Non-additive interactions in liquid helium solvent effects†

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The Sinanoğlu solvent effect method is here modified to include the exchange-overlap three-body SCF term in addition to the usual triple-dipole term. This is accomplished using an analytical fit which gives a better picture of short range non-additive interactions. The application of this modified model to the dimers $(^4He)_2$, $(^3He)_2$ and $^3He-^4He$ in a liquid ^4He environment leads to the lowering of the effective-pair potential energy curve. As a consequence the new terms play a significant role, within the limitations of the method, in the calculation of a bound state of helium dimers immersed in a liquid helium medium.

Recently, Sinanoğlu's treatment of solvent effects to formulate an effective interaction between atoms was applied to the $^4He-^4He$ diatomic system embedded in liquid helium [1]. The question was considered whether the liquid helium solvent could stabilize and bind a dimer, $(^4He)_2$, whose existence is quite uncertain in the gas phase [2, 3]. Liquid helium is an extreme case, when compared to those considered in the original formulation by Sinanoğlu [4], mainly because the quantum effects must certainly cause modification in the calculation of solvent effects. In fact, in the case of helium the effective-pair potential which includes solvent effects, is sensitive to changes in the effective radius used while averaging over different layers of the liquid medium (4). For helium these changes are significant because of the shallow-pair potential well.

The usual applications [1, 4] of Sinanoğlu's approach replace the intrinsic three-atom potential energy, V_3, by the triple-dipole dispersion energy and afterwards perform an average over different mobile layers. Thus, an effective pair potential is obtained. This new potential curve is a function of the distance R between the two molecules in the presence of the liquid environment. In this work we want to stress that the effective-pair potential obtained from solvent effects does indeed change if a more complete three-body potential model is

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taken into consideration. For this purpose, we include in the helium effective potential another non-additive effect : the exchange-overlap energy. It should be stressed that exchange-overlap non-additive potentials are obtained through quantum mechanical studies of the intermolecular interactions of small aggregates of closed shell systems [5]. Consequently their numerical values and geometry dependence have been established independently of the role they may play in solvent effect studies, which is what we want to analyse here, or for that matter for other better known applications such as the study of dense states of matter, solids [6] and liquids [7]. These exchange-overlap three-body terms are particularly well known in the case of helium trimers for which results practically valid up to the Hartree–Fock limit have been derived for a variety of trimer geometries [5]. Such self-consistent field results however, are reported as tables of numerical values and are therefore not in a form amenable to use in Sinanoğlu's theory.

However, an analytical fit that represents both the tripole-dipole and the quantum mechanical exchange-overlap non-additive effects for helium has been derived by Bruch and McGee [8]

$$V_3(R, r, s) = \{ -A \exp [-\alpha(R+r+s)] + C/(Rrs)^3 \}$$
$$\times (1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3), \quad (1)$$

where r, s and R are the sides and θ_1, θ_2 and θ_3 the interior angles of the triangle formed by the three particles. The values of the constants are : $C = 2 \cdot 1 \times 10^{-13}$ erg Å^9, $A = 1 \cdot 33 \times 10^{-9}$ erg, $\alpha = 1 \cdot 936$ Å^{-1}.

The V_3-model of equation (1) is based on a significant extrapolation from the short separation SCF results [5] for helium and should be used cautiously in the intermediate separation region since the balance of exchange and dispersion terms for neon is apparently reversed [9]. For intermediate separations the helium V_3-model given in equation (1) shows that the exchange-overlap term is not only much larger in absolute value than the dispersion terms, but furthermore it is of opposite sign. But it is not obvious that after averaging out V_3 over many geometrical configurations (only r and s vary), the balance between exchange-overlap and dispersion will remain the same as for one isolated geometry. Furthermore, Sinanoğlu's averaging procedure contains a parameter κ which is introduced when structure in the pair distribution function $g(R)$ is neglected and a gas-like averaging is performed. Therefore, the result of averaging the Bruch–McGee V_3-model for helium using Sinanoğlu's procedure leads to an effective potential with a κ dependence as seen in the Appendix. In previous studies on quasi-spherical solvents [4] in which only the triple-dipole term was included, a value $\kappa = 0 \cdot 5$ was used. We examined the sensitivity of the new solvent effects for helium to κ values in the range $0 \cdot 2$ to $0 \cdot 5$ and found that both exchange-overlap energy E_e and dispersion E_d contributions to the effective potential were enhanced for the smaller κ values as seen in figure 1.

