the ''disturbed'' motion along the z direction cannot be considered as a perturbation. Let the wave functions $\psi_{in}^{(0)}(\vec{\rho}_i)$ be eigenfunctions of the equation,

$$\hat{H}_i^{(0)}(\vec{\rho}_i)\psi_{in}^{(0)}(\vec{\rho}_i)=E_{in}^{(0)}\psi_{in}^{(0)}(\vec{\rho}_i). \tag{3}$$

Here the index n labels different quantum-mechanical states and $E_{in}^{(0)}$ are the corresponding eigenvalues of the energy. The solution to the Schrödinger equation $\hat{H}\Psi=E\Psi$ will then be sought in the form,

$$\Psi(\vec{\rho}_1,z_1;\vec{\rho}_2,z_2)=\phi(\vec{\rho}_1,\vec{\rho}_2)\chi(z_1,z_2),$$

$$\phi(\vec{\rho}_1,\vec{\rho}_2)=\sum_{kn} C_{kn}\psi_{1n}^{(0)}(\vec{\rho}_1)\psi_{2k}^{(0)}(\vec{\rho}_2). \tag{4}$$

Multiplying the Schrödinger equation by $\psi_{1m}^{(0)*}(\vec{\rho}_1)\psi_{2l}^{(0)*}(\vec{\rho}_2)$ and integrating over $d\vec{\rho}_1 d\vec{\rho}_2$ one can easily find,

$$C_{lm}(\hat{h}_1^{(0)}+\hat{h}_2^{(0)})\chi+\sum_{kn} C_{kn}\int \psi_{1m}^{(0)*}\psi_{2l}^{(0)*}\hat{V}\psi_{1n}^{(0)}\psi_{2k}^{(0)}\chi d\vec{\rho}_1 d\vec{\rho}_2$$
$$=C_{lm}\epsilon_{lm}\chi, \tag{5}$$

where $\epsilon_{lm}=E-E_{1m}^{(0)}-E_{2l}^{(0)}$. To the first order of the perturbation theory for the motion in the x-y plane (specified by the coordinates $\vec{\rho}_1$ and $\vec{\rho}_2$) we should put $C_{lm}=1$, and $C_{kn}=0$ if $l\neq k$ and $m\neq n$. Thus we obtain

$$(\hat{h}_1^{(0)}+\hat{h}_2^{(0)})\chi+\langle\hat{V}\rangle\chi=\epsilon_{lm}\chi,$$
$$\langle\hat{V}\rangle=\int \psi_{1m}^{(0)*}\psi_{2l}^{(0)*}\hat{V}\psi_{1n}^{(0)}\psi_{2k}^{(0)}d\vec{\rho}_1 d\vec{\rho}_2. \tag{6}$$

When separating as usual the relative motion of particles from the center-of-mass motion one gets,

$$\hat{h}_r^{(0)}\chi_r+\langle\hat{V}\rangle\chi_r=(\epsilon_{lm}-E_c)\chi_r, \tag{7}$$

where E_c is the energy corresponding to the center-of-mass motion, $E_c=p^2/4M$, $\vec{p}=\vec{p}_1-\vec{p}_2$, and the subscript r labels quantities pertaining to the relative motion of the particles, e.g. $\hat{h}_r^{(0)}$ is related to the ''kinetic energy'' of a particle with reduced mass,

$$\hat{h}_r^{(0)}=\frac{q^2}{M},\quad \vec{q}=\frac{\vec{p}_2-\vec{p}_1}{2}. \tag{8}$$

Let us recall that the pseudopotential V is assumed to meet the perturbation theory criterion. The 1D Schrödinger equation (7) can therefore be solved exactly when the exact potential $\hat{V}$ is replaced with the pseudopotential V.[6] The solution reads,

$$\epsilon_{lm}-E_c=\epsilon_r=\frac{M}{4\hbar^2}\left[\int_{-\infty}^{\infty}\langle V\rangle dz\right]^2. \tag{9}$$

Equation (9), indeed, turns out to be consistent with the expression in Ref. 5 for the binding energy, obtained in terms of an ''effective'' potential.

The integral that enters Eq. (9) can be rewritten as follows:

$$I=\int_{-\infty}^{\infty}\langle V\rangle dz=\int V(\sqrt{\rho^2+z^2})F(\vec{\rho})d\vec{\rho}dz,$$
$$F(\vec{\rho})=\int\left|\psi_{1m}^{(0)}\left(\vec{\eta}-\frac{\vec{\rho}}{2}\right)\right|^2\left|\psi_{2l}^{(0)}\left(\vec{\eta}+\frac{\vec{\rho}}{2}\right)\right|^2 d\vec{\eta}. \tag{10}$$

Let the quantity D be the characteristic localization range in the xy plane (for the wave functions $\psi_{1m}^{(0)}$ and $\psi_{2l}^{(0)}$). If the localization radius is sufficiently large, so that $D\gg r_0$, where r_0 is the interaction range, one can easily convince oneself that

$$I=\frac{1}{L^2}\int V(r)d^3r,\ \frac{1}{L^2}=\int|\psi_{1m}^{(0)}(\vec{\eta})|^2|\psi_{2l}^{(0)}(\vec{\eta})|^2 d\vec{\eta},\ \ L\sim D. \tag{11}$$

Combining Eq. (11) and the renormalization relation (1) yields

$$\epsilon_r=4\pi^2\frac{\hbar^2}{Ma^2}\left(\frac{a}{L}\right)^4. \tag{12}$$

One can see from Eq. (12) that the binding energy ϵ_r is expressed in terms of the true scattering amplitude and does not contain the pseudopotential, which shows that the use of the Fermi method here is fully justified. It is convenient to choose the pseudopotential in its traditional form,

$$V(\vec{r})=\frac{4\pi\hbar^2}{M}a\,\delta(\vec{r}). \tag{13}$$

In the opposite limiting case, $D\ll r_0$, the integral I reduces to

$$I=\int_{-\infty}^{\infty}V(z)dz, \tag{14}$$

and the binding energy ϵ_r explicitly depends on the pseudoptential chosen. In this case the renormalization method is no longer valid. To find the binding energy (if a bound state still exists) one should solve the 1D Schrödinger equation with the real ^{3}He-^{3}He interaction potential. [The point is we have laid down the condition [i.e., the ''quasi-1D condition,'' when the integral I in Eq. (10) does not depend explicitly on the pseudopotential V(z) nor the actual potential $\hat{V}$, and I separates into a product of known quantities] whereby a pseudopotential can always be used in such bulk-1D hybrid systems. The actual interaction $\hat{V}$ between ^{3}He is then irrelevent in determining the first term of the energy expansion, apart from providing the first term or so in a Fourier expansion of the potential (as in Ref. 5) which is equivalent in the Born approximation to taking a delta-function potential (as in the present paper). Fermi's essential insight is that the first term of a Fourier expansion will do even when the interparticle interaction contains a singularity, if the particles have space to move around each other. In one dimension, this is expressed in the quasi-1D condition. We remark that there are numerous circumstances in which singularities are quite naturally ''smoothed over'': compare Eqs. (54) and (60) in this paper, in which the averaging effect of Maxwell-Boltzmann motion smooths over the singularity in the zero-temperature absorption cross section.]

To estimate the binding energy ϵ_r of a (^{3}He)$_2$ dimer one has to know the ^{3}He impurity wave functions, $\psi_{1m}^{(0)}(\vec{\rho})$, for the motion in the xy–plane in the external potential of the capillary walls. In principle, these wave functions should be found on the basis of the Schrödinger equation involving the interaction potential of the impurity with the walls and the actual profile of the pore. (These can get quite complicated: for example, the 1D channels of K-L zeolite are formed within ''cages'' interconnected via many narrow apertures[13]). However, if the average radius of the pore is large enough, so that $R\gg d$, and the temperature (or the concentration, in the case of a degenerate mixture) is sufficiently low, so that the de Broglie wavelength of the ^{3}He quasipar-

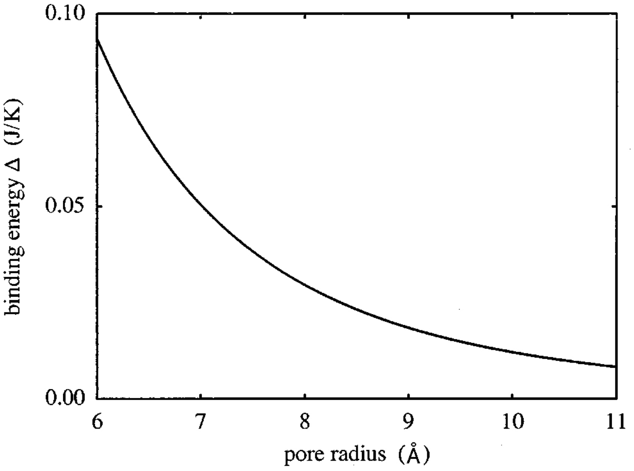

FIG. 1. Binding energy of the $(^3\mathrm{He})_2$ dimer in a superfluid ^{4}He background. The quasi-one-dimensional geometry of the narrow pore causes a power law relationship with pore radius, giving a sizeable value for the binding energy at small radii.

ticle is much larger than the typical scale of wall roughness, the approximation of a particle in a 2D potential box looks quite reasonable. Assuming the channel has axial symmetry, the normalized wave function reads,

$$\psi_{1m}^{(0)}(\vec{\rho}) = \frac{(-1)^{(m+1)}}{\pi^{1/2} J_1(\xi_m) R} J_0\left(\frac{\rho}{R}\xi_m\right), \quad m=1,2,3,\ldots, \tag{15}$$

where $J_0(\xi)$ and $J_1(\xi)$ are Bessel functions of the first kind, and ξ_m are the zeros of the function $J_0(\xi)$. Substituting the wave functions (15) into Eqs. (11) and (12) yields

$$\epsilon_r = 16 B_{nm}^2 \frac{\hbar^2}{Ma^2}\left(\frac{a}{R}\right)^4. \tag{16}$$

The numerical coefficient B_{nm} is defined as follows:

$$B_{nm} = \frac{1}{J_1^2(\xi_n) J_1^2(\xi_m)} \int_0^1 J_0^2(\xi_n z) J_0^2(\xi_m z) z\, dz. \tag{17}$$

Equation (16) gives the binding energy of a ^{3}He dimer in a cylindrical pore. The two ^{3}He atoms are confined in the xy plane by means of the walls of the pore whereas their relative motion along the z axis is finite due to the attractive interparticle interaction. In other words, two ^{3}He impurities can travel along the z axis only as a whole, i.e., as a 1D quasimolecule $(^3\mathrm{He})_2$.

