Thus $z_0 \simeq 0.7$, $\alpha p/\sqrt{2} \simeq 6.5$, and we evaluate G_1 in the limit $y_0 \gg 1$, $\alpha p/\sqrt{2} \gg z_0$. The result is

$$G_1 = A(2p^2)^{3/2} e^{-\alpha a} e^{-z_0^2} \left\{ \frac{1}{4y_0}\left(\frac{1}{y_0^2}\right) + z_0\left(\frac{1}{2y_0^2} - \frac{3}{4y_0^4} + \cdots\right) + \frac{z_0^2}{2y_0^2}\left(1 - \frac{1}{2y_0^2} + \frac{3}{4y_0^4} - \cdots\right)\right\}.$$

G_2 is given by

$$G_2 = -\frac{B}{3a^3}\{(1-2z_0^2)e^{-z_0^2} + 2(\pi)^{1/2} z_0^3 (1 - \operatorname{erf} z_0)\}.$$

It should be noticed that the expression for G_1 and G_2 involve the term $\exp(-z_0^2) \propto \exp(-\gamma T)$, which cannot be obtained from an expansion in powers of $(1/kT)$. The tabulation of $G = G_1 + G_2$ as a function of temperature for $a = 2.175$ Å is given in Table I and Fig. 4.

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Intermolecular Three-Body Forces and Third Virial Coefficients*

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Nonadditivity corrections to the third virial coefficients $C(T)$ of the noble gases have been calculated for the three-body exchange interactions in the first and second orders of perturbation theory using approximate formulas of Jansen based on the Gaussian model. Denoting these corrections by ΔC_1 and ΔC_2, respectively, and the correction for the triple dipole interaction by ΔC_3, it is found that $\Delta C_1 < 0$, $\Delta C_2 > 0$, $\Delta C_3 > 0$, $\Delta C_1 + \Delta C_2 < 0$, and the total nonadditivity correction $(\Delta C_1 + \Delta C_2 + \Delta C_3)$ is small because of cancellations. The values of ΔC_1 and ΔC_2 are somewhat inaccurate, principally because of uncertainty in the Gaussian-density width parameter. Qualitatively, the results provide support for the additivity hypothesis, and do not help to explain existing discrepancies with experiment.

INTRODUCTION

SIGNIFICANT discrepancies occur at low temperatures between the measured third virial coefficients of the noble gases and the values calculated from the Lennard-Jones (12, 6) potential as well as other pairwise-additive empirically determined potential functions.[1,2] These discrepancies are larger than the experimental errors and polynomial-fitting uncertainties.[3] The object of this investigation, as stated previously,[4] is to determine to what extent the discrepancies can be traced to the neglect of three-body interactions, i.e., to the nonadditivity of intermolecular forces.

The three-body interactions can be classified into three types: (1) the first-order triple-overlap exchange interaction[5] which corresponds to the nonadditivity of the valence forces, (2) the second-order single-overlap exchange contribution,[6] and (3) the third-order triple-dipole potential.[7] The effect of the triple-dipole interaction on the third virial coefficient $C(T)$ has been investigated by several authors.[4,8,9] These calculations all show that the nonadditivity effects are appreciable and tend to remove a good part of the discrepancy. Whereas the triple-dipole potential is represented by a

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reliable and simple general formula, there are no comparable expressions available for the three-body exchange interactions of types (1) and (2). By assuming a Gaussian distribution of charge in the atom and neglecting multiple exchange effects, Jansen has obtained approximate expressions for the three-body exchange interactions[5,6,10] and has used these to determine the relative stability of the cubic and hexagonal lattice structures of the noble-gas solids.[10] (In Ref. 10 the multipole expansion of Ref. 6 is avoided and triatomic exchanges are taken into account.) Hitherto no calculations of the nonadditivity corrections to $C(T)$ have been made for the three-body exchange interactions of types (1) and (2). We wish to report the results of such a calculation based on the Jansen formulas.

CALCULATIONS

The nonadditivity correction to the third virial coefficient (per molecule) is

$$\Delta C=-\frac{1}{3V}\int\int\int \exp\left(-\frac{\sum u_{ij}}{kT}\right)\times\left[\exp\left(-\frac{w_{123}}{kT}\right)-1\right]d\tau_1 d\tau_2 d\tau_3, \qquad (1)$$

where u_{ij} is the pair potential between atoms i and j and w_{123} is the three-body potential. The two-body Boltzmann factors make the integrand very small when any pair of atoms is closer than the atomic diameter σ and, therefore, the expressions for w_{123} are not required to be accurate for distances r_{ij} appreciably less than σ. The type (2) and type (3) interactions are not reliable at close distances where higher multipoles also contribute, but they are dominated by the first-order interaction which is the largest when the atoms are all close together. As one atom moves away, the type (1) interaction goes rapidly to zero and, when the three atoms move apart into the region of van der Waals attraction, the type (2) interaction also disappears. Thus the long-range triple-dipole potential is dominant over the largest domain of the configuration space.

