Ab Initio Calculation of a Three-Body Potential To Be Applied in Simulations of Fluid Neon

Elena Ermakova, Jan Solca, Gerold Steinebrunner, and Hanspeter Huber*

Abstract: A three-body potential for neon was calculated by ab initio methods and fitted to an analytic form for further use in simulations of fluid neon. Counterpoised calculations were performed on the same level as in a previous calculation of a pair potential used in simulations. The non-pair-additive part of the potential decays rapidly with distance and is typically below 1% of the dimer potential at its equilibrium distance. The calculated third virial coefficient shows fair agreement with the scarce experimental data.

Keywords: ab initio calculations • computer chemistry • neon • supercritical fluids • three-body potential

Introduction

As part of an effort to calculate bulk properties of liquids ab initio we have previously published two pair potentials for neon, NE1[1] and NE2.[2] Both of them, as well as an ab initio potential for argon published by Woon,[3] have been applied in simulations of many fluid properties.[4–11] It was shown by indirect arguments that many-body interactions are small or negligible for certain properties like the radial distribution function, transport properties and several thermodynamic properties derived from energies and pressure. However, they make a significant contribution to energies and pressure at high density. To confirm these arguments by direct computations we have calculated a three-body ab initio potential.

We are not aware of any analytical Ne_3 potentials in the literature, but several authors have calculated single points on the Ne_3 potential surface.[12–14] More work has been published recently on He_3. Parish and Dykstra[15] have reported an analytical three-body potential for helium. Bhattacharya and Anderson[16] and Tao[17] have calculated single points and come to the surprising conclusion that, at the correlated level, the three-body interaction converges with the basis set much faster than the two-body interaction. Røeggen et al.[18,19] used a new model to obtain three-body energies that are free of basis set superposition errors (BSSE). In general the three-body interactions were found to decay rapidly, usually being less than 1% of the dimer interaction at the dimer-equilibrium distance. Bulski and Chalasinski[20] showed that, for equilateral triangles of helium and neon, the exchange-repulsion and the triple-dipole nonadditivity have different signs and cancel to a great extent in the region of the dimer-equilibrium distance. Barker[21,22] discusses the many-body effect for energies and pressure of rare gases in several papers. He showed that excellent empirical pair potentials combined with the Axilrod–Teller triple-dipole term yield good energies and pressures, leading to the conclusion that overlap-dependent many-body interactions must add up to something close to zero for a range of densities. Sadus and Prausnitz[23] conclude from an empirical study of a Lennard-Jones pair potential with added Axilrod–Teller and repulsion terms that three-body repulsion makes a significant contribution to the three-body interactions in the liquid phase and that the effect of three-body dispersion is offset substantially by three-body repulsion. Recently, Cohen and Murrell[24] reported an analytical function for an ab initio three-body potential of He_3. They state that the third-order, triple-dipole dispersion energy is of minimal importance in comparison with the three-body exchange term except at very large internuclear separations. Wind and Røeggen[25] calculated ab initio the three-body interaction in the $(H_2)_3$ trimer including all the fifth-order corrections, which should yield accurate triple-dipole dispersion energies. They found that the Axilrod–Teller term gives a qualitatively correct picture, but that higher order terms should be included for a quantitative description; for distances less than 10 au higher order terms contribute significantly and at short range, the RHF term is most important. For a further discussion of the controversy about the significance of many-body effects see recent reviews.[26,27]

Indirect arguments about the importance of quantum effects on the radial pair distribution function of liquid argon

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and neon[9,10] were confirmed by simulations with quantum-effective potentials, resulting in the first ab initio calculated structures of liquids with experimental accuracies.[11] Similarly, the potential calculated in this work is used for a direct investigation of the influence of many-body effects on different liquid properties in the following paper.