Consider the case where both ^{3}He particles are in the ground state $m=1$, $\psi_{1m}=\psi_{2m}=\psi_1$. Using the typical values $M=2.33m_3$ and $a\approx -1.0$ Å,[20,4] we obtain the binding energy as a function of pore radius (Fig. 1). Considering a mordenite sample in which, typically, $R=7$ Å, we have $\epsilon_r = \Delta = 0.05$ K, which is quite a sizable effect from the viewpoint of modern low temperature experiment. Due to the power-law relationship, the binding energy is sizeable even at large radii. (The *upper* bound for the radius is provided by the criterion that the spacing between the transverse energy levels must be large compared to the temperature of the fluid.) The normalized wave function $\chi(z)$ of the bound state is

$$\chi(z) = (2\nu)^{1/2}\exp(-\nu|z|), \quad \nu^2 = \frac{M\Delta}{\hbar^2}, \quad z = z_2 - z_1. \tag{18}$$

The size of the dimer is

$$z_0 = \int_{-\infty}^{\infty} |z||\chi(z)|^2 dz = \nu^{-1} = \frac{\hbar}{(M\Delta)^{1/2}} = \frac{1}{4B_{11}}|a|\left(\frac{R}{a}\right)^2, \tag{19}$$

which leads to a quite macroscopic value $z_0 = 11.7$ Å. The smallest pore radius for which the dimer size exceeds R—if the system is then still within the ‘‘superfluid bulk-1D hybrid’’ regime—is $R=4.2$ Å. [The salient result is not particular values of $\epsilon(R)$, but the power-law dependence of the binding energy, which arises because of the restricted geometry.]

So far nothing has been said with regard to the spin structure of the dimer. In the case where both ^{3}He particles forming the dimer are in the ground state of the xy motion, the total wave function $\Psi(\vec{\rho}_1, z_1; \vec{\rho}_2, z_2)$ is symmetric, corresponding to a singlet (spinless) pairing of the ^{3}He impurities. If the ^{3}He particles were in different energy states, $|n\rangle \neq |m\rangle$, dimers of both the singlet and triplet type could exist. The correct wave function should then be constructed by a proper symmetrization or antisymmetrization.

III. THERMODYNAMIC FUNCTIONS: HIGH TEMPERATURES

The thermodynamic properties of a ^{3}He system in a superfluid ^{4}He background are strongly temperature dependent. The simplest and most practical limiting case is the high temperature regime in which quantum degeneracy effects may be neglected and the ^{3}He impurities forming an ideal Maxwell-Boltzmann gas are in the ground state for motion in the xy plane,

$$T_F^* \ll T \ll T_{\mathcal{E}}^*, \tag{20}$$

where $T_F^* = \pi^2\hbar^2 n_3^2/2M$ is the 1D Fermi degeneracy temperature for ^{3}He atoms, and $T_{\mathcal{E}}^*$ is the highest temperature at which a ^{3}He atom remains in the ground state. In this temperature regime, even if $T \gg \Delta$ and the number of dimers is negligibly small, the heat capacity per ^{3}He atom, $c_v = 1/2$, differs drastically from its value in bulk, $c_{v(\mathrm{bulk})} = 3/2$ due to the reduced geometry of the porous structure.

[The impurities in the superfluid background always form a weakly-interacting (almost ideal) gas or fluid—irrespective of the ^{3}He density—as long as one stays away from the phase separation concentration. The impurities form either a Maxwell-Boltzmann ideal gas or a highly correlated, degenerate weakly-interacting fluid (of bosons, fermions, or a mixture of both). In this sense, the impurity density (ignoring phonons etc. in the background superfluid) has no effect on the van der Waals interparticle interaction. Note also that this is a two-body interaction because the average interparticle spacing is always far greater than the interaction range, which falls off exponentially.

We note that the saturation concentration may be affected by a change in scattering length as channel radius is decreased (the mixture going from bulk to quasi-1D). We use the bulk value as an indicative upper bound. The existence, when the mixture is dilute enough, of ideal impurity gas conditions was shown in the relatively very high temperature experiments cited in footnote 3. The precise relationship between saturation concentration and radius is an open question, and an interesting possibility for experiment.]

To find the number density of dimers in equilibrium one should consider the ''chemical reaction'' $^3\mathrm{He}+{}^3\mathrm{He}\rightarrow({}^3\mathrm{He})_2$. The corresponding equilibrium condition is, $2\mu_1=\mu_2$, where μ_1 and μ_2 are the chemical potentials of the ^{3}He and $(^3\mathrm{He})_2$ components respectively. It is convenient to introduce the degree of dimerization, α, defined as

$$\alpha=\frac{2n_2}{n_3}, \quad n_1+2n_2=n_3. \tag{21}$$

Here n_1 and n_2 are the numbers of unpaired ^{3}He atoms and $(^3\mathrm{He})_2$ dimers, respectively, per unit length, and n_3 is the total number of ^{3}He atoms per unit length in the mixture. The thermodynamic functions in the high-temperature regime were calculated in Ref. 5. Reformulating the results obtained in that paper, using the Free Energy together with the chemical equilibrium condition, one can easily find that the total heat capacity C_v can be expressed in the form

$$C_v=\mathcal{N}n_3\left[\frac{1}{2}-\frac{\alpha}{4}+\frac{1}{2}\alpha\frac{1-\alpha}{1+\alpha}\left(\frac{\Delta}{T}+\frac{1}{2}\right)^2\right], \tag{22}$$

where $\mathcal{N}$ is the areal density of pores in the sample, and the degree of dimerization α is given by the equation,

$$\alpha=1+X-(X^2+2X)^{1/2},$$

$$X=\frac{1}{2\pi^{1/2}}\frac{\sqrt{MT}}{\hbar n_3}\exp\left(-\frac{\Delta}{T}\right)=\sqrt{\frac{\pi}{8}}\left(\frac{T}{T_F^*}\right)\exp\left(-\frac{\Delta}{T}\right). \tag{23}$$

The degree of dimerization tends to unity exponentially rapidly as $T\rightarrow T_{F+}^*$ (Fig. 2). As one would expect, a higher density facilitates dimerization. [The nature of this ''density dependence'' is the following. At sufficiently high temperature, Boltzmann statistics holds for the ^{3}He quasiparticles. For low density, the Fermi energy $T_F^*\ll\Delta$. Now suppose the mixture is cooled from some high initial temperature. Due to thermal agitation, there are virtually no dimers when $T_F^*\ll\Delta\ll T$. As the mixture is cooled below the binding energy Δ, with $T_F^*\ll T\lesssim\Delta$, the number of unpaired ^{3}He impurities decreases exponentially rapidly, $\alpha\rightarrow 1$. Impurities want to dimerize before the temperature reaches T_F^*, and they find it easy to do so because $T\lesssim\Delta$. This can be seen in the expression for the free energy (2.3) in Ref. 5. At higher densities within the Boltzmann regime, T_F^* is higher, so rapid dimer formation occurs sooner as T becomes comparable to Δ. Thus, ''higher density facilitates dimerization.'' But if the density is too high and channel radius too large, then it may happen that $T_F^*\gg\Delta$, and the fermi particles cannot effectively dimerize in the Maxwell-Boltzmann regime. Favorable circumstances for observing dimers occur when $T_F^*\ll\Delta$, and complete dimerization ($\alpha\rightarrow 1$) can occur before the system becomes degenerate. The ^{3}He density must be low enough (but not too low, if the experimental apparatus cannot reach T_F^*) and the channel narrow enough (but not too narrow, otherwise either the background stops being superfluid, or the dimer size z_0 will be smaller than the channel width, resulting in a rotational degree of freedom). Depending on the relative sizes of z_0^{-1} and n_3, we can have strong coupling, weak coupling, or anything in between, after the system becomes highly correlated.]