Whereas the triple-dipole potential contains no adjustable parameter, the three-body exchange interactions both depend sensitively on the inverse-width parameter β of the Gaussian charge distribution. Since the type (1) interaction represents the nonadditivity correction to the sum of the first-order pair potentials, it is appropriate to select a value of β which will make the Gaussian-density first-order pair potential agree with the empirical valence repulsion energy. We have chosen β values to give the best fit between the Gaussian-density repulsive potential and the modified Buckingham exponential repulsion in the neighborhood of the van der Waals minimum.[11]

Jansen[5,6,10] has selected the parameter β by equating the Gaussian-density second-order dipole-dipole interaction to the attractive term in the empirical (12, 6) potential; this procedure leads to values of β that are nearly 30% smaller than ours for Kr and Xe. The Gaussian-density first-order repulsive energy is more than ten times larger than the Buckingham repulsive energy in the neighborhood of the van der Waals minimum (and the nearest-neighbor distance in the crystal) when the Jansen parameters for Kr and Xe are used. These parameters also lead to cohesive energies of the solids that, in the case of Ar, are reduced as much as 21% (fcc) and 25% (hcp) by the three-body interactions, according to Jansen.[10] If the Gaussian dipole-dipole coefficient is equated to the quantum-mechanical instead of the empirical coefficient of r^{-6}, the values of β for Kr and Xe are about 15% smaller than the ones we used [cf., A. E. Kingston, Phys. Rev. **135**, A1018 (1964); J. Chem. Phys. **42**, 719 (1965)]. The use of Jansen's β values in our work would lead to unreasonably large negative values of ΔC and, conversely, the use of our β values in the solid-state calculation would substantially reduce the size of the three-body effect. It should be pointed out that Jansen has needed only to determine the relative stability of the cubic and hexagonal lattices and this requires a less precise knowledge of β than the calculation of an absolute correction.

The second-order three-body interaction, in the Jansen-McGinnies[6] dipole-dipole approximation, has been taken into account in two separate calculations, the results of which are in close agreement.[12] We first calculated ΔC using the Sutherland model for the two-body potential; this calculation was largely analytic and closely analogous to our previous work with the triple-dipole potential.[4] In the second computation the (12, 6) potential was used for the two-body interaction and the integration performed numerically. The calculation of ΔC for the type (1) interaction could only be done numerically and was programmed for an IBM 7090 computer, again using the (12, 6) potential for the two-body forces. Denoting the nonadditivity corrections to $C(T)$ due to the three types of three-body interaction by ΔC_1, ΔC_2, and ΔC_3, respectively, we find that all three are of the same order of magnitude at the temperatures of interest, in agreement with the qualitative observation that the long-range third-order interaction is dominant over a larger domain of the configuration space than the stronger first-order interaction. Furthermore $\Delta C_1<0$, $\Delta C_2>0$, $\Delta C_3>0$, and $\Delta C_1+\Delta C_2<0$ at these temperatures.

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[11] The second and higher order exchange energies have been neglected in this comparison [cf., H. Margenau, Phys. Rev. **56**, 1000 (1939)].

[12] L. Jansen (private communication) has stressed the inaccuracy of calculating ΔC from the dipole-dipole approximation for the second-order three-body interaction, which is strictly valid only when one of the three atoms is far from the other two. The inaccuracy is reduced by the formulation given in Eq. (2) and also by the automatic cutoffs at small distances ($r_{ij}<\sigma$) provided by the two-body Boltzmann factors, as discussed above. Although it would have been preferable in calculating ΔC_2 to have used the full expression for the second-order three-body energy derived in Ref. 10 without the use of the multipole expansion, the already large amount of numerical work would have been increased an order of magnitude.

Evaluating ΔC for each of the three types of interaction separately is valid only if the interactions (for $r_{ij}\sim\sigma$) are small compared to kT. In order to avoid this approximation for the exchange interactions, the calculations were formulated in the following manner. The type-(1) interaction was divided by the total Gaussian first-order pair energy and then multiplied by the total empirical repulsive energy in order to reduce the sensitive dependence on β. Similarly, the type-(2) interaction was put in fractional form and multiplied with the total empirical attractive energy in order to partly compensate for the lack of higher terms in the multipole expansion. The explicit formulation of the three-body exchange-force correction to $C(T)$ that we used is