Computational Methods

Ab initio calculations were performed for 47 points on the interatomic potential energy surface of the neon trimer. The basis set and the correlation method used here are the same as those applied by Eggenberger et al.[1] to obtain a neon dimer potential. The basis set consists of Huzinaga's (14s 10p)/[7s 6p] basis increased by four *d* functions (exponents: 2.21, 0.89, 0.35 and 0.14) and one *f* function (exponent: 0.3). Electron correlation was treated by fourth-order Møller–Plesset perturbation theory including up to quadruple excitations (MP4(SDTQ)). The calculations were performed with the GAUSSIAN program set.[28] The basis set superposition error (BSSE) was corrected by the full counterpoise correction.[29] Some problems related to its calculation in the case of the virial coefficient will be discussed below. The computer time needed for the calculation of one point was about 4 days on a 135 MHz DEC-alpha workstation or 1 hour on a NEC-SX3.

The basis set and level of correlation are identical with those used to obtain the pair potential NE 1.[1] They were chosen to be consistent with the previous calculations for comparison purposes and as a compromise between quality and consumption of computer time. As this level is not fully adequate for the calculation of the long-range Axilrod–Teller–Muto effect, direct conclusions about its size cannot be drawn. However, as fluid properties deviate mainly at high densities we assume that the short-range exchange effect is of much greater importance. This short-range effect should be reliably obtained in the present calculations.

Different configurations were selected to study the potential surface by changing the angle α (see Figure 1) in steps of 30° from 30° to 180°. With the distances R_{12} and R_{23} always kept equal, one length was selected at 30°, 13 different lengths were selected at 60°, 9 at 90°, 5 at 120°, 7 at 150° and 7 at 180°. Two additional points were then selected at very long distances for small angles to check the decay to zero and, hence, the numerical accuracy. Finally, three random positions were chosen (see Table 1). The three dimer interactions were subtracted from the complete interaction energy at these points and the remaining nonadditive part was fitted to an analytical expression as discussed in the next section.

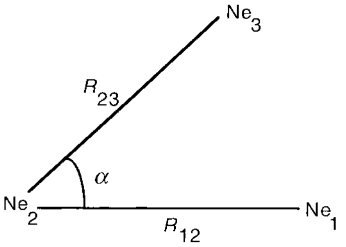

Figure 1. Definition of the neon trimer structure.

Abstract in German: *Zur späteren Verwendung in Simulationen von flüssigem und superkritischem Neon wird ein Drei-Teilchen-Potential für Neon ab initio punktweise berechnet und durch einen analytischen Ansatz wiedergegeben. Die counterpoise-korrigierten Rechnungen wurden auf dem gleichen Niveau durchgeführt, auf dem früher ein Paarpotential für Simulationen berechnet wurde. Der nicht-paar-additive Teil des Potentials fällt für grössere Abstände schnell ab und beträgt normalerweise weniger als 1 % des Dimerpotentials am Gleichgewichtsabstand. Die berechneten dritten Virialkoeffizienten liegen im Streubereich der wenigen experimentellen Daten.*

In Table 1 only three mixed points were used for the fit, which might look like a parsimonious selection. However, the potential surfaces are generally smooth.[30] The sides of the triangle are limited to a relatively small range (below $\approx 0.8\,\sigma$ the total potential becomes extremely repulsive, above $\approx 1.2\,\sigma$ the non-pair-additive part gets very small) and, hence, can deviate only little from an isosceles triangle.[*] The three additional points at the bottom of Table 1 deviate from the fitted curve (see below) by the same magnitude as the points included in the fit. A similar argument is probably responsible for the fact that the points can be fitted with a two-parameter equation, one parameter representing the overall size (ρ), and one the overall shape (Q, see below).

To obtain the third virial coefficient a three-dimensional integration has to be carried out. This was performed with the standard subroutine DQAND from the IMSL library.[31] The integration from 0 to 3000 pm for the two distances and 0° to 180° for the angle leads to many cancellations and, therefore, to numerical inaccuracies due to the different signs in the repulsive and attractive part. Hence, each variable was divided into 30 integration areas. The total numerical error is estimated to be less than 1 % for C_{add} (pair-additive) and less than 4 % for ΔC (the non-pair-additive part of the third virial coefficient).

