

Dimerization of ^3He in ^3He - ^4He mixture films

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abstract

^3He atoms dissolved in superfluid ^4He may form dimers $(^3\text{He})_2$ in two-dimensional geometries. We study dimer formation in films of dilute ^3He - ^4He mixture. After designing a schematic ^3He - ^3He interaction potential we calculate the dimer binding energy for various substrates. It is shown that ^3He impurity states localized near the substrate give rise to the highest magnitudes of the binding energy.

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1 Introduction

^3He atoms dissolved in bulk ^4He have always been considered an ideal system for testing the Landau approach describing the macroscopic properties of quantum fluids in terms of elementary excitations (quasiparticles) [1]. At low enough temperatures one can neglect the contribution of the excitations pertaining to superfluid ^4He (phonons and rotons). The system is then described in terms of an interacting gas of ^3He quasiparticles imbedded in the uniform background of superfluid ^4He . A bare quasiparticle (a single ^3He atom) has a particle-like energy spectrum [2] with an effective mass larger than the bare mass. The quasiparticle interaction at long distances is the bare ^3He - ^3He interatomic interaction renormalized by a phonon-induced term [3]. At small distances a strong repulsive core is predominant. However, the overall effect turns out to be attractive, as was demonstrated on the basis of theoretical calculations [4, 5] and experimental data [6, 7] on the s -wave scattering length a ($a < 0$).

Despite the fact that the effective attraction between two ^3He quasiparticles is too weak to lead to a bound state in the bulk, such a bound state – a $(^3\text{He})_2$ dimer – should certainly exist in helium systems with reduced dimensionality (restricted geometry) [8, 9]. It is well known that in one and two dimensions *any* attractive potential satisfying the perturbation theory criterion gives rise to a bound state (see *e.g.* Ref. [10]). The situation is not that obvious in the case of a nonperturbative potential like the ^3He - ^3He interaction with a strong repulsion at short distances. Nevertheless, one can rigorously prove that spinless $(^3\text{He})_2$ dimer *must* exist in quasi-2D and quasi-1D geometries (like films and narrow capillaries of ^4He) provided a is negative and the characteristic scale of confinement of the ^3He atoms is much larger than the interaction range – which is of the order of $|a|$ – (see [9] and appendix A). When the system is cooled down to temperatures lower than the corresponding binding energy, the single impurity quasiparticles form $(^3\text{He})_2$ Bose-dimers, and the Fermi component of ^3He is replaced by a new Bose quantum fluid of $(^3\text{He})_2$ of reduced dimensionality. This phenomenon should strongly affect the macroscopic properties of dilute mixtures resulting in an extra superfluid transition, new features of the phase diagram, anomalous sound absorption, *etc.* [8]. This is the reason why calculating the binding energy is the main issue in the theory of dimerized ^3He - ^4He solutions. To be specific we will concentrate on dilute ^3He - ^4He mixtures in various 2D geometries (*i.e.* in films on various substrates).

In ^4He films, ^3He impurities are localized in the direction normal to the substrate over a characteristic width w which can be much smaller than the film thickness. When extrapolated to small w (of the order of a few atomic layers) the theory of Ref. [8, 9] provides an estimate for the binding energy which seems to be quite attainable for experimental study. However, it is difficult to assess how accurate such an estimate could be because the theory in question certainly does not hold to describe the ^3He - ^3He interaction in such restricted geometry, *i.e.* in a real 2D situation (when $w \sim a$). In a pure 2D case one cannot *a priori* be sure if a bound state of two ^3He atoms exists at all. Therefore, theoretically calculating the binding energy for an arbitrary film thickness and various substrates would provide a direct clue of which experimental conditions are the best suited for the detection of $(^3\text{He})_2$ dimers. Such calculations are the primary goal of this paper. Here we focus on two cases where ^3He impurities adopt a 2D configuration :

- (i) The Andreev states of ^3He at the free surface of ^4He (see [11, 12, 13] and references therein).
- (ii) The ^3He states localized at the interface between a ^4He film and the substrate, as predicted in

[14, 15].

Case (ii) seems particularly favorable for the creation of dimers because ^3He quasiparticles near the substrate have a large effective mass (due to the higher ^4He density) and a narrow wave-function (localized within the first ^4He liquid layer). The localization length (the width of the wave function in the direction across the film) is of the order of a few angströms. In Sec. 2 some possible realizations of a quasi-2D ensemble of ^3He impurities in superfluid ^4He films on various substrates are briefly reviewed. In Sec. 3 we derive a schematic ^3He - ^3He interaction and then evaluate in Sec. 4 the corresponding $(^3\text{He})_2$ binding energy. We give our concluding remarks in Sec. 5.

2 ^3He impurities in ^4He film

We assume in the following that inhomogeneities of the substrate in the $x - y$ plane parallel to the surface play a negligible role and we impose translational invariance on the helium densities (^3He and ^4He). This does not imply that possible corrugation of the surface is neglected. Indeed, in that case, ^4He atoms will certainly fill the dips of the surface until it is more or less flat ; the effective substrate to be considered is then a mixture of the original substrate and these helium atoms, the effect of which is to weaken the potential. The question of how many atoms can be trapped on the defects of the surface can be answered experimentally, and will appear as an overall shift in coverage, when comparing theory and experiment.

The first question to address is to determine the state of a helium film on a given substrate. The different situations to expect, as a function of increasing attractive strength of the substrate potential, are the following : non wetting, wetting with prewetting[16], and solidification of one or two layers. We limit our study of the ^3He states to cases where the ^4He film is *completely liquid* : there is a clear qualitative change of ^3He impurity states when ^4He solidifies ; the ^3He atoms occupy substitutional states in solid ^4He and move through the lattice via tunneling processes (see *e.g.* Ref. [17]). Our continuous description of the solid misses this phenomenon, since the coupling of ^3He atoms with the ^4He matrix is represented here through a density dependent ^3He effective mass fitted on properties of liquid mixtures (see details in [14]).

Hence, in order to specify the validity of our approach we need a criterion assigning a solid or liquid character to each of the first ^4He layers. This has been done in Ref. [18] where different substrates were characterized by their interaction with helium through two coefficients C_3 and D

$$V_{sub}(z) = \frac{4}{27D^2} \left(\frac{C_3}{z^3} \right)^3 - \frac{C_3}{z^3}. \quad (1)$$

Here D is the depth of the attractive part of $V_{sub}(z)$ and C_3 characterizes the van der Waals tail. According to Ref. [18] one can draw in the $C_3 - D$ plane the lines corresponding to solidification of the first and second layer (see Fig. 1). For completeness, we have also reproduced, from Ref. [16], the line separating the non-wetting region from the wetting one. Note here that the criterion used in [18] is only approximate and that there are also large uncertainties in the parameters of the potentials (up to $\sim 30\%$ on D [19]). As an extreme case, for hydrogen the value $C_3 = 1000 \text{ K}\text{\AA}^3$ extracted from different experiments (see [20] and references therein) is significantly larger than the theoretical value of $360 \text{ K}\text{\AA}^3$ from Ref. [19]. So, the predictions are uncertain for cases close to a line : it may well be that the first layer does solidify on Mg, and that the second layer solidifies on MgO, Cu and Ag.

