Third Virial Coefficients for Ar, Kr, and Xe Including Nonadditive Effects

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In this work we adopt the RMMV potential function proposed by Davis and calculate third virial coefficients for Ar, Kr, and Xe. Nonadditive effects due to dipole-dipole-dipole and dipole-dipole-quadrupole terms are included. We found good agreement between theoretical and experimental values for Ar and Kr, but not for Xe.

In a recent paper [1] Davis proposed a three parameter piecewise pair potential $u(r)$ called RMMV potential, which has the form

$$\begin{aligned}
&\varphi(x) = \infty && 0.0 < x \leqq 0.1\,,\\
&\varphi(x) = \exp[-2\alpha(x-x_m)] \\
&\qquad -2\exp[-\alpha(x-x_m)] && 0.1 < x \leqq 1.0\,,\\
&\varphi(x) = A(x^{-n}-x^{-m}) && 1.0 < x \leqq 2.0\,,\\
&\varphi(x) = -C^* x^{-6}\exp(\beta x^{-2})\,, && 2 < x\,, \qquad (1)
\end{aligned}$$

where $x = r/r_0$, $x_m = r_m/r_0$ and $\varphi(x) = u(x)/\varepsilon$, with r_0 and r_m the separation at the zero and the minimum of the potential, respectively, and ε the depth at the minimum. This potential function fits the experimental second virial coefficients in the short and long range limits [1] for argon, krypton, and xenon. The corresponding potential parameter are listed in Table III and V of Reference 1. In this work we calculate the third virial coefficients as an additional test of the suitability of the RMMV function as an intermolecular potential for argon, krypton, and xenon.

It has been noted [2–4] that for the argon third virial coefficient, using different potentials, it is enough to take into account nonadditive terms up to and including the dipole-dipole-quadrupole term. We have made similar computations for argon, krypton, and xenon using the RMMV potential. In Table 1 and 2 we show the results corresponding to additive and nonadditive integrals in reduced form for $n = 13$ (argon), and $n = 12.5$ (krypton and xenon). The notation is that of Fowler and Graben [2]. The method of numerical computation has been described previously [3].

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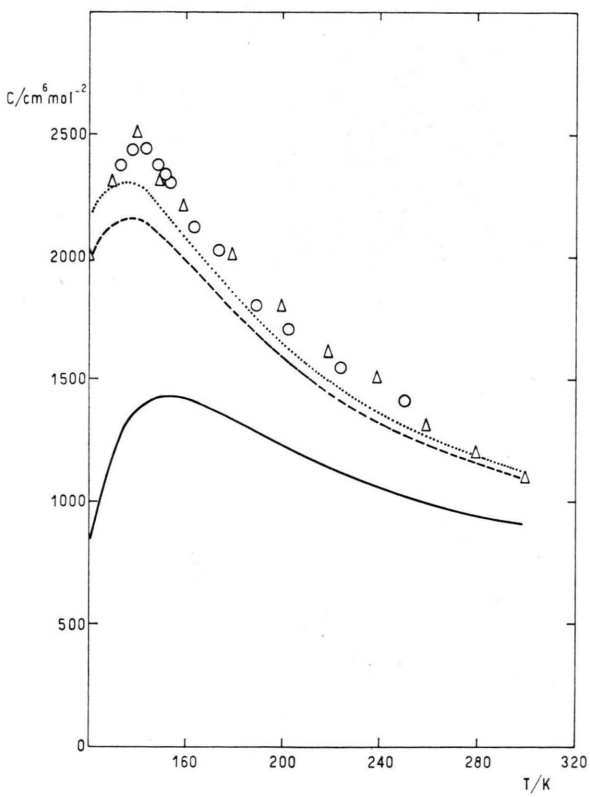

Fig. 1. The third virial coefficient C of argon plotted against the temperature T. ——— C (additive); — — — C (additive + ddd term); ··· C (additive + (ddd) term + (ddq) term). Experimental data: ○ A. Michels, J. M. Levelt, and A. De Graaff, Physica **24**, 659 [1958]. △ J. M. H. Levelt Sengers, M. Klein, and J. S. Gallagher, 1972, AIP Handbook.

Table 1. Reduced third virial coefficient integrals for the RMMV potential. $n=13.0$.

T^*	C_{add}^*	δC_{111}^*	$3\,\delta C_{121}^*$
0.8	−0.2227	28.84	70.44
0.9	0.3560	20.27	48.00
1.0	0.5485	15.26	35.19
1.1	0.5976	12.06	27.20
1.2	0.5925	9.88	21.87
1.3	0.5680	8.32	18.13
1.4	0.5382	7.17	15.39
1.5	0.5090	6.28	13.32
1.6	0.4824	5.58	11.71
1.7	0.4591	5.01	10.42
1.8	0.4390	4.55	9.38
1.9	0.4218	4.16	8.53
2.0	0.4072	3.83	7.81
2.2	0.3842	3.31	6.68
2.4	0.3675	2.92	5.83
2.6	0.3551	2.61	5.18
2.8	0.3459	2.36	4.66
3.0	0.3389	2.15	4.24
3.5	0.3274	1.77	3.47
4.0	0.3206	1.51	2.95
4.5	0.3160	1.32	2.57
5.0	0.3124	1.17	2.29

Table 2. Reduced third virial coefficient integrals for the RMMV potential. $n=12.5$.