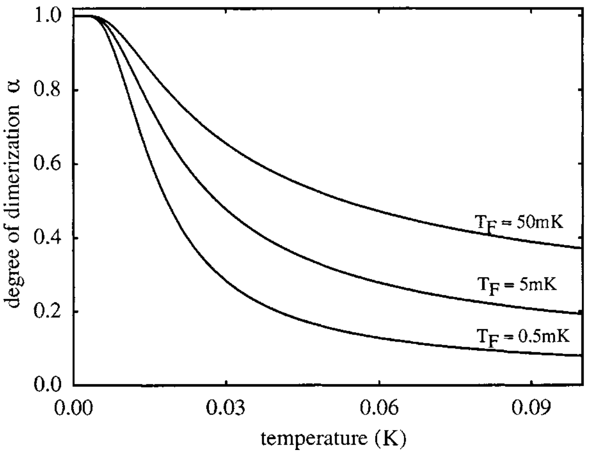

FIG. 2. Degree of dimerization of the ^{3}He component in superfluid ^{4}He as a function of temperature, in the high temperature regime. As the temperature is lowered, at low density, there is a region ($T\sim 10$ mK, for $R\sim 7$ Å) of exponential growth of the number of dimers, resulting in virtually complete dimerization at the degeneracy temperature. The ^{3}He component thus turns into a Bose gas of dimers. The ^{3}He Fermi temperature is limited above because of phase separation: in bulk mixture, this occurs at a concentration of $x\sim 0.06$, i.e., $T_F^*\sim 85$ mK. In channels, the actual phase separation concentration may depend on channel radius (see Sec. III). There is no lower limit on density, apart from that imposed by the limitations of the apparatus: if the apparatus cannot reach T_F^*, and since the degree of dimerization is an increasing function of n_3, the density cannot be too low if the sample is to contain a good proportion of dimers. In other words, given a particular apparatus, the ^{3}He impurity density n_3 must be high enough for dimers to be easily observable. But for larger channel widths, the density cannot be too high, otherwise $T_F^*\sim\Delta$ and complete dimerization cannot occur.

Since it is the singlet (spinless) dimerization that occurs predominantly in the ^{3}He component, directly measuring the magnetic susceptibility or conducting NMR experiments would probably be the best means of detecting the dimers. The magnetic susceptibility, χ, is given simply by the number of the unpaired ^{3}He atoms,

$$\chi=\frac{\beta^2}{T}\mathcal{N}n_3(1-\alpha), \tag{24}$$

where β is the nuclear magnetic moment of ^{3}He. The temperature dependence of the heat capacity and magnetic susceptibility is shown in Figs. 3(a) and 3(b). The effect seems to be sizable enough to be experimentally observable.

It may be noted that the effective interaction between the dimers themselves could prove attractive, which could lead to the formation of quadrumers. Generalizing this possibility one could end up with a polymer state involving $n\geqslant 2$ atoms of ^{3}He or even with an antiferromagnetlike chain $n\rightarrow\infty$ at

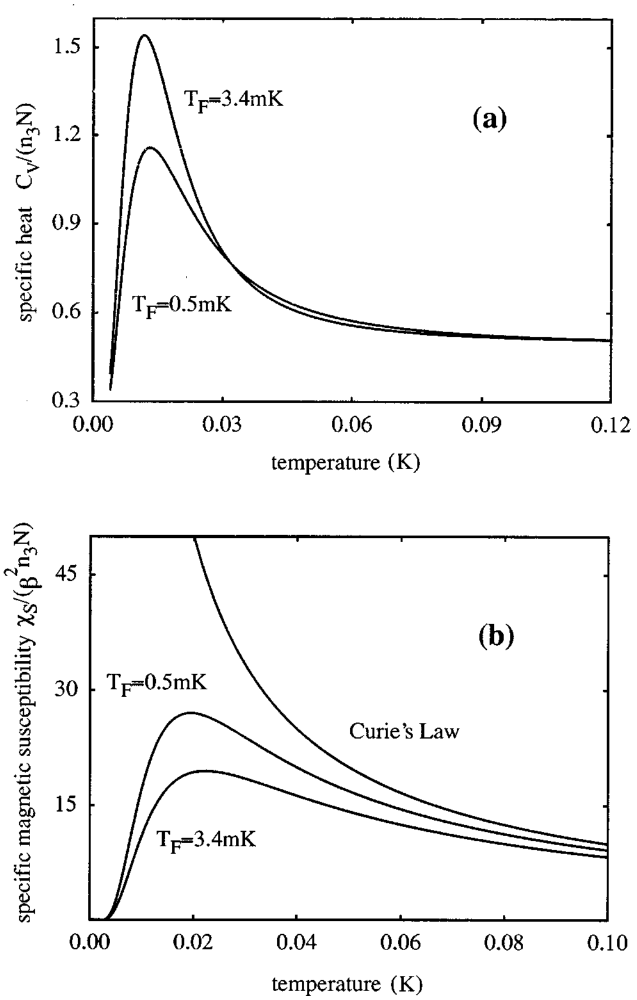

FIG. 3. Specific magnetic susceptibility and specific heat of a dilute mixture of ^{3}He in superfluid ^{4}He. At $T \sim 10$ mK, dimerization causes pronounced deviation from the behavior expected if dimers were absent. In (a), the specific heat deviates from the high temperature value of $c_v = 1/2$. In (b), the magnetization deviates markedly from Curie's Law.

$T \to 0$. To describe such states one would need somehow to take many-particle effects into consideration. To some extent collective effects are considered in the next section on the basis of the Bethe ansatz.

[Such a 1D chain could be capable of information transfer: the flipping of a spin at one end would propagate a spin wave through the chain to the other end, causing the spin of the last particle to flip. The decisive factor in the formation of such a 1D wire may well turn out to be the influence of the corrugation of the channel walls, even when the ^{3}He gas does not feel the potential of the channel wall ''substrate.'' This would be analogous to the ''4/7 commensurate phase'' observed when pure ^{3}He is adsorped onto a 2D graphite substrate (see Ref. 38). The 4/7 phase could not exist without substrate corrugation, and the second ^{3}He layer feels only other ^{3}He atoms (in our case it would also feel the background ^{4}He superfluid).]

IV. THERMODYNAMIC FUNCTIONS: LOW TEMPERATURES

In the low temperature limit, $T \lesssim T_F^*$, many-body correlations and quantum-statistical effects pertaining to 1D systems become important and have to be taken into account. Fortunately, in the limiting case $R \gg d$, the problem effectively reduces to one with the δ-function pseudopotential (see above and Ref. 23) and can be solved exactly. To be specific and to avoid extra complications related to the symmetry of the total wave function we will restrict ourselves to considering an ''antiferromagnetic'' chain of ^{3}He particles along the pore in the absence of an external magnetic field. The corresponding Hamiltonian reads

$$\hat{H} = -\frac{\hbar^2}{2M}\sum_{i=1}^{N_3}\frac{d^2}{dz_i^2} - \frac{4\pi\hbar^2|a|}{ML^2}\sum_{i<j}\delta(z_i - z_j). \tag{25}$$

Here N_3 is the total number of ^{3}He atoms in the pore, and L is defined by Eq. (11). For the case where the ^{3}He impurities are in the ground state,

$$T \lesssim T_F^* \ll \frac{\hbar^2}{2MR^2}(\xi_2^2 - \xi_1^2), \tag{26}$$

the characteristic length L can be expressed in the form,

$$\frac{1}{L^2} = \frac{2}{\pi R^2}B_{11}. \tag{27}$$

Let the Hamiltonian (25) be rewritten in the following dimensionless form:

$$\hat{H}' = \hat{H}\frac{2M}{\hbar^2 n_3^2} = -\sum_{i=1}^{N_3}\frac{d^2}{d\zeta_i^2} - 2\lambda\sum_{i<j}\delta(\zeta_i - \zeta_j). \tag{28}$$

where new coordinates $\zeta_i = n_3 z_i$ are introduced, and the positive coupling constant λ is defined as follows:

$$\lambda = 4\pi\frac{|a|}{n_3L^2} = 8B_{11}\frac{|a|}{n_3R^2} = \frac{2}{n_3z_0} = \pi\left(\frac{2\Delta}{T_F^*}\right)^{1/2} = 2\eta. \tag{29}$$

Here z_0 is the size of the dimer calculated in Eq. (19). Varying λ by changing the density n_3 one could trace the crossover from a correlated Fermi gas (similar to the Cooper pairing regime in conventional BCS superconductors) where the size of the dimer z_0 would considerably exceed the average spacing between the ^{3}He impurities, to an interacting Bose fluid of dimers in the limiting case of $z_0 \ll n_3^{-1}$.