We now come to the ^3He impurity states. Calculations were performed, as in Ref [14], in the limit of *one* ^3He atom. Each state is a part of the 2D continuum, and when considering finite ^3He coverage, one should introduce 2D Fermi momenta for each state. Also, through self-consistency, the ^4He profile, the average field – and consequently the single particle states – depend on ^3He coverage (see Ref. [13] for a study of finite ^3He coverage on the ^4He bulk surface). We shall neglect these effects in the following discussion, which is valid for small ^3He coverage only.

Typical ^4He film profiles and ^3He substrate wave-functions are shown on Fig. 2 for cesium and lithium substrates. We also display our results for other substrates on Table 1. The existence of 2D ^3He states in liquid ^4He near a solid substrate thus appears as a *general feature* of these interfaces. Notice that the ^3He atoms do not move between two compressed ^4He layers, as it was sometimes considered (see the discussion in [15]). On the other hand, even if the ^3He particles can move between layers and occupy several of them, the bound state $(^3\text{He})_2$ still exists although the magnitude of the binding energy becomes smaller.

We recall that the binding energy of a ^3He atom in bulk ^4He is -2.8 K, so for all the substrates listed in Table 1 the substrate state is not a resonance but a true bound state. As discussed in [14] the existence of this substrate state provides a mechanism allowing to understand some unexplained temperature dependence of third sound velocities found in Ref. [21]. Several experimental tests of its existence were proposed in Ref. [14, 15]. In the following we focus on the most exciting consequence : the possible formation of $(^3\text{He})_2$ dimers with a sizeable binding energy.

3 A schematic ^3He - ^3He interaction

The second step in evaluating the dimer binding energy is to choose a sensible effective interaction between the ^3He quasiparticles. The requirements are three-fold : (1) the long range attraction is the bare term reduced by a factor α^2 where α is the excess volume parameter in ^4He (see [3, 22] and below); (2) as mentioned in the introduction, the short distance term is repulsive and equal to the bare potential; (3) the effective potential should reproduce the *s*-wave scattering length a of ^3He in ^4He ($a \simeq -1.5$ Å).

Let us explain the first requirement ; it will lead us to postulate a generic form of the effective potential. We will estimate here the energy of two ^3He atoms imbedded in ^4He . Our derivation is patterned on the approach of Ref. [22]. We consider two ^3He atoms situated at points \mathbf{r}_1 and \mathbf{r}_2 . Atom i ($i = 1, 2$) occupies a volume Ω_3 centered at \mathbf{r}_i (we denote it as $\Omega_3[\mathbf{r}_i]$) of which the ^4He atoms are expelled (see Fig. 3). So, if the total volume of the sample is Ω the ^4He 's will occupy a volume $\Omega' = \Omega - \Omega_3[\mathbf{r}_1] - \Omega_3[\mathbf{r}_2]$. If ρ_4 is the mean ^4He density, then one can consider that each ^4He atom occupies a volume $\Omega_4 = 1/\rho_4$ and the excess volume parameter is by definition

$$\alpha = \frac{\Omega_3 - \Omega_4}{\Omega_4} . \quad (2)$$

The total potential energy of the system is

$$E = E_{33} + E_{34} + E_{44} , \quad (3a)$$

with obvious notations (for instance E_{34} is due to the ^4He - ^3He interaction). E can be separated in a constant (*i.e.* position independent) term plus a term which is an effective ^3He - ^3He potential :

$$E = C^{st} + V_{eff}(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (3b)$$

The separation (3b) is made unambiguous by imposing that V_{eff} goes to zero at large distance (when the two ${}^3\text{He}$ impurities are far apart).

Let us now study the contributions of E_{33} , E_{34} and E_{44} to the effective potential V_{eff} . If two helium atoms interact *via* the bare Lennard-Jones potential V_{LJ} , E_{33} is simply

$$E_{33} = V_{LJ}(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (4)$$

where the explicit form of V_{LJ} is

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (5)$$

with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å.

The cross term E_{34} is

$$E_{34} = \int_{\Omega'} V_{LJ}(|\mathbf{r}_1 - \mathbf{r}|) \frac{d^3\mathbf{r}}{\Omega_4} + \int_{\Omega'} V_{LJ}(|\mathbf{r}_2 - \mathbf{r}|) \frac{d^3\mathbf{r}}{\Omega_4}. \quad (6)$$

In the r.h.s. of (6) the two integrals are equal. Let us focus on the first one for instance. The integration domain can be separated in two contributions: $\Omega' = (\Omega - \Omega_3[\mathbf{r}_1]) - \Omega_3[\mathbf{r}_2]$. The first subdomain describes the energy due to the introduction of atom 1 alone in the ${}^4\text{He}$ matrix. It corresponds to the "dressing" of the bare ${}^3\text{He}$ particle and plays no role in the quasiparticle interaction (*i.e.* it does not depend on $|\mathbf{r}_1 - \mathbf{r}_2|$ and can be included in the constant term of (3b)). The second subdomain describes the interaction of particle 1 with fictitious ${}^4\text{He}$ atoms occupying $\Omega_3[\mathbf{r}_2]$ and brings a contribution to V_{eff} since it depends of the respective position of the ${}^3\text{He}$ impurities. Hence E_{34} contributes to $V_{eff}(|\mathbf{r}_1 - \mathbf{r}_2|)$ with the following term (the factor 2 comes from the sum of the two equal integrals appearing in (6)):

$$E_{34} \sim -2 \int_{\Omega_3[\mathbf{r}_2]} V_{LJ}(|\mathbf{r}_1 - \mathbf{r}|) \frac{d^3\mathbf{r}}{\Omega_4} \simeq -2 \frac{\Omega_3}{\Omega_4} V_{LJ}(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (7)$$

In the last term of (7) we have replaced the integral by an approximate form valid only if $|\mathbf{r}_1 - \mathbf{r}_2|$ is large compared with the characteristic radius of Ω_3 . If not, the dressings of the two quasiparticles might be affected one by the other (see below).

