EVIDENCE FOR THREE-BODY FORCES FROM THIRD VIRIAL COEFFICIENTS

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The three-body dispersion force or triple-dipole interaction for three atoms has been calculated by third-order perturbation theory,[1] by the variational method,[2] and from the classical Drude model.[3] The interaction energy is

$$w_{123} = \nu(r_{12}r_{23}r_{31})^{-3}(1 + 3\cos\gamma_1\cos\gamma_2\cos\gamma_3), \quad (1)$$

where r_{ij} are the sides and γ_i the interior angles of the atomic triangle. For identical atoms, $\nu = 3\alpha\mu/4$ where α is the polarizability and μ the coefficient of the two-body dispersion potential ($-\mu r^{-6}$). Evidence for w_{123} was sought by Kihara et al.[4] who calculated the correction to the third cluster integral b_3 and also the small quantum correction. The nonadditivity correction to b_3 is

$$\Delta b_3 = \frac{1}{3!V}\iiint \exp\left(-\frac{\sum u_{ij}}{kT}\right)\cdot\left[\exp\left(-\frac{w_{123}}{kT}\right)-1\right]d\tau_1 d\tau_2 d\tau_3, \quad (2)$$

where u_{ij} is the complete two-body interaction [customarily represented by the Lennard-Jones (12, 6) potential]. Assuming Eq. (1) to hold for arbitrarily small r_{ij} and using the (12, 6) potential for u_{ij}, Kihara et al. evaluated Δb_3 numerically and compared their results with "experimental" b_3 values obtained from the second and third virial coefficients $B(T)$ and $C(T)$. The correction improved the agreement for all the noble gases except Xe. This way of comparing with experiment tends to obscure the significance of the three-body forces. The uncorrected b_3 values do not differ much from the "experimental" values because the latter are partly based on $B(T)$ data which the (12, 6) potential has been adjusted to fit. It is preferable to compare $C(T)$ values rather than b_3 values.

At low temperatures the measured values of $C(T)$ for the noble gases show large deviations (~60%) from values calculated with the (12, 6) potential assuming additivity. These discrepancies appear much too large to be experimental error. However, the (12, 6) potential not only reproduces $B(T)$ data fairly accurately but also accounts for transport properties with nearly the same potential parameters. The discrepancies are only slightly reduced by using the (9, 6) instead of the (12, 6) potential[5] and are enhanced when $C(T)$ is calculated with the Sutherland (∞, 6) potential.[6]

We have calculated Δb_3 and ΔC from Eqs. (1) and (2) using the Sutherland model for u_{ij}. The Sutherland potential has a hard core of diameter σ and an attractive term $-\mu r^{-6}$ for $r > \sigma$, and is customarily used with the assumption that $\mu\sigma^{-6} \ll kT$. Equation (1) is inaccurate at close distances where higher multipoles contribute and where two or more atoms overlap.[7] Although the overlap forces are known to be nonadditive, there is no simple expression available to represent w_{123} for small r_{ij}. Equation (2) shows that the three-body interaction at close distances will contribute little to the value of the integral

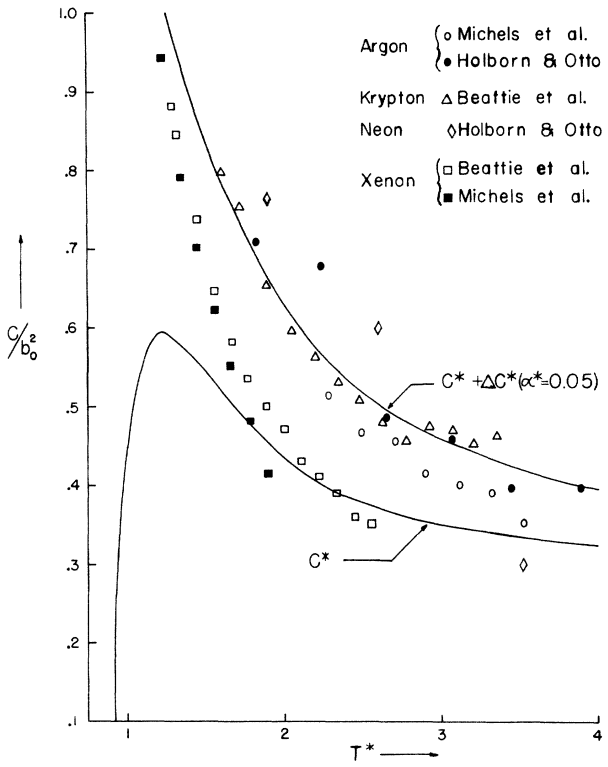

Fig. 1. Reduced third virial coefficient versus reduced temperature. All values of ϵ and σ were taken from Hirschfelder et al. [J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954), p. 1110]. Uncertainties in fitting compressibility data with the virial expansion affect the $C(T)$ values by 10% or less. The Xe data of Beattie et al. have been refitted, but only the high T^* values are affected.

because of the steep rise of the two-body potential.[8] The hard core of the Sutherland model provides an automatic cutoff for w_{123} when $r_{ij} < \sigma$.