A method based on the celebrated Bethe ansatz for finding an exact solution to the Schrödinger equation for a one-dimensional system of particles interacting via a δ-function potential was developed and successfully applied to both bosons and fermions by Yang and Yang,[24] Lieb *et al.*,[25] Takahashi,[26] Gaudin,[27] and others (for review see Ref. 28). In our analysis of the low temperature behavior of thermodynamic functions we will use the results obtained by Lai[29] that describe the thermodynamics of attractive spin one-half fermi particles in one dimension on the basis of the Hamiltonian (28). According to Lai,[29] the energy density $\mathcal{E}$ and number density $\mathcal{N}$ per unit pore length of the system in equilibrium can be presented in the form,

$$\mathcal{E} = 2\int_{-\infty}^{\infty}(k^2 - \eta^2)\rho\,dk + \int_{-\infty}^{\infty}k^2\tau\,dk,$$

$$\mathcal{N}=2\int_{-\infty}^{\infty}\rho dk+\int_{-\infty}^{\infty}\tau dk, \tag{30}$$

where the distribution functions $\rho(k)$ and $\tau(k)$ are defined as follows:

$$\rho(k)=\frac{-1}{2\pi}\frac{\partial\epsilon(k)/\partial A}{1+e^{\epsilon(k)/T}},\quad \tau(k)=\frac{-1}{2\pi}\frac{\partial\psi(k)/\partial A}{1+e^{\psi(k)/T}}. \tag{31}$$

The effective excitation energies ϵ and ψ entering Eqs. (31) are given by the following set of integral equations,

$$\begin{aligned}
\epsilon(k)&=2(k^2-\eta^2)-2A-T\int_{-\infty}^{\infty}K_2(k-k')\ln(1+e^{-\epsilon(k')/T})dk'-T\int_{-\infty}^{\infty}K_1(k-k')\ln(1+e^{-\psi(k')/T})dk',\\
\psi(k)&=k^2-A-T\int_{-\infty}^{\infty}K_1(k-k')\ln(1+e^{-\epsilon(k')/T})dk'-\frac{T}{2}\int_{-\infty}^{\infty}G_1(k-k')\ln(1+e^{-\psi(k')/T})dk'\\
&\quad+\frac{T}{2}\int_{-\infty}^{\infty}G_0(k-k')\ln(1+e^{\phi_1(k')/T})dk',\\
\phi_\nu(k)&=\frac{T}{2}\int_{-\infty}^{\infty}G_0(k-k')\ln(1+e^{\phi_{\nu+1}(k')/T})dk'+\frac{T}{2}\int_{-\infty}^{\infty}G_0(k-k')\ln(1+e^{\phi_{\nu-1}(k')/T})dk',\\
&\lim_{\nu\to\infty}\int_{-\infty}^{\infty}G_0(k-k')\{\ln(1+e^{\phi_\nu(k')/T}-\ln(1+e^{\phi_{\nu-1}(k')/T}\}dk'=0,
\end{aligned} \tag{32}$$

where $\nu\geqslant 1$, $\phi_0=\psi$, the other ϕ_{nu} also being excitation energies, and the kernels $K_n(x)$ and $G_n(x)$ are defined as

$$K_n(x)=\frac{1}{\pi n\eta}\frac{1}{1+\left(\dfrac{x}{n\eta}\right)^2},$$

$$G_n(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{e^{-i\omega x}e^{-n\eta|\omega|}}{\cosh\eta\omega}d\omega. \tag{33}$$

The quantity A in Eqs. (31) and (32) is the Lagrange multiplier for the condition $\delta\mathcal{N}=0$ when minimizing the free energy.

Equations (30)–(34) provide a complete thermodynamic description of a system with the reduced Hamiltonian (28) valid at arbitrary values of λ, i.e., at any density n_3. These equations can, in principle, be analyzed numerically for any given density and temperature. Since there are no experimental data available at sufficiently low temperatures in situations where this model is applicable, no computations for any particular densities and temperatures will be considered here. Instead we will discuss general features of the solutions and the temperature dependence of thermodynamic functions in the two limiting cases of high densities (small λ) and of a dilute gas of dimers (large λ).

The first case, $\lambda\ll 1$, corresponds to a sufficiently high number density, n_3, per unit length along the pore,

$$\frac{1}{z_0}\ll n_3\ll\frac{1}{R}. \tag{34}$$

The right-hand side of criterion (34) is equivalent to Eq. (20) and expresses the condition under which most ^{3}He impurities occupy the ground state for the motion in the xy plane. In this situation where a formally calculated dimer size is greater than the average interparticle separation, one cannot actually consider the dimer as a real particle. Rather, one should talk about a correlated fermion pair with the characteristic coherence length of the order of z_0. In the extreme limiting case $\lambda\to 0$, the kernels in the integrals in Eqs. (32) reduce to delta-functions, $K_n(x)\to\delta(x)$ and $G_n(x)\to\delta(x)$. Under these conditions all the equations drastically simplify and, as was shown in Ref. 29 and as is, indeed, quite natural, reduce to the ones pertaining to a free fermion gas with the chemical potential A. The heat capacity of the gas is proportional to the temperature and can be expressed in terms of the density of states in the standard fashion (usual units),

$$C=\frac{\pi^2}{3}T\left(\frac{dk}{d\epsilon}\right)_A=\frac{MT}{3\hbar^2 n_3}. \tag{35}$$

The second case of interest, $\lambda\to\infty$, is more tricky. This situation implies a sufficiently low density of ^{3}He particles,

$$n_3\ll\frac{1}{z_0}, \tag{36}$$

so that the size of the dimer is much smaller than the average distance between ^{3}He impurities and one can definitely identify dimers as real one-dimensional molecules. The system of ^{3}He atoms can thus be viewed as a dilute mixture of $(^3\mathrm{He})_2$ dimers and unbound ^{3}He particles (monomers). As $\lambda\to\infty$, the integrals containing the kernels K_2, K_1, and G_1 do not contribute. Taking this into account one can conclude that with good accuracy the potentials ϕ_ν from Eqs. (32) are positive constants that satisfy the following functional relations:

$$2x_\nu = \ln(1+x_{\nu+1})(1+x_{\nu-1}), \quad x_\nu = \frac{\phi_\nu}{T}. \tag{37}$$

After simple algebra we obtain

$$\epsilon(k) = 2k^2 - 2A_0, \quad A_0 = 2(\eta^2 + A),$$

$$\psi(k) = k^2 - A_1, \; A_1 = A - \frac{T}{2}\ln(1+x_1). \tag{38}$$

As was spelled out above, in the case in question one can always distinguish between the contribution of dimers and unpaired atoms. Quantity A does not make sense as an effective chemical potential any longer. Instead one has to deal with the chemical potentials μ_1 and μ_2 of both species, i.e., of the ''monomers'' and dimers, respectively. The equilibrium densities of both components, n_1 and n_2 should again be found from the conditions

$$2\mu_1 = \mu_2, n_1 + 2n_2 = n_3. \tag{39}$$

However, one can easily convince oneself that at zero temperature and in the low-density limit Eq. (39) does not have a solution, simply because $\mu_1 \to \Delta_0$ as $n_3 \to 0$ (in an ideal gas $\mu_3 \propto n_3^2$, and Δ_0 is the binding energy with the superfluid background) whereas $\mu_2 \to -|\Delta| + 2\Delta_0$ under the same conditions. In other words, at $T=0$ and $\lambda \to \infty$ where the chemical potential μ_2 of the dimers is always smaller than that of the unbound particles, μ_1, there are no ''monomers'' at all and only the dimerized phase of $(^3\mathrm{He})_2$ survives. When formulated in terms of the reduced dimensionless Hamiltonian (28) and the corresponding variables in Eqs. (31) and (38) this criterion is equivalent to the situation in which at $T=0$ the function $\psi(k)$ can never be negative, i.e., $\psi(k) \geqslant 0$ for all k. In this case the terms containing the ''monomer'' distribution function τ do not contribute to the thermodynamics. Simple calculations using Eqs. (30), (31) and (38) at $T=0, \lambda \gg 1$ lead to

$$A = \frac{\pi^2 \mathcal{N}^2}{16} - \frac{\lambda^2}{4} < 0,$$

$$\mathcal{E} = \frac{\mathcal{N}}{4}\left(\frac{\pi^2 \mathcal{N}^2}{12} - \lambda^2\right),$$

$$\mu_2 = -\frac{\lambda^2}{2} + \frac{\pi^2 \mathcal{N}^2}{8}. \tag{40}$$

At finite but sufficiently low temperatures, $T \neq 0$, even in the case of $\lambda \to \infty$ a small number of unpaired particles can appear in the system due to the thermal decay of the dimers. However, the contribution of these ''monomers'' is exponentially small as the temperature is lowered and can still be neglected. On the other hand, the temperature dependent corrections to A and consequently to A_0 provide an important contribution to thermodynamic properties and should be taken into account. Substituting the low-temperature expansion of the distribution function $\rho(k)$,

$$\frac{1}{1+\exp\frac{\epsilon(k)}{T}} = \Theta(e)\Theta(A_0 - e) - \frac{\pi^2}{24}T^2 \frac{\partial}{\partial e}\delta(e - A_0), e = k^2, \tag{41}$$

into Eqs. (30) and (31) one immediately obtains

$$\mathcal{E} = \frac{4}{\pi}\int_0^{A_0} e\frac{dk}{de}de + \frac{\pi}{6}T^2\left[\frac{\partial}{\partial e}\left(e\frac{dk}{de}\right)\right]_{e=A_0} - \eta^2 \mathcal{N},$$

$$\mathcal{N} = \frac{4}{\pi}\int_0^{A_0}\frac{dk}{de}de + \frac{\pi}{6}T^2\left[\frac{\partial}{\partial e}\left(\frac{dk}{de}\right)\right]_{e=A_0}. \tag{42}$$

Differentiating $\mathcal{E}$ with respect to the temperature and taking into account the obvious relation

$$\frac{\partial \mathcal{N}}{\partial T} = \frac{4}{\pi}\left[\frac{dk}{de}\right]_{e=A_0}\frac{\partial A_0}{\partial T} + \frac{\pi}{3}T\left[\frac{\partial}{\partial e}\left(\frac{dk}{de}\right)\right]_{e=A_0} = 0, \tag{43}$$

one can easily end up with the sought after specific heat,

$$C = \frac{\pi}{6}T\frac{1}{A_0^{1/2}} = \frac{2T}{3\mathcal{N}}, \tag{44}$$

or in conventional units,

$$C = \frac{4MT}{3\hbar^2 n_3}. \tag{45}$$

Thus the temperature dependence of the heat capacity cannot be a decisive factor in distinguishing between Fermi-like (unbound particles) and Bose-like (dimers) behavior as this dependence proves to be linear in both cases. In other words, the difference between the properties of a Fermi gas and of a Bose gas in one dimensional geometry is much more subtle than in the 3D case, a point which has already been discussed in the literature.