Results and Discussion

The ab initio calculated points used for the fit are listed in Table 1. The total interaction energy $\Delta E_3(\varphi_3)$ [Eq. (1)], the counterpoised interaction energy of the trimer, was calculated from the Ne_3 energy $E_3(\varphi_3)$ subtracting the three monomer energies $E_1(\varphi_3)$, which in turn were obtained from the full Ne_3 basis set.

$$\Delta E_3(\varphi_3) = E_3(\varphi_3) - 3E_1(\varphi_3) \qquad (1)$$

The φ_i values symbolise a basis set corresponding to i atoms, and E_1, E_2 and E_3 the monomer, dimer and trimer energy, respectively. This definition of the interaction energy was called the site–site function counterpoise method by Wells and Wilson.[32]

Whereas the above definition of the counterpoised three-particle energy $\Delta E_3(\varphi_3)$ yields a potential to be used in the following paper without ambiguity, there are two possible ways to define a counterpoised non-pair-additive part of the energy that have some relevance in the calculation of the virial coefficient. To obtain the nonadditive part $\Delta\Delta E_3(\varphi_3)$ one has to subtract the three dimer interactions ΔE_2 from the total interaction energy $\Delta E_3(\varphi_3)$. The results of the two different procedures (a and b) are displayed in the last two columns of Table 1.

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[*] A measure for this deviation can be defined by taking the three possible ratios <1 of the three sides and selecting the largest of them. The closer this value is to 1, the closer to isosceles is the triangle. The three mixed points used for the fit represent values of 0.87, 0.91, and 0.94 respectively. The smallest value possible within the above limits can be shown to be 0.82 $[(0.8/1.2)^{1/2}]$. The three additional points at the bottom of the table not used for the fit have values of 0.80, 0.85 and 0.91 (the first including a side below $0.8\,\sigma$).

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Table 1. Points on the neon trimer surface where ab initio calculations were performed and the resulting energies. For structure definition see Figure 1; for different corrections a and b of the BSSE, see text.

α (°)	R_{12} (pm)	R_{23} (pm)	R_{13} (pm)	Total interaction $\Delta E_3(\varphi_3)$ (mE_h)	Nonadditive interaction $\Delta\Delta E_3(\varphi_3)^a$ mE_h)	Nonadditive interaction $\Delta\Delta E_3(\varphi_3)^b$ (mE_h)
180	220.0	220.0	440.0	10.12211	–0.00500	0.05660
	260.0	260.0	520.0	0.93253	–0.01077	0.00264
	280.0	280.0	560.0	0.06912	–0.00495	0.00030
	300.0	300.0	600.0	–0.18243	–0.00188	–0.00012
	315.0	315.0	630.0	–0.21956	–0.00084	–0.00014
	330.0	330.0	660.0	–0.20836	–0.00036	–0.00014
	370.0	370.0	740.0	–0.13037	–0.00005	–0.00007
150	240.0	240.0	463.6	3.43080	–0.01048	0.01143
	260.0	260.0	502.3	0.93451	–0.00679	0.00242
	290.0	290.0	560.2	–0.09947	–0.00185	0.00003
	300.0	300.0	579.6	–0.18248	–0.00112	–0.00007
	315.0	315.0	608.5	–0.21986	–0.00055	–0.00010
	330.0	330.0	637.5	–0.20873	–0.00029	–0.00009
	370.0	370.0	714.8	–0.13058	–0.00004	–0.00005
120	240.0	240.0	415.7	3.42257	–0.00236	0.01005
	290.0	290.0	502.3	–0.10336	–0.00068	0.00036
	310.0	310.0	537.0	–0.21810	–0.00031	0.00008
	330.0	330.0	571.6	–0.21085	–0.00017	0.00000
	370.0	370.0	640.9	–0.13163	–0.00000	0.00002
90	180.0	180.0	254.6	70.91055	–0.56341	–1.22780
	220.0	220.0	311.1	10.02105	–0.02308	0.00530
	240.0	240.0	339.4	3.35940	–0.00382	0.00734
	260.0	260.0	367.7	0.88428	–0.00040	0.00404
	280.0	280.0	396.0	0.03493	0.00010	0.00189
	300.0	300.0	424.3	–0.20643	0.00010	0.00085
	315.0	315.0	445.5	–0.23788	0.00004	0.00049
	330.0	330.0	466.7	–0.22233	0.00000	0.00028
	370.0	370.0	523.3	–0.13724	0.00005	0.00008
60	150.0	150.0	150.0	400.23495	–27.01480	–26.33715
	220.0	220.0	220.0	14.85970	–0.36608	–0.30410
	240.0	240.0	240.0	5.09190	–0.09534	–0.07083
	260.0	260.0	260.0	1.40488	–0.02237	–0.01247
	280.0	280.0	280.0	0.11471	–0.00412	0.00004
	290.0	290.0	290.0	–0.14007	–0.00135	0.00136
	300.0	300.0	300.0	–0.26600	–0.00020	0.00166
	310.0	310.0	310.0	–0.31640	0.00022	0.00154
	315.0	315.0	315.0	–0.32406	0.00030	0.00143
	320.0	320.0	320.0	–0.32406	0.00030	0.00132
	340.0	340.0	340.0	–0.28287	0.00024	0.00081
	370.0	370.0	370.0	–0.19395	0.00015	0.00036
	750.0	750.0	750.0	–0.00253	0.00001	–0.00001
30	500.0	500.0	258.8	0.49863	0.00013	0.00018
21.2	800.0	800.0	295.0	–0.07264	0.00002	–0.00001
16.3	800.0	800.0	226.6	3.59994	0.00004	0.00000
Mixed	480.0	415.7	240.0	1.68251	0.00023	0.00050
	340.0	310.0	280.0	–0.16006	0.00024	0.00176
	330.0	310.0	290.0	–0.25463	0.00022	0.00164
[a]	355.0	284.0	227.0		–0.00090	
[a]	307.0	260.0	220.0		–0.01842	
[a]	266.0	242.0	220.0		–0.07517	