The term E_{44} is

$$E_{44} = \frac{1}{2} \int \int_{\Omega' \times \Omega'} V_{LJ}(|\mathbf{r} - \mathbf{r}'|) \frac{d^3\mathbf{r}}{\Omega_4} \frac{d^3\mathbf{r}'}{\Omega_4}. \quad (8)$$

The integration domain can again be separated as above in several subdomains. The position dependent part of E_{44} gives a contribution to V_{eff} which represents the interaction of fictitious ${}^4\text{He}$ atoms occupying the volumes $\Omega_3[\mathbf{r}_1]$ and $\Omega_3[\mathbf{r}_2]$

$$E_{44} \sim \int \int_{\Omega_3[\mathbf{r}_1] \times \Omega_3[\mathbf{r}_2]} V_{LJ}(|\mathbf{r} - \mathbf{r}'|) \frac{d^3\mathbf{r}}{\Omega_4} \frac{d^3\mathbf{r}'}{\Omega_4} \simeq \left(\frac{\Omega_3}{\Omega_4} \right)^2 V_{LJ}(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (9)$$

As in (7) the last term of Eq. (9) is a long distance approximation.

Gathering the contributions (4,7,9) we see as stated in the beginning of this section that the long range quasi-particle interaction is equal to the bare interaction reduced by a factor α^2 . Essentially the same result was obtained in [3] using thermodynamical arguments in momentum space. In the terminology of Ref. [3] the contribution of $E_{33} + E_{34}$ would correspond to the direct part of the effective interaction and E_{44} would give the phonon-induced term. Of course, derivations based on excluded volume arguments such as in [3] or as presented here (from [22]) are only valid for long wavelengths i.e. for large distances between the ^3He atoms. Working in real space has the advantage of providing a simple way to build an effective interaction sensible also at short distance : if the two atoms get closer one can mimic the interaction of the dressed particles by introducing a correlation term $g(r)$ describing phenomenologically effects such as the disturbance of the ^4He cloud around a ^3He atom by the other particle. We choose for the correlation function the following form ($r = |r_1 - r_2|$) :

$$g(r) = \exp\left\{-\left(\frac{r_c}{r}\right)^5\right\}. \quad (10)$$

Then the contribution of E_{34} to V_{eff} is approximatively given by its long range approximation (the r.h.s. of (7)) multiplied by a factor $g(r)$. Similarly the contribution of E_{44} is multiplied by $g^2(r)$, leading to a total effective interaction

$$V_{eff}(r) = (1 - (1 + \alpha)g(r))^2 V_{LJ}(r). \quad (11)$$

The short range and long range behavior of the effective interaction (11) follow the requirements (1) and (2) above. Requirement (3) will be fulfilled by a correct choice of the free parameter r_c in (10). The value $r_c = 3.725 \text{ \AA}$ gives the correct s-wave scattering length $a = -1.5 \text{ \AA}$. The potential V_{eff} is shown on Fig. 4 where it is compared to the bare Lennard-Jones interaction. We have checked that working with a more realistic bare interaction such as the Aziz potential [23] does not affect the qualitative picture presented below. Also the potential in films should be different from the bulk interaction : at the free surface for instance, ripplon — and not phonon — exchange should dominate the long range behaviour. Or equivalently, the excess volume parameter should be replaced by an "excess surface parameter". We will not discuss this effect in the paper.

In order to test the sensibility of the final results to the effective interaction we designed an other potential \tilde{V}_{eff} having the required properties and roughly imitating the potential derived by Owen using the hypernetted chain approximation [24]. The potential was chosen to be :

$$\tilde{V}_{eff}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \alpha^2 \left(\frac{\sigma}{r}\right)^6 - C \left(\frac{\sigma}{r}\right)^7 \cos\left(2\pi \frac{r - \sigma}{R}\right) \right]. \quad (12)$$

This form obviously fulfills requirements (1) and (2) above. The parameters C and R are chosen so that \tilde{V}_{eff} has a zero at $r = 4 \text{ \AA}$ as in Owen's results (this imposes $R = 5.776 \text{ \AA}$) and that the s-wave scattering length has the correct value (this fixes $C = 1.16$). The corresponding \tilde{V}_{eff} is plotted on figure 4. Note that the potential of Ref. [24] is deeper than \tilde{V}_{eff} (it has a minimum at approximatively 19 K) and might lead to dimers more bound.

4 (^3He)₂ dimers

The Hamiltonian describing two ^3He quasiparticles in the film has the form:

$$H = \frac{\mathbf{p}_1^2}{2m^*} + \frac{\mathbf{p}_2^2}{2m^*} + V_{eff}(|\mathbf{r}_1 - \mathbf{r}_2|) + U_{ext}(z_1) + U_{ext}(z_2), \quad (13)$$

where U_{ext} is the ^3He mean field due to both the substrate and the ^4He film (such as shown on Fig. 2) and m^* the ^3He effective mass for the surface (Andreev) or substrate state (cf Table 1). It should be pointed out that the ^3He particles described by Eq. (13) may, in general, be in two different localized states in the z -direction, i.e. may belong to two different 2D continua. In this case the effective masses of both quasiparticles in the Hamiltonian (13) may be quite different. As explained earlier we restrict ourselves to considering the case of two ^3He particles at the same energy level for the motion along the z -axis, which provides the highest binding energy. In (13) and in the following V_{eff} is used as a generic notation valid for both potentials V_{eff} and \tilde{V}_{eff} . The description (13) might in general be improved by phenomenologically introducing a ^3He concentration-dependent effective mass m^* within the local density functional approach to ^3He - ^4He mixtures [13]. However, when looking for the binding energy such a correcting term is certainly beyond the accuracy of the theory (see below).

We make the following ansatz for the wave function of the two ^3He atoms :

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2\pi} e^{i\mathbf{K}_\perp \cdot \mathbf{R}_\parallel} \chi(\mathbf{r}_\parallel) \varphi(z_1) \varphi(z_2). \quad (14)$$

Eq. (14) describes two fermions with opposite spins. \mathbf{R}_\parallel is the center of mass coordinate in the (x, y) plane. For a dimer at rest (as we consider in the following) the corresponding momentum \mathbf{K}_\parallel is zero. Variable \mathbf{r}_\parallel is the relative coordinate in the plane. We have separated the (x, y) and z direction. The functions $\varphi(z_1)$ and $\varphi(z_2)$ describe the motion along the z -axis. We assume (which is exact to the first order of perturbation theory) that they are of the type shown on Fig. 2, not being affected by the coupling between the two atoms. So the main point here is that the interaction between ^3He atoms just slightly disturbs the motion in the z -direction but entirely changes the relative motion in the plane and leads to a bound state. In other words a perturbation theory can be applied for describing the normal motion only but the transverse dynamics of particles should be determined from the exact Schrödinger equation. In practice this means that one has to solve the 2D Schrödinger equation with a potential averaged over the unperturbed wave functions of ^3He quasiparticles in the z coordinate. The function φ is determined by the solution the equation :

$$\left[\frac{p_z^2}{2m^*} + U_{ext}(z) \right] \varphi(z) = \epsilon \varphi(z), \quad (15)$$