We have considered the exact solution of Lai's model in the two limiting cases of high and low densities of ^{3}He particles where the ^{3}He component manifests itself as a Fermi gas of ''monomers'' and pure Bose fluid of dimers, respectively. The critical concentration, n_{3c}, at which the crossover between two those regimes occurs, is of the order of z_0^{-1} and should be found by exactly solving Eqs. (30)–(33) at arbitrary $\lambda \sim 1$. The situation very much resembles the crossover between the Cooper pair and Bose molecule regimes in three-dimensional BCS superconductors[30,31,33] and 2D Fermi fluids.[7,32]

V. ABSORPTION OF SOUND

The presence of $(^3\mathrm{He})_2$ dimers can drastically influence the attenuation of the first sound in a dilute ^{3}He-^{4}He mixture. An extra absorption mechanism due to the decay of the dimerized state in the field of the acoustic wave can exhibit itself at sufficiently low temperatures. It was shown in Ref. 5 that the sound absorption coefficient in a dimerized quasi-1D ^{3}He system should have a clearly pronounced resonant character. To come up with quantitative figures that can be used when running an experiment, one has to take into account the quantum-mechanical indistinguishability of two ^{3}He particles and the Doppler effect due to the thermal motion of the dimers.

The calculation of the sound absorption coefficient proceeds in a natural way once the wave function for the acoustically split ^{3}He particles is known. Since the $(^3\text{He})_2$ dimer in the ground state is spinless, the dissociated ^{3}He particles have opposite spin (equal to a half). In concordance with the validity of the Fermi renormalization method (in the Born approximation), and by virtue of the Hamiltonian of Eqs. (25) and (28), the motion in the narrow pore reduces to that of fermions interacting with an attractive delta function pseudopotential in one dimension. The explicit exact solution to this two body problem, obtained by McGuire,[34] shows that when the length of the pore is much greater than the scattering length of the delta function potential, the momentum eigenvalues of the unpaired particles are independent of the attraction strength to an exponentially small error; that is, apart from an exponentially small (but finite) term, the particles are free of each other's influence once they separate and the final spatial wave function is simply a symmetric superposition of plane waves corresponding to a singlet state of free fermions.

To begin with, the transition probability is calculated in the center-of-mass system for the case of no thermal motion of dimers (i.e., $T=0$, no Doppler shift). The absorption mechanism exists because of the inelastic single-phonon process whereby the $(^3\text{He})_2$ dimer is split by a sound wave of definite frequency $\omega_0 \geqslant |\Delta|/\hbar$. The golden rule reads

$$dw = \frac{2\pi}{\hbar} |\langle \psi_f | \hat{H}_{int} | \psi_i \rangle|^2 \delta(-\Delta + \hbar\omega - E) \frac{dp}{2\pi\hbar}, \quad (46)$$

where E and p are the energy and momentum of the relative motion of the particles in the final state, $\psi_i = \chi(z)$, given by Eq. (18), is the normalized wave function of the initial state, and ψ_f is a symmetric superposition of plane waves propagating along the z axis, which in the c.m.s. is

$$\psi_f = 2^{1/2} \cos\frac{pz}{\hbar}. \quad (47)$$

To construct the operator $\hat{H}_{int}$ for the interaction of a $(^3\text{He})_2$ dimer with the phonon field in the superfluid ^{4}He background, we start with the interaction $\hat{V}_{int}$ of a single ^{3}He impurity with the acoustic wave,[35,4,20] which has the form

$$\hat{V}_{int} = \frac{\partial \epsilon_0}{\partial \rho} \delta\hat{\rho} + \frac{1}{2} \frac{\delta M}{M} (\hat{p}\hat{v}_s + \hat{v}_s \hat{p}), \quad (48)$$

where $\epsilon_0 \approx -2.8$ K is the binding energy of a single impurity atom with the superfluid ^{4}He background, ρ is the density of the pure ^{4}He in equilibrium, $\hat{p} = -i\hbar\partial/\partial z$ is the momentum operator, $\delta\hat{\rho}$ and $\hat{v}_s$ are hydrodynamic operators for the density and velocity (respectively) of the ^{4}He superfluid under acoustic perturbation, and $\delta M = M - m_3$, m_3 being the atomic mass of ^{3}He. The operators $\delta\hat{\rho}$ and $\hat{v}_s$ are defined by the expressions,

$$\delta\hat{\rho} = a e^{-i\omega_0 t + iqz}, \quad \hat{v}_s = b e^{-i\omega_0 t + iqz}. \quad (49)$$

Here $\hbar q = \hbar\omega_0/c$ is the momentum of the acoustic phonon, assumed definite for simplicity, c is the speed of first sound in liquid ^{4}He, and a and b are normalizing constants. In the zeroth order of ^{3}He concentration, the equation of continuity

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho v_s = 0 \quad (50)$$

yields the relation

$$a = \frac{\rho b}{c}. \quad (51)$$

The intensity of the sound wave is $\rho c \overline{v_s^2} = \frac{1}{2}\rho c |b|^2$, which gives the constant b normalized to one phonon,

$$|b|^2 = \frac{2\hbar\omega_0}{\rho c}. \quad (52)$$

Combining Eqs. (48), (49), and (52) for two ^{3}He particles that form a $(^3\text{He})_2$ dimer we arrive at the Hamiltonian $\hat{H}_{int}$ of the dimer-phonon interaction in the c.m.s.,

$$\hat{H}_{int} = 2b \frac{\rho}{c} \frac{\partial \epsilon_0}{\partial \rho} \cos\frac{qz}{2} + i \frac{\delta M}{M} b \left(\hat{p} \sin\frac{qz}{2} + \sin\frac{qz}{2} \hat{p} \right). \quad (53)$$

To avoid lengthy expressions we will restrict ourselves to calculating the cross section of sound absorption in the dipole approximation only, in which the phonon momentum $q \to 0$, and the second term in Eq. (53) is neglected. The phenomenon is then similar to the well known effect in classical electrodynamics in which neither dipole radiation nor absorption exist in a system of charged particles that have the same charge-to-mass ratio. For this reason the recoil momentum $\hbar q$ in the operators $\delta\hat{\rho}$ and $\hat{v}_s$ is then also neglected. The criterion of validity for the dipole approximation is $qd \ll 1$ which is consistent with the hydrodynamic conditions applying here.

Substituting the Hamiltonian (53) and Eq. (52) into Eq. (46) yields the zero-temperature cross section per particle $\sigma(\omega_0)$ for acoustic splitting at constant pore radius,

$$\sigma(\omega_0) = \frac{2M\omega_0}{p} \frac{\rho}{\hbar c^3} \left(\frac{\partial \epsilon_0}{\partial \rho} \right)^2 [\chi(k) + \chi(-k)]^2,$$

$$\chi(k) = \frac{2\nu^{3/2}}{\nu^2 + k^2}, \quad \hbar k = p. \quad (54)$$

Here $\chi(k)$ is the Fourier transform of the wave function (18) of the initial dimerized state, and ν is the inverse dimer size given in Eq. (19). Taking into account the energy conservation law

$$\frac{p^2}{M} + \Delta = \hbar\omega_0, \quad (55)$$

one obtains the expression

$$\sigma(\omega_0) = 32 \frac{\rho}{\hbar c^3} \left(\frac{\partial \epsilon_0}{\partial \rho} \right)^2 \frac{\eta^{3/2}}{(1-\eta)^{1/2}}, \quad \eta = \frac{\Delta}{\hbar\omega_0}. \quad (56)$$

In agreement with general principles regarding the behavior of cross sections near reaction thresholds,[6] the cross section (56) is proportional to the momentum p and thus diverges like $(\hbar\omega_0-\Delta)^{-1/2}$ as $\eta\to 1$.

In a realistic experiment, thermal motion of dimers as well as nonmonochromaticity of the emitted sound signal will cause the singularity to be smoothed over. We proceed now to consider the effect on the singularity of thermal motion in the high temperature regime in which the $(^3\mathrm{He})_2$ dimers form a classical Maxwell-Boltzmann gas.

In the high temperature regime the dimers in equilibrium are in random thermal motion along the length of the pore, their velocities distributed according to the Maxwell distribution. The frequency of phonons arriving at the dimers is Doppler shifted according to

$$\omega=\omega_0\left(1+\frac{v_z}{c}\right). \tag{57}$$

For a phonon of definite source frequency ω_0, one must take into account all scattering events for which the arrival energy $\hbar\omega\geqslant\Delta$, which is the single fact that gives rise to the smoothing of the singularity. The total cross section per particle for acoustic splitting at constant pore radius is

$$\sigma_{MB}(\omega_0)=\int_{\Delta/\hbar}^{\infty}\sigma(\omega)g(\omega)d\omega, \tag{58}$$

where $g(\omega)d\omega$ is the Maxwell-Boltzmann probability per particle of a phonon arriving at a dimer with Doppler shifted energy $\hbar\omega$,

$$g(\omega)d\omega=\frac{1}{\pi^{1/2}\omega_0}\zeta^{1/2}\exp\left[-\zeta\left(\frac{\omega}{\omega_0}-1\right)^2\right]d\omega, \tag{59}$$

where we have introduced the dimensionless parameter $\zeta=Mc^2/T$. Expressing the cross-section integral (58) in terms of the parameters ζ and η, we have

$$\sigma_{MB}(\zeta,\eta)=\frac{32}{\pi^{1/2}}\frac{z_0}{n_3}\theta J(\zeta,\eta), \tag{60}$$

where θ is a dimensionless parameter,

$$\theta=\frac{\rho}{\hbar c^3}\left(\frac{\partial\epsilon_0}{\partial\rho}\right)^2\frac{n_3}{z_0}, \tag{61}$$

and

$$J(\zeta,\eta)=\eta\zeta^{1/2}e^{-\zeta(\eta-1)^2}\int_0^{\infty}t^{-1/2}(1+t)^{-1}e^{-at-bt^2}dt,$$

$$a=2\zeta\eta(\eta-1),\quad b=\zeta\eta^2. \tag{62}$$

Using a saddle-point method, one finds to order $O(1/(2\zeta^{1/4}\eta^{1/2}))$,

$$J(\zeta,\eta)\sim\sqrt{\pi}\frac{\eta^2+\eta-1}{\eta^{1/2}}\zeta^{1/4}e^{-\zeta(\eta-1)^2}H_{-1/2}(\zeta^{1/2}(\eta-1)), \tag{63}$$

where $H_{-1/2}(x)$ is a Hermite function.