[a] Not used for the fit.

a) $\Delta\Delta E_3(\varphi_3)^a$ [Eq. (2)] was obtained by subtracting the counterpoised pair potential published previously [Eq. (3)][1] (for very short distances a few additional dimer points were calculated and directly subtracted from the total interaction energy). These are the values used for the fit and, together with the dimer potential, for the calculation of the third virial coefficient (see below).

$$\Delta\Delta E_3(\varphi_3)^a = \Delta E_3(\varphi_3) - 3\Delta E_2(\varphi_2) \quad (2)$$

$$\Delta E_2(\varphi_2) = E_2(\varphi_2) - 2E_1(\varphi_2) \quad (3)$$

b) $\Delta\Delta E_3(\varphi_3)^b$ [Eq. (4)] was obtained by a more expensive procedure. For each distance occurring in the trimers a dimer calculation with the (ghost) orbitals of the corresponding third neon atom was performed. The monomer energies $E_1(\varphi_3)$ obtained with the full Ne_3 basis set were subtracted from the dimer energy $E_2(\varphi_3)$ (Equation (5), pair interaction counterpoised with trimer basis).

$$\Delta\Delta E_3(\varphi_3)^b = \Delta E_3(\varphi_3) - 3\Delta E_2(\varphi_3) \quad (4)$$

$$\Delta E_2(\varphi_3) = E_2(\varphi_3) - 2E_1(\varphi_3) \quad (5)$$

The results of these two procedures are quite different and yield different results, but one should be aware that the effects are mostly very small. Procedure b) is consistent in relation to the counterpoise correction, since for all calculations involved the trimer basis set is used. However, in relation to the concept of dividing the overall interaction into different many-body interactions it is inconsistent, as the pair interaction $\Delta E_2(\varphi_3)$ depends on a third virtual body. For simulations this division into additive and non-additive interactions is irrelevant, as only the total interaction is of importance. However, for the virial coefficients procedure b) leads to difficulties as it is inconsistent for the many-body interations. Therefore, we used procedure a) for a fit of the nonadditive trimer interaction. This fitted curve was then used for the calculation of the third virial coefficient below.