By expanding the exponentials in Eq. (2) the integral can be evaluated analytically for the Sutherland model. The first two terms of the expansion of $\exp[-u(r)/kT]$ when $r > \sigma$, i.e., $1 + (\mu/kT)r^{-6}$, give a better approximation to the exponential expression for the (12, 6) potential than the unexpanded formula. The correction to the third virial coefficient, obtained analytically in "corresponding states" form, is

$$\Delta C^* = (15\alpha^*/4T^*)[1 + (2.1067 - 0.0693\alpha^*)/T^*], \quad (3)$$

where C^* is the reduced value of C, T^* the reduced temperature, and α^* the reduced polarizability. We set $\mu = 4\epsilon\sigma^6$ and $b_0 = 2\pi N\sigma^3/3$. Then $C^* = C/b_0^2$, $T^* = kT/\epsilon$, and $\alpha^* = \alpha/\sigma^3 \approx 0.05$ for most noble gases. The Lennard-Jones parameters σ and ϵ can be approximately identified with the Sutherland parameters σ and ϵ as defined. When adjusted to fit $B(T)$ data, they have nearly the same numerical values.

Figure 1 shows a plot of C^* vs T^* for the (12, 6) potential assuming additivity. The correction ΔC^*, obtained from Eq. (3), is also plotted and it is seen that the experimental points tend to agree with the corrected curve. Thus Eq. (3), which contains no adjustable constant, removes most of the disagreement at low temperatures. The error incurred in using the Sutherland model for ΔC^* is a small correction on a correction. We conclude that the third virial coefficients of the noble gases provide evidence for the predicted three-body dispersion forces.

[1]B. M. Axilrod, J. Chem. Phys. 19, 719 (1951).

[2]Y. Midzuno and T. Kihara, J. Phys. Soc. Japan 11, 1045 (1956).

[3]W. L. Bade, J. Chem. Phys. 27, 1280 (1957).

[4]S. Koba, S. Kaneko, and T. Kihara, J. Phys. Soc. Japan 11, 1050 (1956).

[5]T. Kihara, J. Phys. Soc. Japan 6, 184 (1951).

[6]If the discrepancies are attributed to the (12, 6) potential being an inadequate representation of the true two-body potential, the fact that the deviations increase rapidly with decreasing temperature would suggest that it is the attractive London term which is mainly at fault. But the form of this term is certainly correct and the coefficients μ can be checked in several ways.

[7]L. Jansen and R. T. McGinnies, Phys. Rev. 104, 961 (1956).

[8]Furthermore, the triple-dipole forces will be more influential than the three-body overlap forces at the low temperatures for which the discrepancies occur.

ENHANCED DIFFUSION IN AN rf DISCHARGE IN THE PRESENCE OF A MAGNETIC FIELD*

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In a great number of plasmas such as arcs, positive columns, PIG discharges, etc., it has been observed that the diffusion in a direction transverse to a static magnetic field B is anomalous in that it does not decrease monotonically[1-8] like B^{-2}. In plasmas of the type just mentioned, one generally assumes the existence of a static longitudinal electric field $\vec{E}$ and a direct current $\vec{I}$, both of which are parallel to B; however, in other plasmas the existence of the directed current $\vec{I}$ has not been demonstrated with certainty. Kadomtsev and Nedospasov[9] have recently proposed an explanation for anomalous diffusion which is based on the existence of a directed current $\vec{I}$. Our purpose is to show that anomalous diffusion seems also to occur in plasmas where a directed current $\vec{I}$ does not exist; namely, in an rf discharge.

Glass tubes of length ~60 cm and of diameter ϕ varying from 1.25 cm to 5 cm were placed in a solenoid of length $L \sim 40$ cm. The magnetic field was variable from zero to approximately 1000 gauss. The electrodes to which the rf voltage was applied were separated by approximately 40 cm, and consisted of strips of copper foil wrapped around the outside surface of the glass cylinder. A leak valve was used to vary the pressure and type of gas in the glass tube. The working pressure was in the range of 20 microns to 200 microns of Hg and was measured with a MacLeod gauge. Hydrogen and argon were the two gases utilized in the experiment. In Fig. 1, the experimental setup is presented.

The applied rf voltage is of the order of 200 volts peak to peak and is maintained constant. It is furnished by a 0.1-kW rf push-pull oscillator operating at 23 Mc/sec. The plasma density is