where p_z is the z component of the momentum ($z = z_1$ or z_2) :

$$\frac{\mathbf{p}_1^2}{2m^*} + \frac{\mathbf{p}_2^2}{2m^*} = \frac{p_{z_1}^2}{2m^*} + \frac{p_{z_2}^2}{2m^*} + \frac{\mathbf{P}_\parallel^2}{2M} + \frac{\mathbf{P}_\parallel^2}{2\mu}. \quad (16)$$

with M and μ being respectively the total mass ($2m^*$) and the reduced mass ($m^*/2$). Then writing the Schrödinger equation for the entire wave function Ψ , multiplying by $\varphi^*(z_1)\varphi^*(z_2)$ and integrating over $dz_1 dz_2$ one can easily find :

$$\left[\frac{P_{\parallel}^2}{2\mu} + \langle V_{eff}(r_{\parallel}) \rangle \right] \chi(r_{\parallel}) = E_{dim} \chi(r_{\parallel}), \quad (17)$$

where

$$\langle V_{eff}(r_{\parallel}) \rangle = \int \varphi^2(z_1) \varphi^2(z_2) V_{eff}(r_1 - r_2) dz_1 dz_2. \quad (18)$$

According to our perturbation scheme, all the x -dependence has been removed from formula (17). The substrate and ${}^4\text{He}$ density intervene indirectly through μ (i.e. m^*) and the z -wave function in (18).

It appears that for all the cases we are interested in (the Andreev state or the substrate state) the z -wave function can be represented to a fairly good approximation by a simple gaussian (characterized by its half-width). So instead of giving results for all the substrates listed in Table 1 we will independently vary the effective mass m^* and half-width w of a normalized gaussian fitting for $\varphi^2(z)$ in (17,18).

In the limit of a large half-width, although common perturbation theory cannot be directly applied when seeking the solution of the Schrödinger equation, one can use the Fermi renormalization technique (see [25] and appendix A) to obtain the binding energy with logarithmic accuracy:

$$|E_{dim}| \simeq \frac{\hbar^2}{m^* r_0^2} \exp\left(-\frac{m_b^* L}{m^* |a|}\right), \quad (19)$$

where r_0 is a quantity of the order of the interaction potential range, m_b^* is the effective mass of a ${}^3\text{He}$ quasiparticle in bulk ${}^4\text{He}$, and L is defined as:

$$\frac{1}{L} = \int |\varphi(z)|^4 dz. \quad (20)$$

Here L is of the order of the half-width, w , and it is a measure of the spatial extension of the z -wave function. The result above is valid only for large values of $L/|a|$ (see the appendix). One can see from Eq. (19) that in this limit the requirements of Sec. 3 are enough to determine the order of magnitude of the dimer binding energy.

In the opposite limit of very localized states — such as those we are primarily interested in — our numerical results show a great sensibility of the binding energy to the details of the potential (the results for E_{dim} as a function of the half-width for different effective masses are shown on Fig. 5 for V_{eff} and on Fig. 6 for \bar{V}_{eff}). For instance, for $m^*/m = 2.95$ the binding energies estimated with V_{eff} and \bar{V}_{eff} differ from each other by two orders of magnitude. Under these conditions a precise quantitative prediction would thus be illusive. We just note that if V_{eff} mimics accurately the exact quasiparticle interaction, it would be very difficult to observe the formation of $({}^3\text{He})_2$ bound states in experiment. On the other hand, if the effective potential \bar{V}_{eff} can be applied in the case in question, then for a magnesium substrate ($m^*/m = 2.9$ and $w = 0.9 \text{ \AA}$) the dimer binding energy would be $E_{dim} = -6.3 \text{ mK}$, which is a reachable temperature with modern experimental techniques. A problem might occur though because the first ${}^4\text{He}$ layer on a Mg substrate could be solid (see the discussion in Sec. 2). The next candidate for dimer formation would then be hydrogen. Using the two potentials designed in Sec. 3 we could not get a reasonable dimer binding energy, mainly because m^* in this case is not large enough. However, other pseudo-potentials might give a different result.

Although not quantitatively predictive, our study allows us nevertheless to draw a very clear qualitative picture. In highly compressed substrate layers the ^3He effective mass is large. This reduces the kinetic energy and favours the creation of $(^3\text{He})_2$ bound states. The small spatial extension of the wave function in these layers is also favorable to the formation of dimers as can be seen from Eq. (19) and Fig. 5 and 6. From these figures one can also see that there is an optimal width of the order of 0.5 Å. It is interesting to note that the more attractive the substrate, the closer one approaches this value (see Table 1). The proper way to observe dimers would then be to choose a substrate for which the first ^4He layer is close to be solid but still remains liquid.

5 Concluding remarks

After having classified various substrates according to their ability to solidify one or two layers of a multilayer helium film, we have concentrated on cases in which helium remains liquid. In addition to the already known Andreev states we have shown that ^3He impurities were able to form a new 2D Fermi system near the substrate. After designing a sensible schematic interaction we have computed the binding energy of $(^3\text{He})_2$ dimers in the limit of small ^3He concentration. We found that for attractive substrates (such as magnesium or hydrogen) there was a reasonable hope to form dimers with sizeable binding energy. Note here that the binding energy of dimers in Andreev surface states is extremely small according to all our estimates, so the eventual observation of $(^3\text{He})_2$ dimers would be a direct consequence of the existence of ^3He substrate states.

In this paper the quantitative calculation of the dimer binding energy was based on a semi-empirical effective interaction and the one-particle wave functions obtained within a density-functional approach. It would be very useful to carry out the appropriate calculations with the help of other theoretical approaches (*e.g.* Ref. [27]). This would allow a better understanding of the accuracy of the present computations.

We hope that these results will motivate experimental study of the substrate ^3He states as was proposed earlier in [14, 15]. The eventual formation of $(^3\text{He})_2$ dimers would be a very interesting consequence of the existence of these states leading to an amazingly rich phase diagram. An experimentalist could face an extra Kosterlitz-Thouless phase transition, liquefaction of $(^3\text{He})_2$ or polymerization of ^3He , crossover from a Bose gas of dimers to a 2D Fermi fluid (with strong pair correlation) upon increasing the ^3He concentration, *etc.* [8, 9, 28, 29, 30, 31]. The dimer binding energy is a *cornerstone* characteristic of all these phenomena which are exciting objectives for experimental and theoretical studies.

Among the open problems, the study of "polymerization" of ^3He , *i.e.* the possible formation of N -mers with $N > 2$, is the natural continuation of the present work. Although Fermi statistics favours polymers with even numbers of ^3He atoms, there might be no upper limit for N , and our results could be a hint of the existence of a 2D liquid phase of ^3He . This eventuality is made sound by the recent finding of Brami *et al.* [32] whose variational results lead to propose at low temperature a new "self-condensed" fluid phase for pure ^3He films on graphite. As the presence of ^4He favours the formation of ^3He dimers it could also favour the formation of a liquid phase.