T^*	C_{add}^*	δC_{111}^*	$3\,\delta C_{121}^*$
0.8	−0.3349	29.40	71.74
0.9	0.3109	20.63	48.82
1.0	0.5332	15.50	35.75
1.1	0.5963	12.24	27.61
1.2	0.5977	10.02	22.18
1.3	0.5761	8.43	18.38
1.4	0.5474	7.26	15.59
1.5	0.5183	6.35	13.49
1.6	0.4914	5.64	11.85
1.7	0.4676	5.07	10.55
1.8	0.4468	4.60	9.50
1.9	0.4290	4.20	8.63
2.0	0.4137	3.87	7.90
2.2	0.3894	3.34	6.75
2.4	0.3715	2.94	5.90
2.6	0.3582	2.63	5.24
2.8	0.3482	2.38	4.71
3.0	0.3405	2.17	4.28
3.5	0.3277	1.78	3.50
4.0	0.3200	1.52	2.98
4.5	0.3146	1.33	2.60
5.0	0.3105	1.18	2.31

Figure 1 shows the computed and experimental third virial coefficients for argon. It should be noted that our calculations for the RMMV potential with $n=13$ result in a third virial coefficient for argon which is slight by smaller than that obtained for the Bobetic-Barker-Maitland-Smith potential function [4]. The agreement with experimental data is good.

In Fig. 2 we show the computed and experimental third virial coefficients for krypton. The computed third virial coefficients using the RMMV potential function are similar to the corresponding values obtained by Barker, Johnson and Spurling [5] using the Bobetic-Barker-Klein potential function. The agreement with experiment is improved by the inclusion of nonadditive terms. More precise experimental determinations of third virial coefficients would be of great value since one finds discrepancies up to 20 per cent in C between the results from different laboratories.

The computed third virial coefficients for xenon are shown in Fig. 3 together with the experimental values. The agreement between calculated and ex-

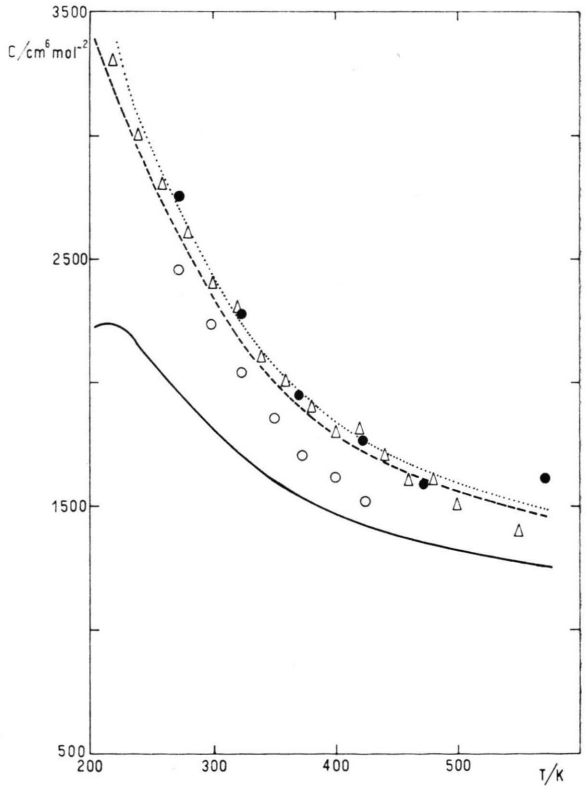

Fig. 2. The third virial coefficient C of krypton plotted against the temperature T. Labeling of theoretical curves as in Figure 1. Experimental data: ● J. A. Beattie, J. S. Brierly, and R. J. Barriault, J. Chem. Phys. **20**, 1615 [1952]. ○ N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, Physica **32**, 1503 [1966].. △ J. M. H. Levelt Sengers, M. Klein, and J. S. Gallagher, 1972, AIP Handbook.

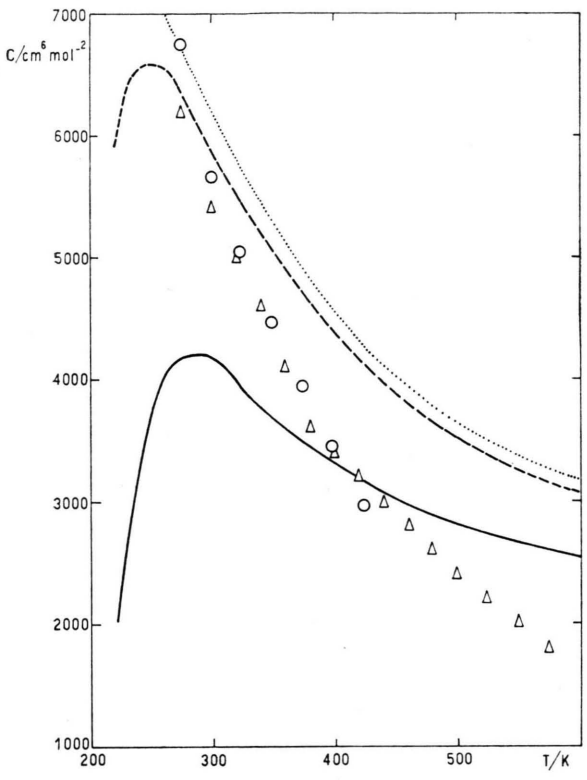

Fig. 3. The third virial coefficient C of xenon plotted against the temperature T. Labeling of theoretical curves as in Figure 1. Experimental data: ○ A. Michels, T. Wassenaar, and P. Louwerse, Physica **20**, 99 [1954]. △ J. M. H. Levelt Sengers, M. Klein, and J. S. Gallagher, 1972, AIP Handbook.

perimental data is poor. We are not aware of computations of the third virial coefficient of xenon using potential functions other than the RMMV potential.

The uncertainty in the polarizability values [6] affects the contribution to the third virial coefficients due to the dipole-dipole-quadrupole term. However, the uncertainty modifies the final third virial coefficient by less than 5 per cent and does not affect the above discussion.

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[6] See M. B. Doran and I. J. Zucker, J. Phys. **C 4**, 307 [1971].