Figure 2 shows sections of the nonadditive part $\Delta\Delta E_3(\varphi_3)^a$ of the trimer potential surface for three angles α (the neon atoms forming an isosceles triangle with equal sides R). The potential is slightly positive at long distances for the smaller angles, but becomes very attractive at short distances. For large angles it is always attractive; in the case of the linear arrangement it becomes strong immediately below the equilibrium distance, whereas at 90° this happens at much shorter distances. The behaviour at long and medium distances is qualitatively equal to the Axilrod–Teller triple-dipole term. At shorter distances, where overlap of the electron clouds becomes important, the energies become negative in all cases, whereas at very short distances the linear arrangement (Table 1) experiences increasing repulsion. Additional calculations for even shorter distances also showed such a repulsion for nonlinear arrangements with obtuse angles.

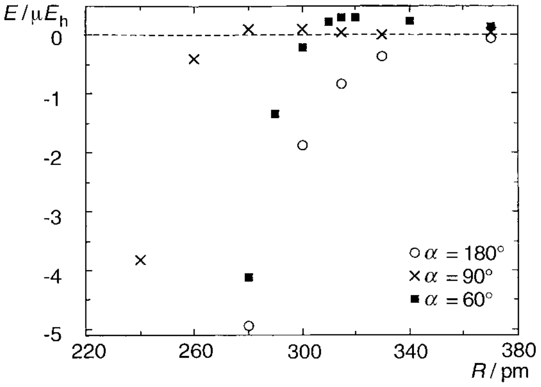

Figure 2. Non-pair-additive interaction energy $\Delta\Delta E_3(\varphi_3)^a$ [Eq. (2)] for an isosceles neon triangle as a function of the side length $R = R_{12} = R_{23}$ for three different angles α.

Figure 3 shows a representation of the nonadditive part $\Delta\Delta E_3(\varphi_3)^a$ of the trimer potential surface as a function of the angle α and the side length R for an isosceles triangle. Whereas the potential is relatively flat at longer distances, it shows a strong maximum at 260 pm (front left side) close to zero energy for 90°, but with large negative values for smaller and larger angles.

Although the numbers are quite different, the qualitative features discussed with the help of Figures 2 and 3 are the same for $\Delta\Delta E_3(\varphi_3)^a$ and $\Delta\Delta E_3(\varphi_3)^b$. The numbers in Table 1 might be compared with results for single points published recently[12–14]. Table 2 gives our values for structures published in the literature, interpolated by cubic splines from the values in Table 1 at constant angles.

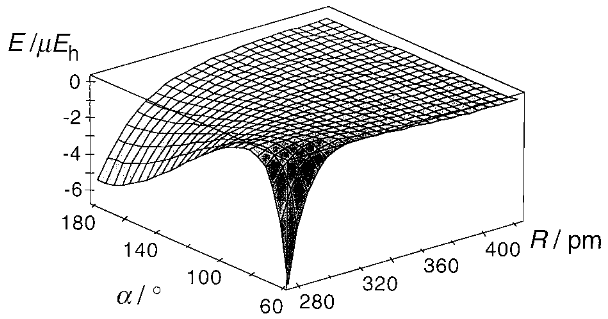

Figure 3. Non-pair-additive interaction energy $\Delta\Delta E_3(\varphi_3)^a$ [Eq. (2)] for an isosceles neon triangle as a function of the angle α and the side length $R = R_{12} = R_{23}$.

Table 2. Comparison of non-pair-additive interaction energies obtained in this work with previous calculations from the literature (energies in μE_h) for several equilateral and isosceles trimers.

