

Solvent effects of liquid helium on He_2 †

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1. INTRODUCTION

The possible existence of a bound state for the helium diatomic molecule is still an open question [1, 2]. The results of reference [2] show a marked sensitivity of the bound state to the energy curve. Thus another question arises immediately ; how are these results modified by the effects of the solvent ? In particular we may consider two He atoms interacting in a liquid helium environment and study the modifications on the He-He potential energy curve.

In a series of papers Sinanoğlu developed a theoretical method [3, 4] and derived the solvent and the solvation structure dependence (related to many-body effects) of the interaction potentials in liquids. The method is based on the introduction of discrete but mobile solvent layers of individual molecules (packed according to relative size) around the solute molecules. In our case the solute molecules are the He_2 and the discrete effects of three and four-body terms are averaged over various packings in the first solvent layers. For the layers beyond the second, structural effects are naturally smeared out, so the rest of it is just integrated over [3].

This method is quite relevant for helium as it has been shown that three and four-body terms are not always negligible and are frequently of opposite signs [5]. Three-body effects are attractive for equilateral configurations, for instance. Such attractions contribute slightly to the stability of the isolated He_3 ground state [6], which, in contrast to the He_2 case, is substantially bound. Three-body terms, however, may also be repulsive, e.g. the case of linear configurations. Four-body terms are quite sizeable, implying that the convergence of many-body expansions is slower for helium than for all other noble gases [7]. So it is quite interesting to see how all these terms average out in the solvent effect.

It should also be remarked that helium is an interesting testing ground for the importance of solvent effects because the very loosely bound nature of the He_2 vibrational ground state [1, 2] makes it particularly sensitive to these effects.

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2. RESULTS AND DISCUSSION

In reference [2] four different analytical fittings of the He_2 potential energy curve were analysed. These were adjusted to the parameters ϵ and σ (the well depth and the value of the distance where the potential vanishes) corresponding to potential energy data which were taken from some recent theoretical calculations, based on the theory of intermolecular forces of Sinanoğlu and Kestner [8, 9], on the He_2 curve [10, 12]. We here use a Lennard-Jones potential with the same ϵ and σ parameters :

$$V_{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right], \quad (1)$$

instead of the more sophisticated potentials of reference [2]. This indeed changes the bound state energy somewhat. We are interested here, however,

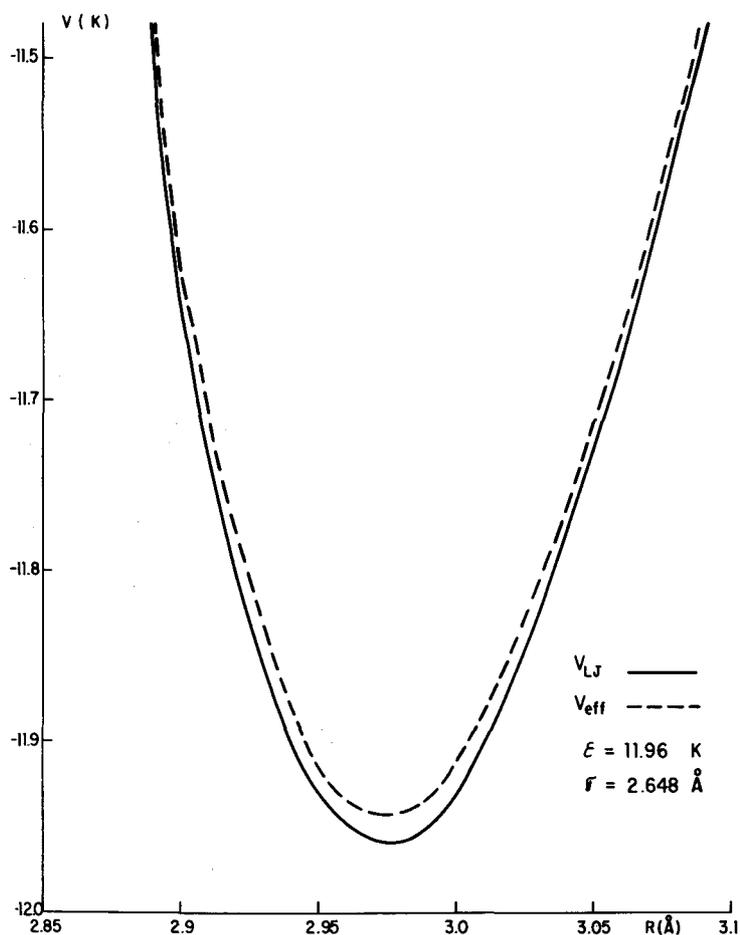


Figure 1. The Lennard-Jones (solid line) and the effective potential (dotted line) for the He_2 molecule. The effective potential includes the solvent effects of the liquid helium medium. Only the region near the well minimum is depicted. The parameter κ of reference [2] is taken as $\frac{1}{2}$.

not on the absolute value of the ground-state energy but its relative change by the introduction of solvent effects. Furthermore, the solvent effect theory of Sinanoğlu [3] takes a particular simple form for the Lennard-Jones potential which transforms to the effective curve

$$V_{\text{eff}} = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \left(1 - \frac{1}{3} \Delta' D_1' L_{AB} \right) \right], \quad (2)$$

where the expressions for Δ' , D_1' and L_{AB} are given in reference [3] and were evaluated at the temperature 3.71 K, that is 0.7 of the critical temperature.