For fluids such as helium with diffuse solvation layers, κ values smaller than $0 \cdot 5$ are more likely to reproduce the true liquid structure. Indeed from a comparison of the helium $g(R)$ [10] with that of a classical liquid such as argon [11], it appears that one should select values of κ smaller than $0 \cdot 5$, to take into account in the averaging procedure the same portion of the first solvation layer. For
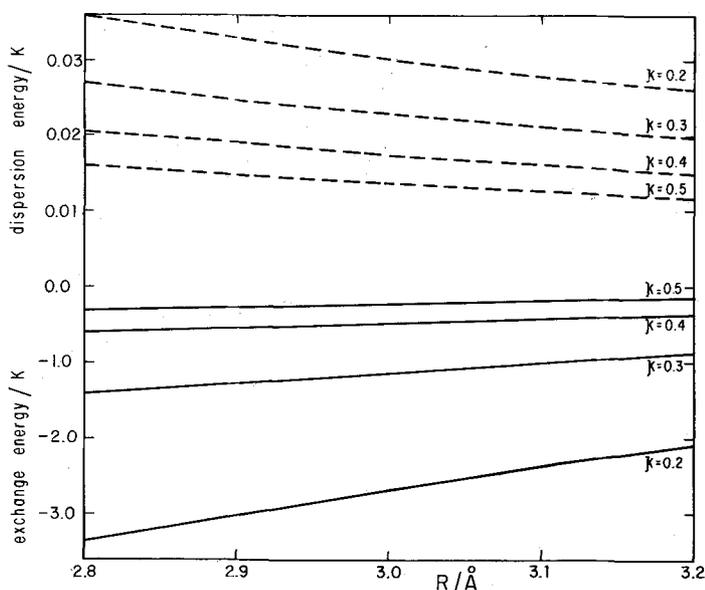
Figure 1. Triple-dipole-dispersion contribution (upper half) and exchange-overlap contribution (lower half) to the $(^4He)_2$ effective pair potential energy for different values of κ. The positive and negative scales are different.

example, when the integral

$$\int_0^{3R_c} g(R)R^2 \, dR,$$

related to the coordination number, is substituted by

$$\int_{(1+\kappa)R_c}^{3R_c} R^2 \, dR,$$

for the pure argon $g(R)$ with Sinanoğlu's assumed value of $\kappa = 0.5$ one obtains 96 per cent of the layer. For the helium case the relation between these integrals depends notably on κ giving 97 per cent, 96 per cent, 95 per cent, 93 per cent, 91 per cent, 81 per cent, for $\kappa = 0.2$, 0.25, 0.3, 0.4, 0.5 and 0.8 respectively.

In any case the result of using the Bruch–McGee V_3-model for solvent effect on helium is indeed that the averaged exchange-overlap term outweighs the averaged triple-dipole term regardless of the choice of κ, as is evident from figure 1. We also would like to stress that the newly introduced three-body term (i.e. the exchange-overlap attractions) are not greatly sensitive to changes in κ, and in fact change less when κ is shifted from 0.2 to 0.5 than the traditional dispersion contribution, as is shown in table 1, for intermolecular distances around the region of the potential minimum.

The consequence is, of course, the deepening of the effective pair potential for ^4He and ^3He dimers immersed in a liquid ^4He environment as is shown in figure 2. The numerical calculations leading to figure 2 were done using the ESMMSV [12] potential which represents the 'bare' or isolated pair-wise interaction of a $(He)_2$ dimer (continuous line) and to which were added the averaged exchange-overlap and dispersion energies to obtain the new effective

Table 1. Ratio of the κ changes in the dispersion contribution $E_d{}^\kappa$ to the κ changes in the exchange overlap contribution $E_e{}^\kappa$ for the solvent effects of $(^4He)_2$ in liquid ^4He.