R/a_o	α(°)	$\Delta\Delta E_3(\varphi_3)^a$	$\Delta\Delta E_3(\varphi_3)^b$	Ref. [12]	Ref. [13]	Ref. [14]
6.00 equilateral	60	0.31	1.38	1.81		
5.75 equilateral		0.05	1.65		– 1.4	
5.50 equilateral		– 1.19	1.41		– 3.5	
5.25 equilateral		– 5.33	– 0.74		– 8.7	
5.00 equilateral		– 17.20	– 9.00		– 20.5	
5.50 isosceles	90	0.16	1.19		0.0	
	120	– 0.65	0.30		0.2	
	150	– 1.75	– 0.03		0.2	
5.9645 isosceles	60	0.30	1.42			– 0.68
	90	0.04	0.48			– 0.01
	120	– 0.25	0.08			0.01
	180	– 0.81	– 0.14			0.02

It can be seen at a first glance that the agreement between numbers from different sources is poor. However, one has to be aware that most values agree in that they are extremely small. Our $\Delta\Delta E_3(\varphi_3)^b$ energy shows fair agreement with the calculation by Chalasinski et al.,[12] which is of coupled cluster type with single, double and noniterative triple excitations and was also calculated with procedure b). The only numbers in the table, which are larger than 2 μE_h, are for the equilateral triangle at short distances. We can see a qualitative agreement between Wells and Wilson's[13] SCF results, which are nearly BSSE-free, and the present work.

Many analytical equations were tested to fit the nonadditive interaction energy $\Delta\Delta E_3(\varphi_3)^a$. Several of them included Axilrod–Teller type terms. However, these terms did not contribute significantly to improving the fits, probably because our level of correlation in the quantum-chemical calculations did not reproduce the long-range part of the potential adequately. Finally, the function given in Equation (6) was chosen for the counterpoise-corrected nonadditive part of the interaction energy.

$$\Delta\Delta E_3(\varphi_3)^{\mathrm{a}} = a_1/(\rho^4(1 + a_2\rho + a_3\rho^2)) + Q(a_4 + a_5\rho)/(\rho^4(1 + a_6\rho + a_7\rho^2)) + Q^2 a_8/\rho^3 \qquad (6)$$

$\rho = R_{12} \times R_{23} \times R_{13}$
$Q = \cos(\alpha_1)\cos(\alpha_2)\cos(\alpha_3)$
$a_1 = -1494.04316399$ $a_5 = 196.84364784$
$a_2 = -2.40436522 \times 10^{-2}$ $a_6 = -1.00003202 \times 10^{-2}$
$a_3 = 1.98381726 \times 10^{-4}$ $a_7 = 4.64397240 \times 10^{-5}$
$a_4 = -3.34763381 \times 10^{4}$ $a_8 = -77.45577385$

α_i are the angles of the triangle formed by the three neon atoms and a_i are parameters in atomic units. Not all figures displayed are significant. We show them only to avoid round-off errors. For the fit 18 additional points for isosceles triangles with sides of length 800 pm and angles smaller than 60° were chosen with an energy set to zero in order to enforce complete decay of the function at large distances. This is justified by a comparison with the numbers from quantum chemical calculations in Table 1. The points could be fitted with a standard deviation of about 0.3 μE_h, which is slightly more than the numerical accuracy of the ab initio energies, which we estimate to be about 0.1 μE_h.

The total interaction energy $\Delta E_3(\varphi_3)$ is then given by Equation (7), where $\Delta E_2(\varphi_2)$ [Eq. (8)] is the original NE1 pair potential and a_i are parameters in atomic units. The third virial coefficient C consists of a part C_{add} [Eq. (9)] due to the additive pair interactions and a part ΔC [Eq. (10)] due to the nonadditive three-particle interaction.[33]

$$\Delta E_3(\varphi_3) = \Delta\Delta E_3(\varphi_3)^{\mathrm{a}} + 3\Delta E_2(\varphi_2) \qquad (7)$$

$$\Delta E_2(\varphi_2) = a_1 e^{-a_2 R} + a_3 R^{-12} + a_4 R^{-10} + a_5 R^{-8} + a_6 R^{-6} \qquad (8)$$