$$\Delta C_{1+2}=-\frac{1}{3V}\int\int\int\left\{\exp\left[-\left(\frac{\sum u_{ij}^{(r)}}{kT}\right)\times\left(1+\frac{w_{123}^{(1)}}{\sum v_{ij}^{(1)}}\right)-\left(\frac{\sum u_{ij}^{(a)}}{kT}\right)\left(1+\frac{w_{123}^{(2)}}{\sum v_{ij}^{(2)}}\right)\right]-\exp\left[-\frac{\sum\left(u_{ij}^{(r)}+u_{ij}^{(a)}\right)}{kT}\right]\right\}d\tau_1 d\tau_2 d\tau_3,\quad (2)$$

where $u_{ij}^{(r)}$ and $u_{ij}^{(a)}$ are the repulsive and attractive terms of the empirical (12, 6) pair potential, $v_{ij}^{(1)}$ and $v_{ij}^{(2)}$ are the first- and second-order Gaussian-model two-body interactions, and $w_{123}^{(1)}$ and $w_{123}^{(2)}$ are the first- and second-order Gaussian-model three-body interactions. The triple-dipole potential $w_{123}^{(3)}$ is small compared to kT for the lowest temperatures at which $C(T)$ data are available.

RESULTS

Using the (12, 6) potential for the two-body interaction, ΔC_{1+2} was calculated from Eq. (2) for a range of β values.[13] The results for Xe corresponding to the reduced parameter $\beta^*=\beta\sigma=2.828$, which was chosen in the manner described above, are given in Table I for the temperature range of interest. The reduced temperature T^* and the reduced third virial coefficient C^* have their standard definitions[2] in terms of the (12, 6) potential parameters σ and ϵ. The values of σ and ϵ that we have used are the ones obtained in Ref. 9 and they deviate slightly from the parameters given in Ref. 2 in the direction of reducing the disagreement between the experimental results and the calculated values of $C(T)$ assuming additivity. Also shown in Table I are the values of ΔC_3 calculated from Eq. (1) without expansions; these values are close to the ones previously obtained in Refs. 4, 8, and 9. It is seen from Table I that ΔC_{1+2} and ΔC_3 tend to cancel. At the higher temperatures ($T^*>1.40$) the net positive value for ΔC, taken together with the revised value of the additive $C(T)$ obtained from the newer (12, 6) potential parameters, combine to give results in approximate agreement with the experimental data for Xe; however, the discrepancies persist at the lowest experimental temperatures. Similar results were obtained for Kr (where the measurements do not extend to as low temperatures) whereas for Ar the cancellation between ΔC_{1+2} and ΔC_3 was almost complete over the whole low-temperature range.

Table I. Nonadditivity corrections to the third virial coefficient of Xe.

T^*	ΔC_{1+2}^*	ΔC_3^*
1.00	−1.0268	0.9341
1.20	−0.5749	0.5991
1.40	−0.3774	0.4314
1.60	−0.2740	0.3339
1.80	−0.2129	0.2711
2.00	−0.1735	0.2278
2.50	−0.1191	0.1630

Because of the partial cancellation between the triple-dipole term ΔC_3 and the exchange terms ΔC_1 and ΔC_2 and because of the sensitive dependence of the latter terms on the parameter β, no reliable *quantitative* conclusions can be drawn from these calculations about the *total* nonadditive effect. We have found that a 7% variation in the β values, which cannot be excluded, considerably alters the quantitative results for the total effect. The hybrid nature of the calculation based partly on the empirical (12, 6) potential and partly on the Gaussian model, the approximations inherent in this model and the uncertainty in the parameter β, and the use of expressions based on multipole expansions to represent the two- and three-body interactions, all combine to make the results quantitatively uncertain.

The three-body contributions to intermolecular forces in the first and second orders of perturbation theory are not at all small and it has appeared difficult to reconcile this with the degree of success achieved in calculating thermodynamic properties with the assumption of pairwise additivity. The calculations reported here suggest that the success of the additivity hypothesis may be due to an unexplained cancellation of the nonadditivity effects in successive orders of perturbation theory.

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[13] The error functions appearing in the formula for $w_{123}^{(1)}$ were calculated by a rational approximation due to Hastings [C. Hastings, Jr., *Approximations for Digital Computers* (Princeton University Press, Princeton, New Jersey, 1955)]. In discussing his numerical work, Jansen (Ref. 5) states that the ratio $w_{123}^{(1)}/\sum v_{ij}^{(1)}$ is somewhat irregular when the three interatomic distances r_{ij} become large, due to the loss in accuracy in combining a large number of small terms. The irregularity, which is associated with $v_{ij}^{(1)}$ becoming negative for $\beta r_{ij}>3.4$, is of no consequence in our calculation because the factor $\sum u_{ij}^{(r)}$ has already reduced the repulsive term to a negligible size.