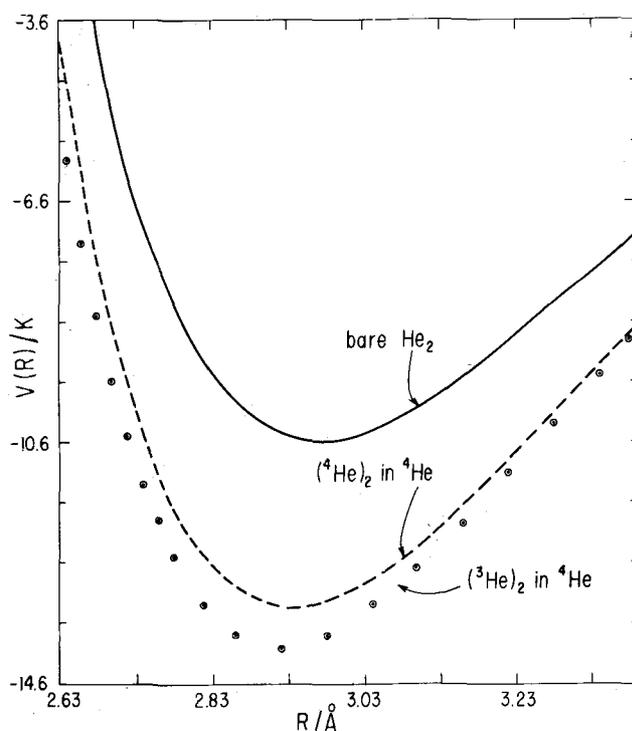| $R/\text{Å}$	$\Delta_d = E_d{}^{0.5}/E_d{}^{0.2}$	$\Delta_e = E_e{}^{0.5}/E_e{}^{0.2}$	Δ_d/Δ_e
2·8	0·443	0·075	5·90
3·0	0·449	0·075	5·98
3·2	0·460	0·076	6·03

Figure 2. Effective potentials for the $(^4He)_2$ and $(^3He)_2$ dimers in a ^4He solvent medium, as compared to the bare ESMMSV [12] helium pair-wise potential.

potential (dashed curve). The circles give the effective potential of the $(^3He)_2$ dimer in a liquid ^4He medium. It should be mentioned that the well of the ESMMSV curve is quite similar to those of other recently proposed potentials [13].

We now discuss the effect of a liquid ^4He medium on the hypothetical bound states of helium dimers. For this, the Schrödinger equation for the movement of the nuclei containing the interatomic potentials of figure 2 was solved using a numerical method [1-2]. We have recalculated this movement by integrating numerically using the ESMMSV potential for free dimers $(^3He)_2$, $(^4He)_2$ and $^3He-^4He$. No bound state is obtained for these three systems. This result is not new because when in reference (2) other (older) potentials were studied, binding energies of the order of one thousandth of a degree kelvin were reported

for $(^4He)_2$ and only positive energies for $(^3He)_2$. The negative energy values were too close to zero to decide the issue of whether $(^4He)_2$ was a bound system or not. The new results are obtained when the effective potential of equation (A 1) is introduced in the Schrödinger equation representing either the pair $^4He-^4He$, $^3He-^4He$ or $^3He-^3He$ modified by a ^4He environment. For $^3He-^4He$ as well as for the lighter pair $^3He-^3He$, in spite of the fact that its effective curve (dots) is the lowest in figure 2, we still obtain a positive energy for values of κ in the range $0 \cdot 2 \leqslant \kappa \leqslant 0 \cdot 8$. This means that, within the approximation of formula (1), in spite of the strong solvent effects, the pairs $(^3He)_2$ and $^3He-^4He$ are not bound.
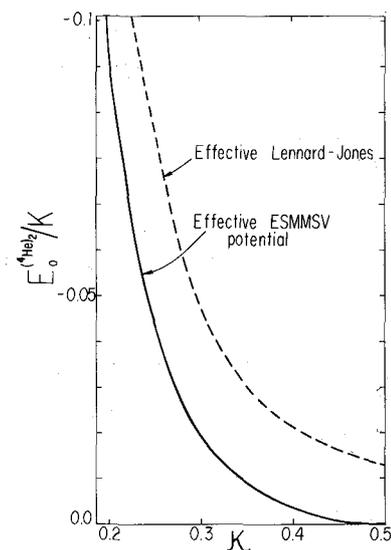