$\mathrm{a}_1 = 148.735474$ $\mathrm{a}_4 = -5160.348$
$\mathrm{a}_2 = 2.3520917$ $\mathrm{a}_5 = -8.3724779$
$\mathrm{a}_3 = 37497.54$ $\mathrm{a}_6 = -6.8028878$

$$C_{\mathrm{add}} = -8\pi^2 N_A^2/3 \iiint [\exp(-V_{12}/kT) - 1] \times [\exp(-V_{13}/kT) - 1][\exp(-V_{23}/kT) - 1] R_{12}R_{13}R_{23}\,dR_{12}\,dR_{13}\,dR_{23} \qquad (9)$$

$$\Delta C = -8\pi^2 N_A^2/3 \iiint [\exp(-\Delta V_3/kT) - 1] \times \exp\{-(V_{12} + V_{13} + V_{23})/kT\} R_{12}R_{13}R_{23}\,dR_{12}\,dR_{13}\,dR_{23} \qquad (10)$$

In Equations (9) and (10) $\Delta V_3 = \Delta\Delta E_3(\varphi_3)^{\mathrm{a}}$ and $V_{ij} = \Delta E_2(\varphi_2)$. Table 3 displays values for C_{add}, ΔC and their sum at different temperatures, which are high enough for quantum effects to be negligible. The numerical accuracy of the calculated data has already been discussed. We do not know the error due to the inaccuracy of the potential, but we estimate it to be much larger than the numerical one. This is especially true for ΔC. The numbers given in the table were obtained with the fitted function from the above integral for the limit of very large R (3000 pm). The fitted function has a small, but very slowly decaying tail that leads to unrealistic values at long distances in the integration. If the integration is taken only to 750 pm, where the values from the ab initio calculations converge to zero, ΔC is about 30% smaller. The main conclusion that may be drawn from Table 3 is that ΔC is very small, usually only a few per cent of the additive part C_{add}, but increases at low temperatures.

Table 3. Third virial coefficients of neon in $\mathrm{cm^6\,mol^{-2}}$. C_{add} is the pair-additive part, ΔC the non-pair-additive part, and C_{calc} and C_{exp} are the calculated and experimental total third virial coefficient, respectively.

T(K)	C_{add}	ΔC	C_{calc}	C_{exp}[a]	C_{exp}[b]	C_{exp}[c]	C_{exp}[d]
123	264	−19.8	244				309
173	253	−14.1	239				199
223	245	−11.2	234				228
273	238	−9.4	227	225	246	220	256
323	232	−8.1	224	224	234	180	
373	225	−7.3	218	224	238		432
423	219	−6.6	212	197	208		
473	213	−6.0	207				335

[a] Ref. [38]. Six-term fit of PV data (max P 2900 atm). [b] Ref. [38]. Three-term fit of PV data (max P 80 atm). [c] Ref. [39]. Three-term fit of PV data (max P 80 atm). [d] Ref. [34,35]. Five-term fit of PV data (P: 100 atm).

Experimental values are shown for comparison in Table 3. It can be seen that there is quite a disagreement between the different sources. We are not aware of any more recent or more accurate data. The results by Holborn and Otto[34,35] show an unusual scattering with temperature and disagree at most temperatures with other experimental and calculated values. Therefore, we assume that they are rather inaccurate.

Two decades ago Les[36] published calculations with a Conway and Murrell[37] pair potential and the Axilrod–Teller potential for the nonadditive part. In the temperature range given in the table, he found values for C_{add} between 216 and 184 $\mathrm{cm^6\,mol^{-2}}$ and for ΔC between −3.3 and −1.3 $\mathrm{cm^6\,mol^{-2}}$, in reasonable agreement with our results.

In the following paper, further comparisons with experiments are made by application of the potential in simulations to investigate the influence of the three-body interactions on different fluid properties at high densities.

Acknowledgements: This investigation is part of the Project 2000-045269.95 supported by the Schweizerischer Nationalfonds zur Förderung der Wissenschaften. We thank the staff of the university computer centre in Basel for their assistance and the Swiss HLR-Rat for a grant of computer time on the national supercomputers.

Received: June 26, 1997 [F738]

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