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Appendix A

In this appendix we derive the expression (19) for the dimer binding energy E_{dim} using the Fermi renormalization technique (see [25]). According to this method we introduce a weak two-particle pseudo-potential $V_f(r)$ which is assumed to meet the perturbation theory criterion. Let us emphasize that such an pseudo-potential has nothing to do with the interaction between quasiparticles which, indeed, cannot be treated in terms of a perturbation theory at all.

The pseudo-potential V_f is supposed to result in the true scattering amplitude when calculated within the Born approximation :

$$a = \frac{m_b^*}{4\pi\hbar^2} \int V_f(r) d^3r, \quad (A1)$$

where m_b^* is the effective mass of a ^3He quasiparticle in bulk ^4He ($m_b^* = 2.38m$). The idea of the method is to carry out all calculations in the framework of a perturbation theory for V_f and then to express the final formulae through the true s-wave scattering length a only by means of the renormalization (A1). Thus the method works while all obtained expressions contain the pseudopotential V_f only in the integral form (A1).

The solution of the Schrödinger equation, i.e. of Eq. (17) with V_f replacing V_{eff} , may be expressed in the form (see e.g. Ref. [10, 26])

$$E_{dim} \simeq -\frac{\hbar^2}{2\mu r_0^2} \exp \left[-\frac{\hbar^2}{\mu} \left| \int_0^\infty \langle V_f \rangle \rho d\rho \right|^{-1} \right], \quad (A2)$$

where $r_0 \sim |a|$ is of the order of the interaction range and $\langle V_f \rangle$ is defined by (18) with V_f replacing V_{eff} . Let us recall once again that the pseudopotential V_f is assumed to meet the criterion of a perturbation theory : for instance the integral entering Eq. (A2) should converge. Denoting this integral as I one can write :

$$I = \int_0^\infty \langle V_f \rangle \rho d\rho = \int V_f(\sqrt{\rho^2 + z^2}) F(z) \rho d\rho dz, \quad (A3)$$

where

$$F(z) = \int |\varphi(t - z/2)|^2 |\varphi(t + z/2)|^2 dt. \quad (A4)$$

Let the quantity w be a characteristic localization range in the z -direction for the wave function φ (w describes the half-width introduced in section 4). If the localization length is sufficiently large, $w \gg r_0$, one can easily find that

$$I = \frac{1}{2\pi L} \int V_f(r) d^3r \quad \text{with} \quad \frac{1}{L} \equiv F(0) = \int |\varphi(t)|^4 dt. \quad (A5)$$

Evidently L is of the same order as w (if φ^2 is a normalized gaussian of half-width w , then $L = w\sqrt{\pi/\ln 4}$). Combining Eq. (A5) and the renormalization relation (A1) yields :

$$E_{dim} \simeq -\frac{\hbar^2}{m^* r_0^2} \exp \left[-\frac{m_b^* L}{m^* |a|} \right]. \quad (A6)$$

In (A6) we have replaced the reduced mass by its value for the state $\varphi(z)$ considered: $\mu = m^*/2$. We see that the binding energy is expressed in terms of the true scattering amplitude and does not contain a pseudopotential in any explicit form. Thus using the Fermi method is completely justified in the limiting case $w \gg r_0$. Note, however, that it is difficult to exactly determine the quantity r_0 (see [26]) which could, in general, be pseudo-potential dependent. On the other hand, its order of magnitude is known ($r_0 \sim |a|$) and, in fact, it does not enter the exponential factor which determines the dominant behavior of E_{dim} .

In the limiting case $w \ll r_0$ the integral I obviously reduces to

$$I = \int V_f(\rho) \rho d\rho, \quad (A7)$$

and the binding energy explicitly depends on what kind of a pseudopotential is chosen. It means that the renormalization method is no longer valid and the 2D Schrödinger equation with the real interaction potential should be solved to find the binding energy. In this paper we have chosen to perform the calculation of E_{dim} by means of semi-empiric pseudopotentials which gave rise to reasonable estimates for quantities measured in experiment (see Sec. 2).

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Table captions

Table 1. Energy (ϵ), effective mass (m^*) and half-width (w) of the ^3He impurity state on various substrates and for the Andreev state. In the case of H_2 , the value $C_3 = 1000 \text{ K}\text{\AA}^3$ extracted from different experiments [20] is different from the theoretical value of $360 \text{ K}\text{\AA}^3$ [19].

substrate	$C_3 [\text{K}\text{\AA}^3]$	$D [\text{K}]$	$\epsilon [\text{K}]$	m^*/m	$w [\text{\AA}]$
Cs	673	4.4	-4.74	1.51	2.0
Rb	754	5.0	-4.23	1.78	1.9
K	812	6.3	-4.15	1.84	1.8
Na	1070	10.4	-4.04	2.02	1.4
Li	1360	17.1	-4.17	2.28	1.2
Mg	1780	32.0	-5.00	2.90	0.9
H_2	360	28.0	-5.51	2.41	0.9
	1000	28.0	-5.00	2.61	0.9
^4He free surface			-5.20	1.35	3.6

Figure captions

Figure 1. Phase diagram of ^4He on various substrates at zero temperature (form [18]). The dotted line is the wetting line [16].

Figure 2. ^4He liquid density (dotted line), ^3He substrate state wave-function (with arbitrary units) and ^3He average field on a Cs substrate (less attractive) and Li substrate (more attractive).