Figure 3. Ground energy of the $(^4He)_2$ system including solvent effects as a function of κ.

The situation for the heavier $(^4He)_2$ dimer is different. In figure 3 we show that the ground state energy of $(^4He)_2$ is extremely dependent on the solvent effect parameter κ. As seen there, already for $\kappa = 0 \cdot 4$ the bound state is lowered to values of $-0 \cdot 003$ K by the inclusion of the exchange-overlap non-additive attraction. Moreover, as stated above from considerations on the non-classical nature of liquid helium, the solvent layers are quite diffuse implying that smaller values of κ than in the classical liquid should be considered. For the extreme value of $\kappa = 0 \cdot 2$ the bound state is drastically stabilized to about $-0 \cdot 1$ K. For comparison with reference [1] we have also calculated for the $(^4He)_2$ dimer the ground state of a Lennard–Jones (L–J) potential whose constants ϵ and σ are fitted to the new ESMMSV potential ($\epsilon = 10 \cdot 57$ K, $\sigma = 2 \cdot 625$ Å). The bare L–J ground state is $-0 \cdot 009$ K. If only triple-dipole non-additive corrections are included into the solvent effects the ground level is shifted upward by about 5 per cent. In contrast a downward shift of 50 per cent ($\kappa = 0 \cdot 5$) is obtained by including also the exchange-overlap term in the averaged three-body effects. The changes in κ of the bound state energy of a L–J $(^4He)_2$ system with solvent effects are also shown in figure 3.

The main purpose of this paper is to point out that exchange-overlap three-body terms should and can be incorporated into the solvent effect model. The role they play in the stabilization of helium dimers through the action of the liquid helium medium is quite important and changes previous estimations [1], showing that solvent effects tend to enhance the very weak binding of $(^4\mathrm{He})_2$ systems.

APPENDIX

The effective potential between molecules M_A and M_B is obtained by adding to a pair-wise potential $V_2(R)$ the averaged three-body terms :

$$V_{\mathrm{eff}}(R) = V_2(R) + \frac{1}{n}\left[\frac{C}{R_C{}^3 R^6} L_{\mathrm{AB}}(R) + L'_{\mathrm{AB}}(R)\right], \qquad (A\,1)$$

where $R_C = (3/4\pi\rho)^{1/3}$, ρ = the number density of the solvent, $n = 3$, 2 or 1 depending on whether $M_A = M_B = M_C$, $M_A \neq M_B = M_C$ or M_A and $M_B \neq M_C$, M_C being a solvent molecule. The constant C characterizes the triple-dipole term in equation (1), $L_{\mathrm{AB}}(R)$ is reported in table 1 of reference (4) and $L'_{\mathrm{AB}}(R)$ is the averaged exchange-overlap contribution which in terms of reduced variables $r \rightarrow r/R$ and $s \rightarrow s/R$ [4] is

$$L'_{\mathrm{AB}}(R) = \begin{cases} F(s_0, r_0) & \text{if } R > R_A + R_B + 4R_C \begin{cases} s_0 = R_A + 2R_C \\ r_0 = R_B + 2R_C \end{cases} \\[2ex] F(s_0, r_0) - F(1 + r_0, r_0) & \text{otherwise,} \end{cases} \qquad (A\,2)$$