In figure 1 the solvent effects on one of the Lennard-Jones potentials (L-J 1) are depicted. The effective potential is displaced upwards. This is also true for all the other curves. In fact, in figure 2, the relative shift for the four potentials is represented.

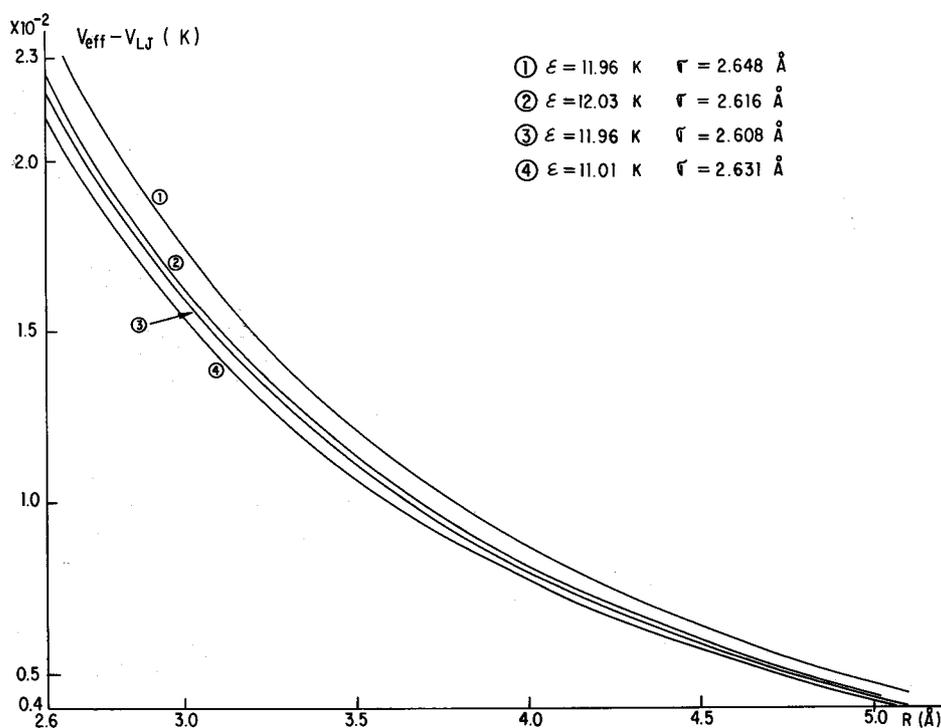


Figure 2. Graph of the relative shift produced by solvent effects, as a function of distance, on the four Lennard-Jones potentials given in the table.

To analyse the effect of such a shift on the ground-state energy we performed a numerical integration of the Schrödinger equation for the nuclear motion. This was done using the programme 'BOUND', references [2] and [13]. The results are reported in the table. It is clear that solvent effects tend to disrupt the (very weakly) bound state of He_2 . Their influence is significant, if not large, amounting to about 5 per cent of the vibrational ground-state energy.

Potential	ϵ (K)	σ (Å)	E_{LJ} (K)	E_{eff} (K)	$\Delta E =$ $(E_{eff} - E_{LJ})$	$\Delta E \times 100/E_{LJ}$
L-J 1 (a)	11.96	2.648	-0.08807	-0.08547	0.00360	4.08 per cent
L-J 2 (b)	11.96	2.608	-0.06514	-0.06300	0.00214	3.29 per cent
L-J 3 (c)	11.01	2.630	-0.02512	-0.02384	0.00128	5.10 per cent
L-J 4 (d)	12.03	2.616	-0.07421	-0.07188	0.00233	3.14 per cent

(a) Lennard-Jones curve adapted to the *ab-initio* values of reference [8].

(b) Lennard-Jones curve adapted to values of reference [10].

(c) Lennard-Jones curve adapted to values of reference [9].

(d) Lennard-Jones curve adapted to values of references [1] and [10].

Parameters for the helium interatomic Lennard-Jones potentials (ϵ and σ). Bound state energies E_{LJ} , bound state energies including solvent effects E_{eff} , numerical change in the bound state energies ΔE and percentage change.

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