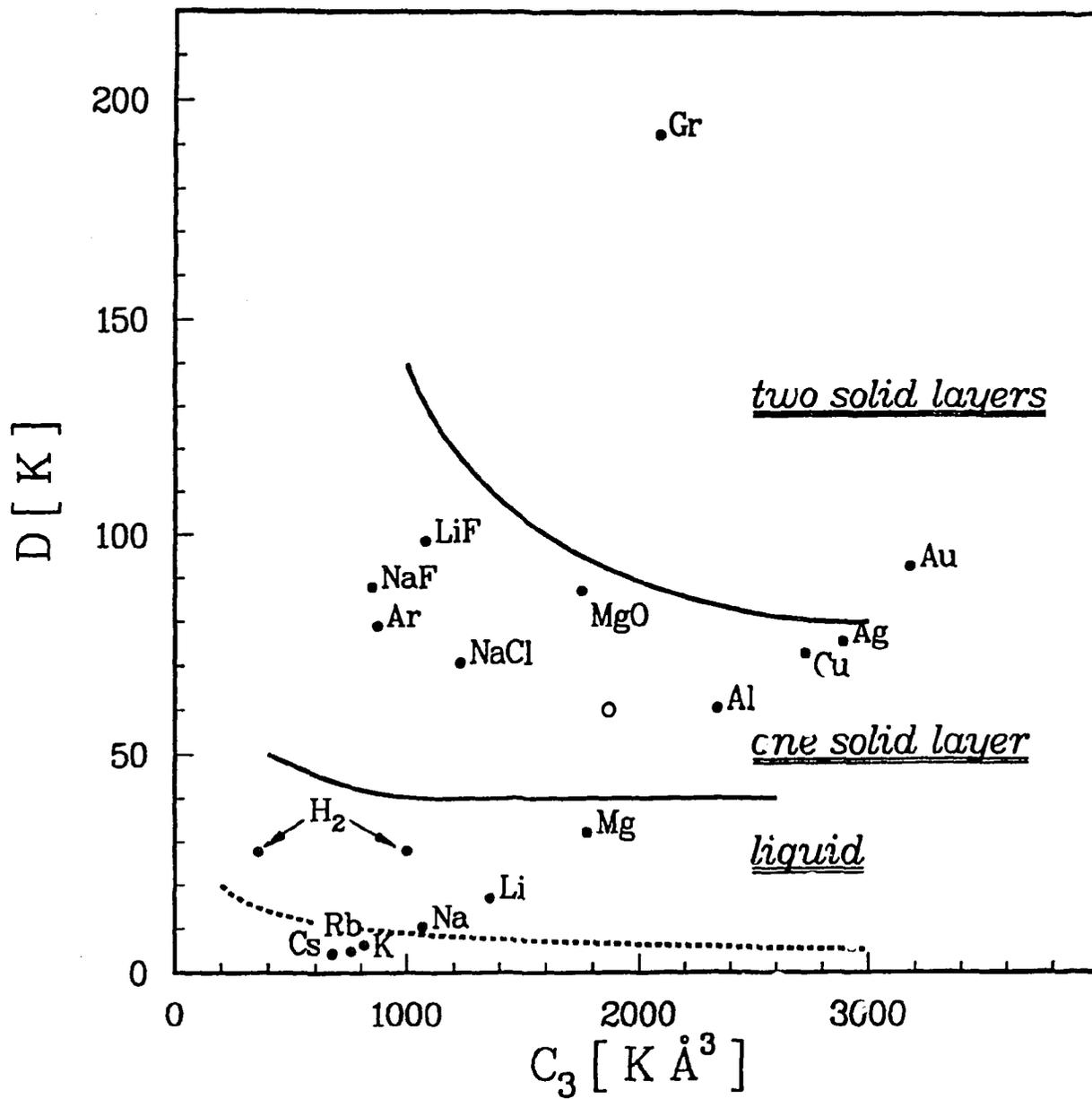
Figure 3. Schematic representation of the behaviour of two ^3He atoms situated at points \mathbf{r}_1 and \mathbf{r}_2 in bulk liquid ^4He . Atom i ($i = 1, 2$) occupies a volume $\Omega_3[\mathbf{r}_i]$ of which the ^4He 's are expelled (see the text). The shaded zone represents the volume occupied by liquid ^4He .

Figure 4. ^3He interaction potentials. The solid line represents the bare Lennard-Jones potential V_{LJ} , the dashed lines represent the effective potentials V_{eff} (long dashes) and \bar{V}_{eff} (short dashes).

Figure 5. E_{dim} as a function of w computed with V_{eff} for the effective masses $m^*/m = 2.95$, 3.0 and 3.05.

Figure 6. E_{dim} as a function of w computed with \bar{V}_{eff} for the effective masses $m^*/m = 2.8$, 2.9 and 2.95. Note the change of energy scale with respect to Fig. 5.

Fig.1



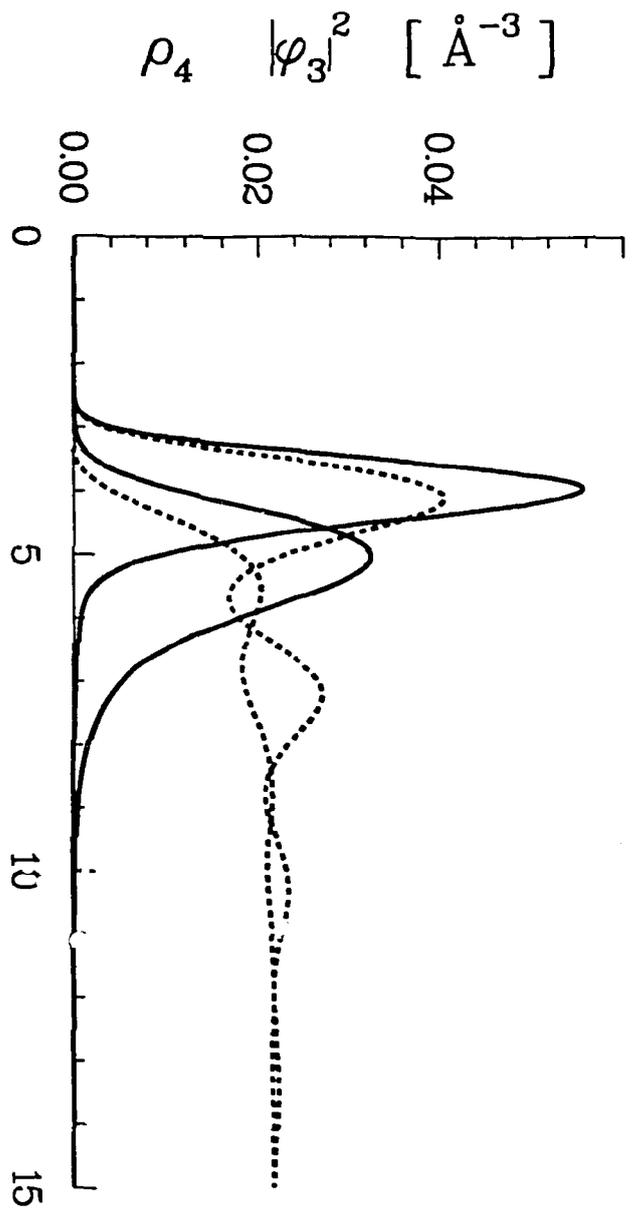
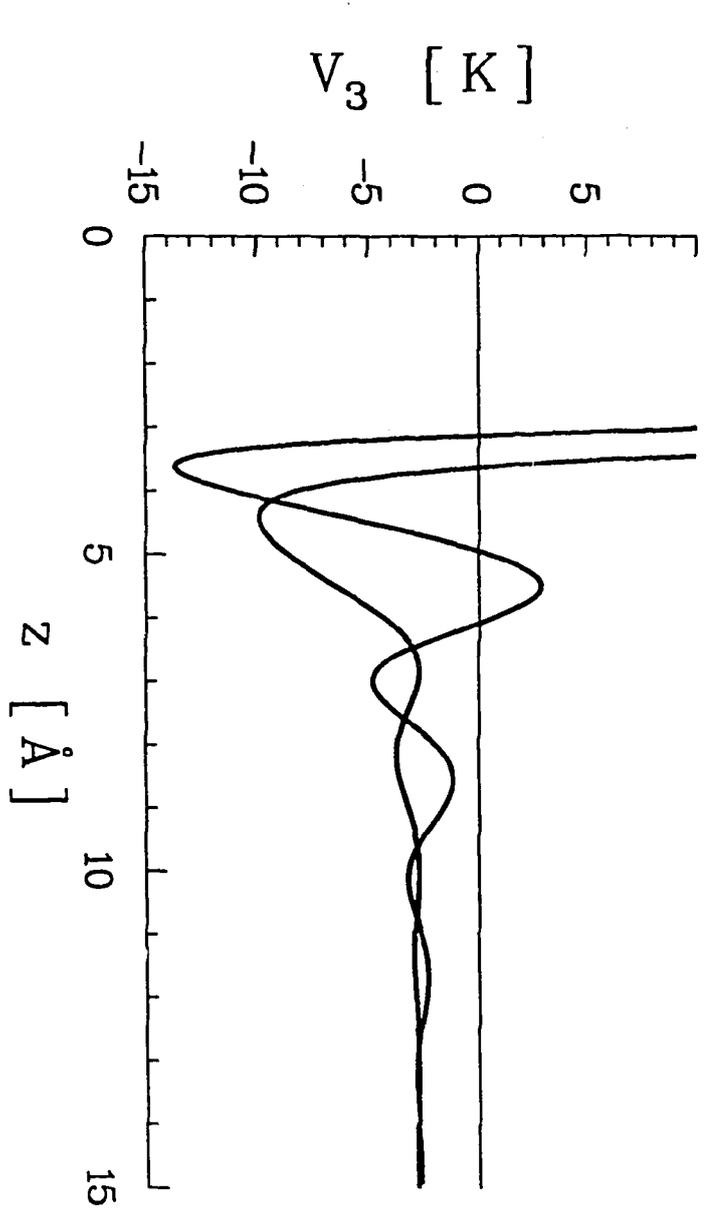