where R_A and R_B are the radii of atoms M_A and M_B forming the dimer calculated at the same reduced temperature as that of the solvent. Three regions are to be specified in the second case above : if

$$R_A + R_B + 4R_C \geqslant R \geqslant R_A + R_B + (2+\kappa)R_C \qquad \text{then} \quad \begin{cases} s_0 = R_A + 2R_C \\ r_0 = R_B + 2R_C, \end{cases}$$

if

$$R_A + R_B + (2+\kappa)R_C \geqslant R > R_A + R_B + 2R_C \qquad \text{then} \quad \begin{cases} s_0 = R_A + \kappa R_C \\ r_0 = R_B + 2R_C, \end{cases}$$

if

$$R_A + R_B + 2R_C > R \geqslant |R_A - R_B| \qquad \text{then} \quad \begin{cases} s_0 = R_A + \kappa R_C \\ r_0 = R_B + \kappa R_C. \end{cases}$$

The function $F(x, y)$ has the following form :

$$F(x, y) = -\bar{A}\{(2\bar{\alpha})^{-1}\{\exp[-\bar{\alpha}(2x+1)]\}f_1 + \tfrac{3}{4}\exp(\bar{\alpha})(f_2 + f_3 + f_4)$$
$$+ 2\exp[-\bar{\alpha}(x+y)]f_5\} - E_1(\bar{\alpha}x)[\tfrac{3}{8}E_1(\bar{\alpha}y) - \exp(-\bar{\alpha}y)f_6]\}, \qquad (A\,3)$$

where $\bar{A} = (3/2R_C{}^3)\, A \exp(-\bar{\alpha})$, $\bar{\alpha} = \alpha R$ and the f_i ($i = 1$ to 6) are given by

$$f_1 = \beta_0 + \beta_1\left(x - \frac{1}{2\bar{\alpha}}\right) + \beta_2\left(x^2 - \frac{x}{\bar{\alpha}} + \frac{1}{2\bar{\alpha}^2}\right) + \beta_3\left(x^3 - \frac{3x^2}{2\bar{\alpha}} + \frac{3x}{2\bar{\alpha}^2} - \frac{3}{4\bar{\alpha}^3}\right)$$

$$+ \beta_4\left(x^4 - \frac{2x^3}{\bar{\alpha}} + \frac{3x^2}{\bar{\alpha}^2} - \frac{3x}{\bar{\alpha}^3} + \frac{3}{2\bar{\alpha}^4}\right) + \beta_5 E_1(2\bar{\alpha}x),$$

$$f_2 = cI_6 + (5c + b)I_5 + (9c + 5b + a)I_4 + (13c + 9b + 5a)I_3 + (c + 13b + 9a)I_2,$$

$$f_3 = \sum_{i=1}^{2}(-)^{i+1}\left[\phi_i \exp(-2\bar{\alpha}b_i)E_1(2\bar{\alpha}(1 + x - b_i)) - \frac{2a}{b_i}E_1(2\bar{\alpha}(1 + x))\right],$$

$$f_4 = \phi_3 E_1(2\bar{\alpha}x),$$

$$f_5 = \left(x - \frac{1}{\bar{\alpha}}\right)\gamma_1 + \left(x^3 - \frac{3x^2}{\bar{\alpha}} + \frac{6x}{\bar{\alpha}^2} - \frac{6}{\bar{\alpha}^3}\right)\gamma_2 + \tfrac{3}{8}\exp(-\bar{\alpha}y)E_1(\bar{\alpha}y)\left[x^5 - \frac{5x^4}{\bar{\alpha}}\right.$$

$$\left. + x^2\left(1 - \frac{20}{\bar{\alpha}^2}\right)\left(\frac{3}{\bar{\alpha}} - x\right) - x\left(1 + \frac{6}{\bar{\alpha}^2} + \frac{120}{\bar{\alpha}^4}\right) + \frac{1}{\bar{\alpha}}\left(1 + \frac{6}{\bar{\alpha}^2} - \frac{120}{\bar{\alpha}^4}\right)\right],$$

