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ments and with the differential scattering experiments of Bickes et al.[8]

Finally we note that in all calculations elastic scattering was assumed and the potential anisotropy was neglected. This appears justified by the observation that the orbiting maxima for Ar measured with pure para-H_2 in the rotational state $j = 0$ have been found to be identical to those for n-H_2. Furthermore, trial close coupling calculations[9] using the full LK potentials, with closed channels included, indicated that the anisotropy of the potential only produces a negligible quenching of the observed resonance maxima.

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NOTES

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Shortly after Alder and Wainwright[1] published a summary of their work on computer simulated dynamics, in which long time tails were observed for the velocity autocorrelation function, a variety of theoretical papers appeared which claimed to explain the phenomenon. Dorfman and Cohen[2] presented a kinetic theory justification of the results of Alder and Wainwright. Zwanzig and Bixon[3] presented a hydrodynamical theory which also explained the long time tail behavior of the autocorrelation function. A semikinetic, semihydrodynamical theory was also presented by Ernst, Hauge, and van Leeuwen,[4] which also explained the long time tails. Another semihydrodynamical approach, the mode coupling theory, was used to explain these same results by Kawasaki[5] and also by Pomeau.[6]

A closely related problem is the problem of the velocity autocorrelation function for a Brownian particle immersed in a fluctuating fluid. The Landau–Liftshitz theory[7] of fluctuating hydrodynamics, as formulated by Fox and Uhlenbeck,[8] has been applied successfully to this problem by Chow and Hermans,[9] and by Hauge and Martin-Löf.[10] Both groups showed long time tail behavior of the type observed by Alder and Wainwright.

It is the purpose of this note to make an observation which appears to have been overlooked so far. The fluctuating hydrodynamic theory directly yields the Alder and Wainwright result through the autocorrelation function of the fluid velocity field, without the introduction of a Brownian particle. The advantage of this approach is its simplicity, because the computation of the free fluid velocity field autocorrelation is rather easy compared with the calculation of the corresponding velocity autocorrelation function for the Brownian particle.

The velocity field satisfies the following linearized, Navier–Stokes equation[7,8]:

$$\rho_0 \frac{\partial v_i}{\partial t} = -\frac{\partial \rho}{\partial x_i} + \eta \nabla^2 v_i + \frac{\partial}{\partial x_j} \tilde{S}_{ij}, \tag{1}$$

in which $\tilde{S}_{ij}$ is the fluctuating stress tensor which has the correlation formula

$$\langle \tilde{S}_{ik}(\mathbf{x}, t) \tilde{S}_{jl}(\mathbf{x}', t') \rangle = 2 K_B T \eta (\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj}) \delta(t - t')$$
$$\times \delta(\mathbf{x} - \mathbf{x}'), \tag{2}$$

in which K_B is Boltzmann's constant, T is the temperature, and η is the shear viscosity. In the above, restriction to the incompressible case is implicit, although not necessary. Szu, Szu, and Hermans[11] have treated the autocorrelation functions for fluctuating hydrodynamics in some detail; so we quote their result for the velocity autocorrelation function of the free fluid, although the derivation, using Fourier transformations, from (1) and (2) is quick and easy. The result is according to Eq. (24) of Szu et al.,

$$\langle v_i(\mathbf{x}, t) v_j(\mathbf{x}, t') \rangle = \tfrac{2}{3} K_B T (1/\rho_0) (4\pi\nu |t - t'|)^{-3/2} \tag{3}$$

in which $\nu = \eta/\rho_0$. This is precisely the formula which provides an explanation of the Alder–Wainwright observations, according to the earlier theories.[2-6]

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Calculation of the second virial coefficients for water using a recent "*ab initio*" potential

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The potential energy function representing the water–water interaction is of considerable importance in the understanding of the physics and chemistry of water. Although empirical formulas have been presented long ago,[1] it is only recently that theoretical potentials[2] of increasing accuracy have started to appear. The most sophisticated one is the one by Matsuoka *et al.* obtained with the method of configuration interaction,[3] (where 6000 configurations are considered). In this work two potentials are reported: the first, hereafter referred to as CI(1), includes only the intermolecular correlation corrections, whereas the second, henceforth called CI(2) includes also the intramolecular correlation corrections. In view of the success of the CI(1) potential function in predicting various properties of liquid water by a Monte Carlo method,[4] it is certainly interesting to see how well this same potential fares in the gas phase. Thus we report the calculations of the second virial coefficients of steam and compare them with the experimental results of Kell *et al.*[5] Also reported are the second virial coefficients obtained from the CI(2) potential as well as an empirical potential designated as ST2, which has been shown to yield realistic results for various properties of liquid water in a molecular dynamic simulation study.[6]

The relative orientation of two water molecules can be specified by giving three positional coordinates (r, θ, φ) and three Euler angles (α, β, γ) of the first molecule while holding the second molecule fixed in the origin. The second virial coefficient $B(T)$ can then be written as

$$B(T) = \frac{N}{16\pi^2} \int_0^\infty r^2 \, dr \int_0^\pi \sin\theta \, d\theta$$

$$\times \int_0^{2\pi} d\varphi \int_0^\pi \sin\beta \, d\beta \int_0^{2\pi} d\gamma [e^{-U/kT} - 1] \, ,$$

where N is the Avogadro number and U is the water–water interaction potential function. The above six-dimensional integration was carried out by a Monte Carlo technique for the three potential functions, CI(1), CI(2), and ST2. The numerical results are given in Table I (where we have reported only as many digit as significant by convergency test). Comparison with the experiments is done in Table I and Fig. 1. For completeness, the results obtained from a Hartree–Fock potential[7] is also plotted in the figure.

The integration has been performed by defining three regions; the first ($r < 2$ Å) yields a constant value of 10 cm^3/mole, the second within the range 2 Å $\leq r \leq 5$ Å, and the third for the range $r > 5$ Å. For the third region, the CI(1) potential is found to be in better agreement than the others with what were obtained using an empirical potential of Lennard-Jones type corrected by other empirical factors.[8]

Figure 1 shows clearly that the CI(1) potential gives the best results, among the four, relative to the experiments. While the results of the ST2 potential yield a curve nicely parallel to the experimental curve, indicating a nearly constant ratio between the two, it is less so for the CI(2) and the CI(1) curves. We note also that while the CI(1) curve seems to converge to the experimental curve at high temperatures, the HF curve is found to be diverging.

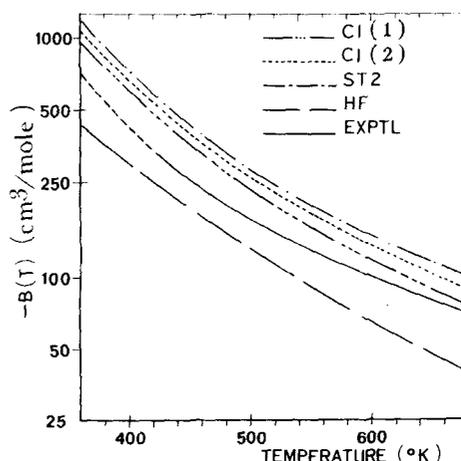The HF, ST2, and CI(1) potential functions have been

FIG. 1. Second virial coefficient as a function of temperature. The potentials are those reported in Ref. 3 for CI(1) and CI(2), in Ref. 2 (the last one) for HF, and in Ref. 6 for ST2; the experimental curve EXPTL is given in Ref. 5 (the dashed part of this curve corresponds to extrapolated values).