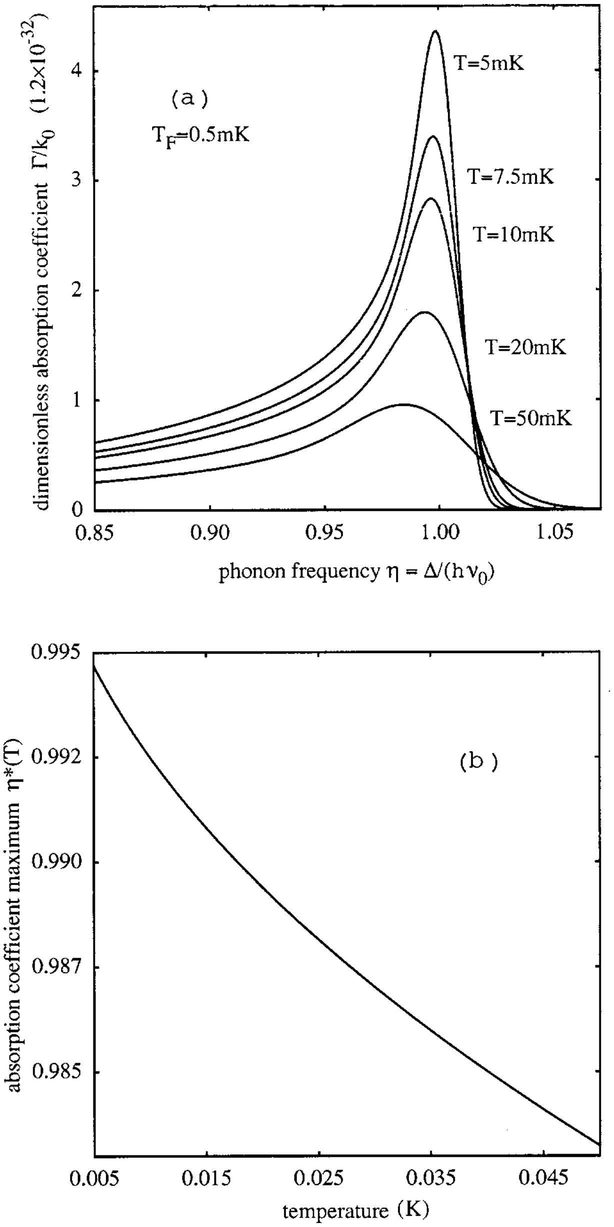

FIG. 4. Resonance peak for acoustic splitting of dimers in a dimerized ^{3}He component in superfluid ^{4}He. (a) is a plot of the exact dimensionless function $\Gamma^*=\Gamma/k_0=\eta\alpha J(\zeta,\eta)$ (1.2×10^{-32}) at a density of $T_F^*=0.5$ mK, where Γ is the absorption cross-section calculated with the Maxwell distribution. Damping is caused at high temperatures by thermal disruption of dimers. (b) shows the displacement of the absorption cross-section peak with temperature. Displacement towards $\eta=1$ slows markedly with falling temperature.

We define the absorption coefficient in one dimension for the narrow pore problem in the high temperature regime as

$$\Gamma_{1D}=\frac{n_2}{A}\sigma_{MB}=\frac{\alpha}{2}\frac{n_3}{A}\sigma_{MB}=\frac{16}{\pi^{1/2}}\frac{z_0}{A}\theta\alpha J(\zeta,\eta), \tag{64}$$

where A is the (fixed) cross-sectional area of the pore, and α is the degree of dimerization defined in Eqs. (21) and (23). The dimensionless ratio of the absorption coefficient and phonon wave number [Fig. 4(a)] is given simply by

$$\Gamma^*_{1D}=\frac{\Gamma_{1D}}{k_0}=16\frac{\hbar c}{\Delta}\frac{z_0}{A}\theta\eta\alpha J(\zeta,\eta), \tag{65}$$

where c is the speed of first sound in superfluid ^{4}He.

The total cross section for acoustic splitting $\sigma(\zeta,\eta)$ is finite and smooth at $\eta=1$. As the temperature is increased from the lower end of the Maxwell-Boltzmann regime, an asymmetric distribution appears which shows the strong influence of the exponential factor in the Maxwell velocity distribution. The maximum of the absorption cross section shifts towards decreasing values of η [Fig. 4(b)]; i.e., towards higher phonon source frequencies ω_0. This can be understood as follows. Although the Maxwell velocity distribution for motion along the pore is a Gaussian that is symmetric about $v_z=0$, only dimers with a sufficiently large velocity towards the phonon source can be acoustically split: there is a threshold energy below which the phonon has no effect, and only these dimers see a sufficiently large Doppler-shifted phonon energy. Thus an asymmetry is introduced into the problem. As the temperature is increased, the Maxwell distribution becomes broader and flatter, which means there are fewer low speed splittable dimers: the most probable energy for splitting shifts towards higher dimer speed and hence higher phonon source frequency. The position of the absorption cross-section peak should be found from the transcendental equation,

$$\frac{H_{-3/2}(\zeta^{1/2}(\eta-1))}{H_{-1/2}(\zeta^{1/2}(\eta-1))}=-2\zeta^{1/2}(\eta-1), \tag{66}$$

which is obtained by only keeping terms to $O(1/\zeta^{1/4})$ in the asymptotic series for the derivative of the exact integral (62) then setting the derivative to zero (otherwise ill-conditioning will cause problems with numerical algorithms). Using properties of cylinder functions (see Ref. 37), analysis of the transcendental equation (66) yields for the position of the absorption cross-section peak, to order $O([\zeta^{1/2}(\eta-1)]^3)$,

$$\eta^*(T)\approx 1-\frac{1+A^2+(1+2A^2-3A^4)^{1/2}}{2A^3}\frac{1}{\sqrt{\zeta(T)}},$$

$$A=\frac{2\Gamma\left(\frac{3}{4}\right)}{\Gamma\left(\frac{1}{4}\right)}. \tag{67}$$

Taking a working density of 3.84×10^7 m^{-1} ($T_F^*=0.5$ mK, concentration $x=0.000026$, one ^{3}He particle every 260 Å along the pore), for $R=7$ Å, the independent parameters are explicitly,

$$\zeta=\frac{Mc^2}{k_BT}\approx\frac{48.4}{T(\mathrm{K})},\qquad \eta=\frac{\Delta}{\hbar\omega_0}\approx\frac{6.6\times 10^9}{\omega_0(\mathrm{rad\,s^{-1}})},$$

$$\theta\approx 6.9\times 10^{-43}n_3\ \ (\mathrm{m}^{-1}), \tag{68}$$

where the last quantity was evaluated using the dimensionless group

$$\frac{\rho}{m_4c^2}\frac{\partial\epsilon_0}{\partial\rho}=1.28, \tag{69}$$

m_4 being the bare mass of a ^{4}He atom. The position of the absorption cross-section peak is then given by

$$\eta^*(T)\approx 1-0.0750\sqrt{T}. \tag{70}$$

The temperatures for which quantum degeneracy and thermal excitation effects can be neglected suggest bounds of the order $2420\lesssim\zeta\lesssim 9680$, while in view of the high frequencies involved (hypersound) we would expect experimental equipment to attain a narrow range in the vicinity of $\eta=1$; say, $0.95\lesssim\eta\lesssim 1.05$. The accuracy of the approximation (63) (i.e., the ratio of second and first terms of the asymptotic expansion) for the sound absorption coefficient is better than 2% at higher temperatures, and gets *worse* as the temperature is lowered, tending to $\eta(\eta-1)/[2(\eta^2+\eta-1)]$ for all low temperatures. Close to the maximum the approximation is better than 0.05% at low temperatures.

It is an open question as to what happens in the cross-over region between the semi-classical and degenerate regimes. As noted above, the dimers may well form quadrumers and longer polymers as the temperature is lowered. In any case, one might expect that thermal effects would ensure the presence of a transition region in which dimers exist in their own right. It is well known that even a small attraction in one dimensional systems causes drastic deviation from ideal gas behavior even in dilute systems. However, here we are considering a quasi-one-dimensional dilute gas in a narrow pore. An experiment that confirms ideal gas behavior for the system in the cross-over region would imply that realistic application of one dimensional models is critically dependent on the confinement length in the x-y plane. To this end, it is worthwhile to calculate the absorption cross section with the assumption that in the cross-over region, the dimers behave like an ideal Bose gas in vacuum.