Fig 2

Fig 3

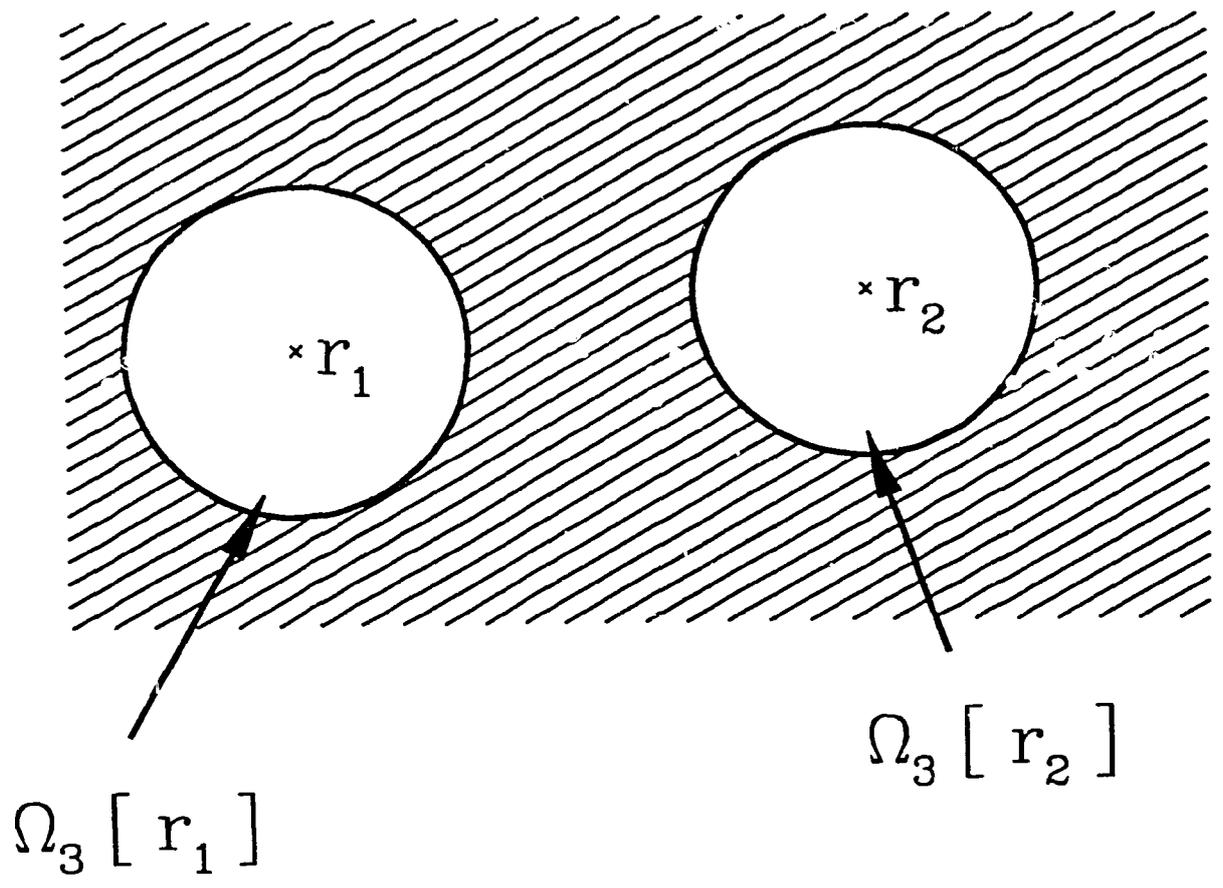


Fig 4