$$f_6 = \frac{1}{\bar{\alpha}}\left[\tfrac{3}{8}\left(y + \frac{1}{\bar{\alpha}}\right)(1 - y^4) + \tfrac{3}{8}\left(y + \frac{3}{\bar{\alpha}}\right)\left(y^2 + \frac{2}{\bar{\alpha}^2} - \frac{20y^2}{\bar{\alpha}}\right) + \frac{3y}{2\bar{\alpha}}\left(\frac{1}{\bar{\alpha}} - y^3\right)\right],$$

with

$$\beta_0 = \frac{3}{4\bar{\alpha}}\left[\tfrac{1}{2} + \frac{7}{\bar{\alpha}} + \frac{27}{\bar{\alpha}^2} + \frac{60}{\bar{\alpha}^3}\left(1 + \frac{1}{\bar{\alpha}}\right)\right],$$

$$\beta_1 = \frac{1}{4\bar{\alpha}}\left(8 + \frac{35}{\bar{\alpha}} + \frac{82}{\bar{\alpha}^2} + \frac{81}{\bar{\alpha}^3}\right),$$

$$\beta_2 = \frac{1}{\bar{\alpha}}\left(2 + \frac{21}{4\bar{\alpha}} + \frac{21}{4\bar{\alpha}^2}\right),$$

$$\beta_3 = \frac{3}{8\bar{\alpha}}\left(1 + \frac{1}{\bar{\alpha}}\right),$$

$$\beta_4 = -\tfrac{3}{8},$$

$$\beta_5 = \frac{3}{\bar{\alpha}}\left(-\tfrac{1}{8} + \frac{1}{8\bar{\alpha}} + \frac{27}{7\bar{\alpha}^2} + \frac{57}{4\bar{\alpha}^3} + \frac{15}{\bar{\alpha}^4} + \frac{15}{\bar{\alpha}^5}\right),$$

$$a = 0.250\,621,$$

$$b = 2.334\,733\bar{\alpha},$$

$$c = \bar{\alpha}^2,$$

$$b_1 = -0.368\,975\bar{\alpha},$$

$$b_2 = -1.611\,751\bar{\alpha},$$

$$\phi_i = a + 3b + c + \frac{2a}{b_i} + \frac{0.804\,650\,3}{\bar{\alpha}(1 - b_i)} + b_i(3c + b + 13a)\,;\quad i = 1, 2,$$

$$\phi_3 = \frac{0.804\,650\,3}{\bar{\alpha}}\frac{(a + b + c)(b_1 - b_2)}{(1 - b_1)(1 - b_2)},$$

E. Blaisten-Barojas *et al.*

$$\gamma_1 = \frac{1}{\bar{\alpha}} \left[\frac{1}{4} \left(y + \frac{1}{\bar{\alpha}} \right) \left(1 + \frac{9}{\bar{\alpha}^2} \right) + \frac{3y^2}{8} \left(y + \frac{3}{\bar{\alpha}} \right) \right],$$

$$\gamma_2 = \frac{3}{8\alpha} \left(y + \frac{1}{\alpha} \right)$$

and where for $m > 1$

$$I_m = \frac{0{\cdot}804\ 650\ 3}{\bar{\alpha}} \exp\left[-2\bar{\alpha}(1+x) \right] \sum_{i=1}^{2} (-)^{i+1} b_i{}^m \left\{ \exp\left[2\bar{\alpha}(1+x-b_i) \right] \right.$$

$$\times E_1(2\bar{\alpha}(1+x-b_i)) + \frac{1}{2\bar{\alpha}} \sum_{k=1}^{m} \binom{m}{k} b_i{}^{-k}(1+x-b_i)^{k-1}$$

$$\times \left[1 + \sum_{p=1}^{k-1} \frac{(k-1)(k-2) \dots (k-p)}{[2\bar{\alpha}(1+x-b_i)]^p} \right] \right\}.$$

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