The Bose-Einstein probability per particle of a phonon of frequency ω_0 arriving at a dimer with Doppler shifted energy $\hbar\omega$ is,

$$f(\omega)d\omega=\frac{4Mc}{hn_3\omega_0}\frac{d\omega}{\exp\left[\gamma+\zeta\left(\frac{\omega}{\omega_0}-1\right)^2\right]-1}, \tag{71}$$

where γ is found from the normalization condition,

$$1=\delta\int_0^\infty\frac{de}{\sqrt{e}(\exp(\gamma+e)-1)},\qquad \delta=\frac{4\sqrt{Mk_BT}}{hn_3}=\sqrt{\frac{2T}{T_F^*}}. \tag{72}$$

The total cross section per particle for acoustic splitting is then given by

$$\sigma_{BE}(\zeta,\eta)=\int_{\frac{\Delta}{\hbar}}^{\infty}\sigma(\omega)f(\omega)d\omega$$

$$=32\frac{z_0}{n_3}\theta\left(\frac{4Mc}{hn_3}\right)\sum_{n=1}^{\infty}e^{-n\gamma}\frac{J_n(\zeta,\eta)}{\zeta^{1/2}}, \tag{73}$$

where

$$J_n(\zeta,\eta)=\eta\zeta^{1/2}e^{-n\zeta(\eta-1)^2}\int_0^\infty t^{-1/2}(1+t)^{-1}e^{-n(at+bt^2)}dt, \tag{74}$$

with a and b as in Eq. (62). Use of the same saddle-point method as before yields

$$J_n(\zeta,\eta)\sim\sqrt{\pi}\frac{\eta^2+\eta-1}{\eta^{1/2}}\zeta^{1/4}\frac{e^{-n\zeta(\eta-1)^2}}{n^{1/4}}H_{-1/2}(\sqrt{n\zeta}(\eta-1)) +O(1/(2\zeta^{1/4}\eta^{1/2})). \tag{75}$$

Expressing the integrand in Eq. (72) as an infinite series and keeping only the first term, one obtains the well-known high temperature asymptotic form of γ, $\gamma_{high}=\log\sqrt{\pi}\delta$. Substituting γ_{high} into Eq. (73) and allowing the temperature to grow large shows that $\sigma_{BE}\rightarrow\sigma_{MB}$. At lower temperatures, as expected, the cross section manifests enhanced acoustic splitting due to the tendency of the Bose particles to attain like velocities as they are cooled [Figs. 5(a) and 5(b)].

It should be emphasized that the above treatment considered the propagation of sound through a liquid that fills narrow pores, rather than a solid matrix (capillary walls). Exciting sound vibrations in the liquid that fills a nanoporous medium may present a difficult technical problem. It may be easier to let a sound wave propagate through an acoustically inhomogeneous system, e.g., a porous sample filled with the fluid, as a whole. In the latter case some expressions such as Eqs. (51) and (52) can no longer be used and the appropriate part of the description should be modified. However, the statement regarding the resonant sound absorption associated with the decay of the dimerized states as well as the description of the resonance peak remain valid. Observing nonmonotonic resonant behavior of the sound absorption would provide direct evidence for the existence of dimers.

VI. CONCLUDING REMARKS

All the above results apply directly to any rarefied system in restricted geometries provided the s-wave scattering length for a two-particle collision is negative. It might be tempting to try to detect dimers in various gases placed in porous media. Experimental data of Wada *et al.*[12,13] on the heat capacity show a one-dimensional gas-like behavior of a sufficiently small amount of ^{4}He in the pores of K-L zeolite. By measuring the isosteric heat of sorption Takaishi *et al.*[36] observed one-dimensional gas states of Xe and Ar atoms in the one-dimensional channel network of mordenite with the pore diameter about 7 Å. So far all low-temperature experiments with fluids filling the 1D channels of various zeolites have been done in the temperature range 0.1–10 K which is well above the estimated value of the binding energy of a dimer. Lower temperatures are more favorable for the observation of the dimerized state. However, when dealing with a gaseous phase at low temperatures the rapidly decreasing saturated vapor pressure may cause serious experimental difficulties.

Another luring experimental possibility would be to attempt tracing dimers in dense quantum liquids of pure ^{3}He and ^{4}He placed in nanoporous media. Of course, the methods used above to describe low-density systems do not work in the case of a dense liquid. On the other hand, one cannot exclude the possibility that the dimerized state, although modified, may survive when increasing the density and some vestige of that state might be detected even at high densities. In the case of a Fermi liquid, the approach applied in this paper can be generalized to consider bound states of the single-particle excitations. It seems unlikely that the s-wave $(^3\text{He})_2$ dimers could exist in liquid ^{3}He as the latter does not

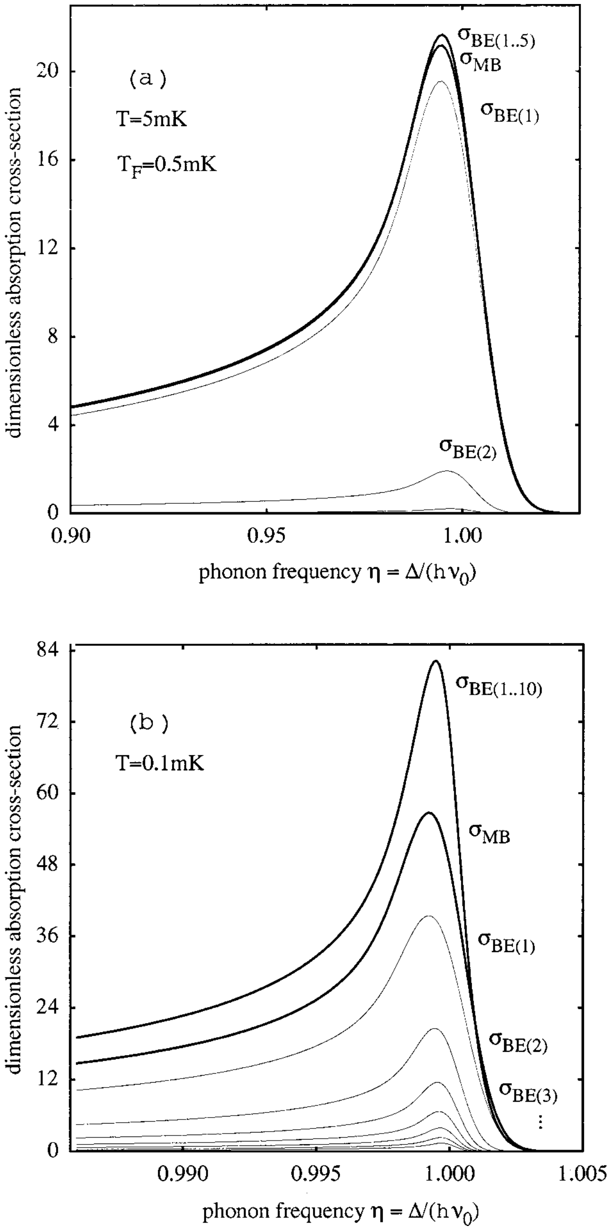

FIG. 5. Resonance peak for acoustic splitting in the cross-over region between semiclassical and degenerate regimes, assuming that the dimers form an ideal Bose gas in this region. The discrepancy with the semiclassical picture is pronounced at $T\sim0.1$ mK. Enhanced acoustic splitting occurs due to the tendency of the Bose particles to attain like velocities as they are cooled. Plotted here is a partial sum of the exact dimensionless absorption cross section given by $(\sqrt{\pi}n_3)/(32z_0\theta)\sigma_{BE(1..N)}=776/\zeta^{1/2}\Sigma e^{-n\gamma}J_n(\eta)$, low order individual terms of the series, as well as the exact semiclassical absorption cross-section given by $(\sqrt{\pi}n_3)/(32z_0\theta)\sigma_{MB}=J(\eta)$. γ is obtained from Eq. (72), keeping two terms in the expansion of the integrand. It is an open question whether the dimers form quadrumers or even longer polymers at lower temperatures.

exhibit superfluidity associated with the *s*-wave pairing, i.e., the $l=0$-harmonic of the effective scattering amplitude corresponds to a repulsion between quasiparticles. Nevertheless, dimers with $l=1$ or higher might well be present in liquid ^{3}He that fills narrow channels. A concentrated solution of ^{3}He in superfluid ^{4}He might be a good candidate to exhibit the *s*-wave $(^3\mathrm{He})_2$ dimers because, according to experimental data (Ref. 4 and references therein), the *s*-harmonic of the effective interaction is attractive. As was noted at the beginning of the paper, two ^{4}He atoms form a bound state, albeit a very shallow one, even in a 3D geometry. For this reason, liquid ^{4}He in porous media is an interesting object of study, the observation of dimerized states with a higher binding energy being likely. Theoretically describing the dimerized states in dense liquids would require more powerful computations and are beyond the scope of this paper.