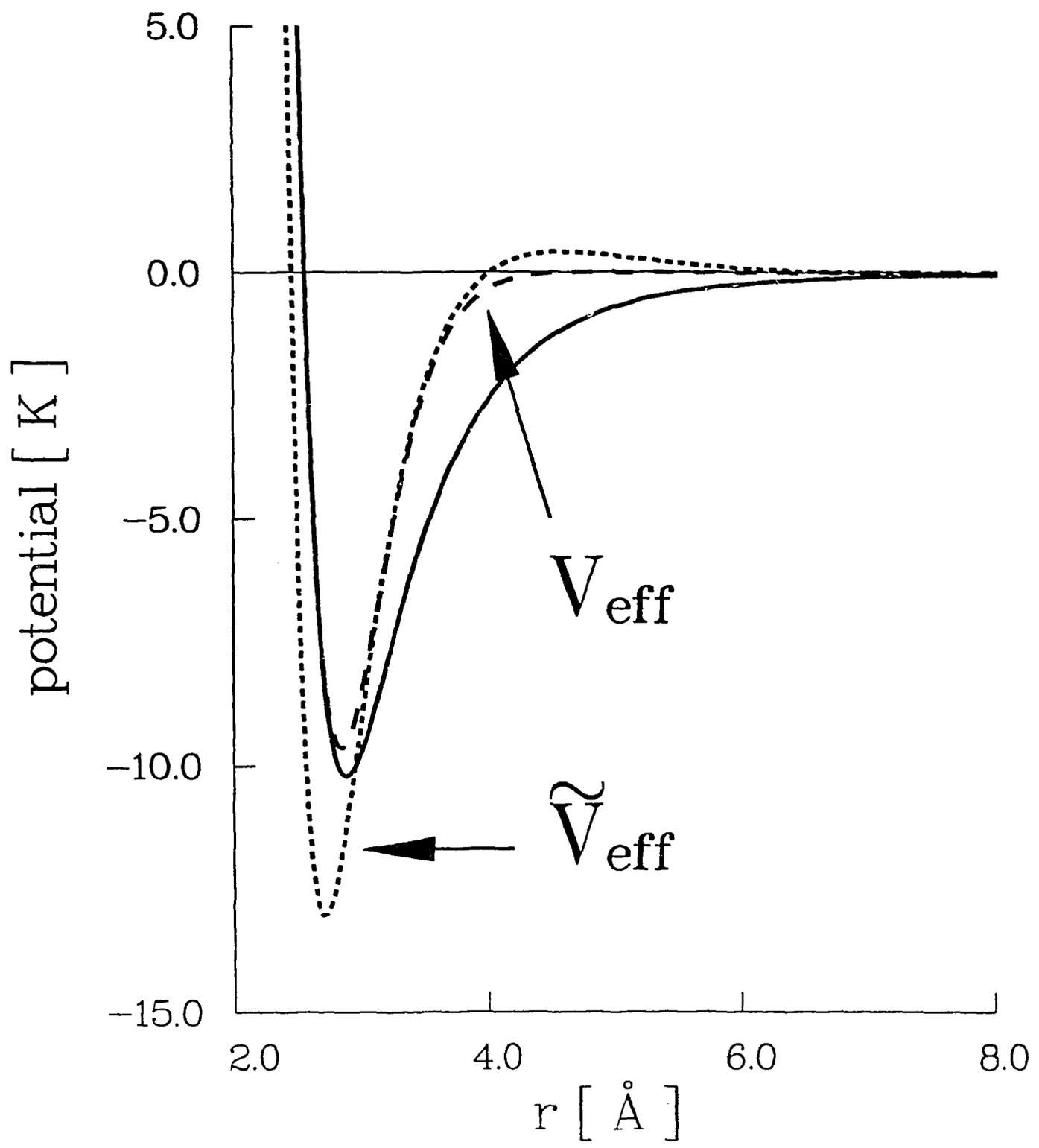


Fig. 5

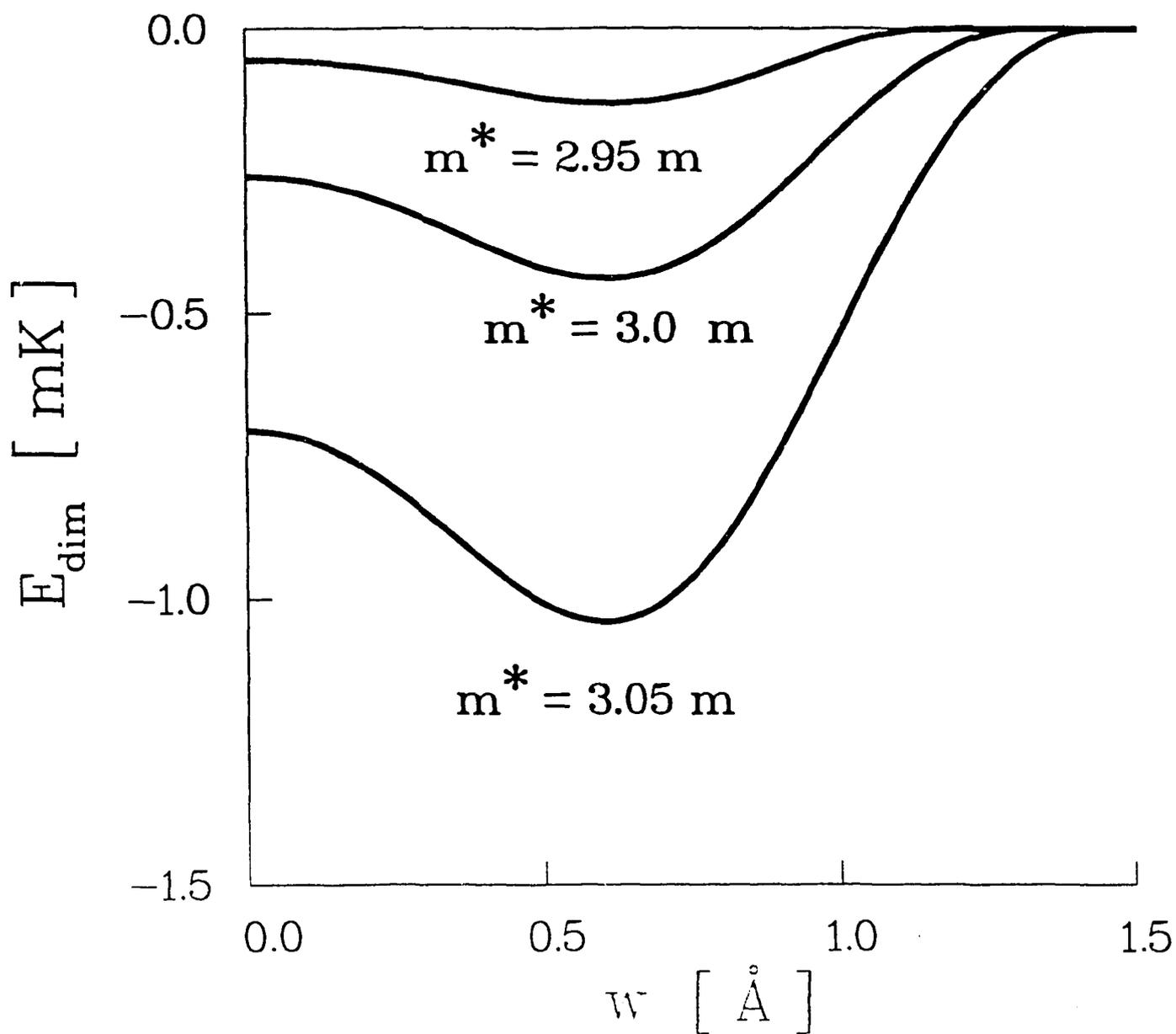


Fig 6