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APPENDIX: EVALUATION OF THE ABSORPTION CROSS-SECTION INTEGRAL

After substituting the parameters ζ and η into Eq. (59), the integral we want is

$$J(\zeta,\eta)=\eta\zeta^{1/2}e^{-\zeta(\eta-1)^2}\int_0^\infty t^{-1/2}(1+t)^{-1}e^{-at-bt^2}dt$$
$$\equiv\eta\zeta^{1/2}e^{-\zeta(\eta-1)^2}J(a),$$
$$a=2\zeta\eta(\eta-1),\quad b=\zeta\eta^2. \tag{A1}$$

We will use the known integral,

$$I_{\nu-1}(a)\equiv\int_0^\infty t^{\nu-1}e^{-at-bt^2}dt=\frac{\Gamma(\nu)}{b^{\nu/2}}H_{-\nu}\left(\frac{a}{2\sqrt{b}}\right),$$
$$I(a)\equiv I_{-1/2}(a). \tag{A2}$$

We use a saddle-point method to find an expansion of $J(a)$ in powers of $1/b$ which converges quickly at low temperatures and shows excellent agreement in the region of interest $\eta\approx1$. We seek an asymptotic expansion of $J(a)$ that is uniformly valid as η passes through unity. The saddle-point of e^{-at-bt^2} in the integrand of Eq. (A1) is at $t_0=-a/(2b)=1/\eta-1$, which is near the end-point of integration when $\eta\to1$. Now write

$$J(a)=\int_0^\infty t^{-1/2}f(t)e^{-at-bt^2}dt,\quad f(t)=\frac{1}{(1+t)}, \tag{A3}$$

and let

$$f(t)=p+q(t-t_0)+t(t-t_0)g(t), \tag{A4}$$

where

$$p=f(t_0),\quad q=\frac{f(t_0)-f(0)}{t_0}=-\frac{1}{1+t_0}. \tag{A5}$$

Substitute Eq. (A5) into Eq. (A4) and find $g(t)$. The integral we want, $J(a)$, is then the sum of two known integrals and a third integral involving $g(t)$ which we call $J_1(a)$. Integrating this by parts, we find that we return to the same form as the original integral (A1) if we define a function $f_1(t)$ to be

$$f_1(t)=\frac{1}{2}g(t)+tg'(t). \tag{A6}$$

Repeat the process. Let $f_1(t)=p_1+q_1(t-t_0)+t(t-t_0)g_1(t)$ with the p's and q's defined in an analogous way. Note that $\lim_{t_0\to0}q_1=0$, therefore define $q_1=0$ when $t_0=0$. Substituting $f_1(t)$ into the expression for $J_1(a)$ we obtain two known integrals and a third integral involving $g_1(t)$. Meanwhile we have also obtained two asymptotic series in negative powers of b. After some rearranging, one arrives at the following expression for $J(\zeta,\eta)$, accurate to order $O(1/b^{3/2})$:

$$\begin{aligned}J(\zeta,\eta)=\sqrt{\pi}e^{-\zeta(\eta-1)^2}\Bigg\{&(p-t_0)b^{1/4}H_{-1/2}\left(\frac{a}{2\sqrt{b}}\right)\\&+\frac{q}{2b^{1/4}}H_{-3/2}\left(\frac{a}{2\sqrt{b}}\right)+\frac{(p_1-q_1t_0)}{2b^{3/4}}H_{-1/2}\left(\frac{a}{2\sqrt{b}}\right)\\&+\frac{q_1}{4b^{5/4}}H_{-3/2}\left(\frac{a}{2\sqrt{b}}\right)+O(1/b^{3/2})\Bigg\},\end{aligned} \tag{A7}$$

where $H_{-\nu}(x)$ are Hermite polynomials, and

$$p=\frac{1}{1+t_0},\quad q=-p,\quad p_1=\frac{p^2}{2}-p^3t_0,\quad q_1=\frac{p_1}{t_0}-\frac{p}{2t_0}. \tag{A8}$$

For low temperatures $T\sim0.01$ K, the main contribution comes from the first term of this expansion (A7), and we have simply the expression in Eq. (61). Finally, since the (exact) classical cross-section integral (59), as T approaches zero, tends to a delta function peaked at $\eta=1$, the expression (61) becomes a good approximation to the exact integral for all frequencies η.

To evaluate the Bose-Einstein cross-section integral (69), the relation,

$$\frac{1}{\exp(d+x^2)-1}=\sum_{n=1}^{\infty}\exp[-n(d+x^2)],\quad d\geqslant0, \tag{A9}$$

gives integrals of the form $(A1)$. It is an easy matter to arrive at an expansion in powers of $1/(nb)$ analogous to Eq. (A7).

[1] E.S. Meyer, J.C. Mester, M.W. Reynolds, T.E. Huber, Z. Zhao, B. Freedman, J. Kim, and I.F. Silvera, Phys. Rev. Lett. **71**, 1343 (1993); Physica B **194-196**, 885 (1994).

[2] F. Luo, G.C. McBane, G. Kim, C.F. Giese, and W.R. Gentry, J. Chem. Phys. **98(4)**, 3564 (1993).

[3] J. Mester, E. Meyer, T. Huber, M. Reynolds, and I.F. Silvera, Physica B **194-196**, 887 (1994).

[4] E.P. Bashkin and A.E. Meyerovich, Adv. Phys. **30**, 1 (1981).

[5] E.P. Bashkin, Zh. Éksp. Teor. Fiz. **78**, 360 (1980) [Sov. Phys. JETP **51**, 181 (1980)].

[6] L.D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1977).

[7] K. Miyake, Prog. Theor. Phys. **69**, 1794 (1983).

[8] E.P. Bashkin, in *Recent Progress in Many-Body Theories*, edited by C. Campbell, B. Clements, E. Krotscheck, and T. Ainsworth (Plenum, New York, 1992), Vol. 3.

[9] E. Østgaard and E.P. Bashkin, Physica B **178**, 134 (1992).

[10] E.P. Bashkin, N. Pavloff, and J. Treiner, J. Low Temp. Phys. **99**, 659 (1995).

[11] D.W. Breck, *Zeolite Molecular Sieves* (Wiley, New York, 1974), Chap. 2.

[12] N. Wada, H. Kato, S. Sato, S. Takayanagi, T. Ito, and T. Watanabe, in *Proceedings of the 17th International Conference on Low Temperature Physics*, edited by V. Eckern *et al.* (North-Holland, Amsterdam, 1984), p. 523.

[13] H. Kato, K. Ishioh, N. Wada, T. Ito, and T. Watanabe, J. Low Temp. Phys. **68**, 321 (1987).

[14] N. Wada, K. Ishioh, and T. Watanabe, J. Phys. Soc. Jpn. **61**, 931 (1992).

[15] N. Wada, H. Kato, and T. Watanabe, J. Low Temp. Phys. **95**, 507 (1994).

[16] N. Wada and H. Kato, Physica B **194–196**, 685 (1994).

[17] N. Wada, A. Inoue, H. Yano, and K. Torii, Phys. Rev. B **52**, 1167 (1995).

[18] M. Hieda, M. Suzuki, H. Yano, and N. Wada, in *Proceedings of the 21st International Conference on Low Temperature Physics* [Czech. J. Phys. **46**, 129 (1996)].

[19] S. Miyamoto and Y. Takano, in *Proceedings of the 21st International Conference on Low Temperature Physics* [Czech. J. Phys. **46**, 137 (1996)].

[20] E.P. Bashkin, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 3 (1977) [JETP Lett. **25**, 1 (1977)]; Zh. Eksp. Teor. Fiz. **73**, 1849 (1977) [Sov. Phys. JETP **46**, 972 (1977)].

[21] K.A. Musaelian and A.E. Meyerovich, Physica B **194–196**, 875 (1994).

[22] E.M. Lifshitz and L.P. Pitaevskii, *Statistical Physics, Part 2* (Pergamon, New York, 1980).

[23] E.P. Bashkin, Pis'ma Zh. Éksp. Teor. Fiz. **40**, 383 (1984) [JETP Lett. **40**, 1197 (1984)].

[24] C.N. Yang, Phys. Rev. Lett. **19**, 1312 (1967); C.N. Yang and C.P. Yang, J. Math. Phys. **10**, 1115 (1969).

[25] E.H. Lieb and W. Liniger, Phys. Rev. **130**, 1605 (1963).

[26] M. Takahashi, Prog. Theor. Phys. **46**, 1388 (1971).

[27] M. Gaudin, Phys. Lett. **24A**, 55 (1967).

[28] P. Schlottmann, Phys. Rep. **181**, 1 (1989).

[29] C.K. Lai, Phys. Rev. Lett. **26**, 1472 (1971); Phys. Rev. A **8**, 2567 (1973).

[30] A.J. Leggett, J. Phys. (Paris), Colloq. **41**, C7-19 (1980).

[31] P. Nozieres and S. Schmitt-Rink, J. Low Temp. Phys. **59**, 195 (1985).

[32] M. Randeria, J. Duan, and Shieh, Phys. Rev. B **41**, 327 (1990).

[33] M. Casas, M. Fortes, M. de Llano, A. Puente, and M.A. Solis, in *Condensed Matter Theories*, edited by M. Casas, M. de Llano, J. Navarro, and A. Polls (Nova Science, Commack, NY, 1995), Vol. 10, p. 233.

[34] J.B. McGuire, J. Math. Phys. **6**, 432 (1965); **7**, 123 (1966); **31**, 164 (1989); Phys. Rev. A **41**, 739 (1990).

[35] J. Bardeen, G. Baym, and D. Pines, Phys. Rev. **156**, 207 (1967).

[36] T. Takaishi, A. Yusa, and F. Amakasu, Trans. Faraday Soc. **67**, 3365 (1971); T. Takaishi, A. Yusa, Y. Ogino, and S. Ozawa, J. Chem. Soc., Faraday Trans. 1 **70**, 671 (1974).

[37] N.N. Lebedev, *Special Functions and their Applications* (Prentice-Hall, Englewood Cliffs, NJ, 1965).

[38] H. Godfrin and H.-J. Lauter, Prog. Low Temp. Phys. **XIV** (1995).