THREE-BODY FORCES IN DENSE SYSTEMS*

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The contributions of long-range triple-dipole three-body interactions to the thermodynamic properties of dense gaseous argon are calculated using a recently developed perturbation theory together with an accurately determined pair potential function. Calculated pressures, internal energies, and critical constants are in reasonable agreement with experiment provided that the three-body contributions are included. The validity of the principle of corresponding states in the presence of three-body forces is discussed.

The extent to which three-body forces contribute to the thermodynamic properties of gaseous, liquid, and solid phases of inert gases is a matter of considerable interest. A recent detailed study of the pair potential for argon[1] and the development of a satisfactory perturbation theory of the liquid state[2] enable us to make rather precise calculations of the three-body contributions for the case of argon, supplementing the estimates given by Graben.[3]

The potential energy of a set of interacting molecules may be written in the form

$$U = \sum_{i<j} u(ij) + \sum_{i<j<k} u(ijk) + \cdots \qquad (1)$$

in which the first term describes pair interactions and the second triplet interactions; the functions $u(ijk\cdots)$ are assumed to approach zero as

one of the molecules $ijk\cdots$ becomes remote from the others. Since the contributions of triplet interactions to thermodynamic functions are only a few percent of the pair contributions, it is reasonable to neglect higher terms in (1), corresponding to nonadditive interactions of four or more molecules. Further, there is strong evidence[1,3,4] that the only important three-body interaction for inert gases is the triple-dipole dispersion interaction, given by

$$u(ijk) = \nu(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)/(R_1 R_2 R_3)^3 \qquad (2)$$

in which $\theta_1, \theta_2, \theta_3$ and R_1, R_2, R_3 are the corresponding angles and sides of the triangle formed by ijk, and the coefficient ν may be calculated from known oscillator strengths.[5]

For the pair potential for argon, which depends only on the distance R between the molecules ij, Barker and Pompe derived the result

$$u(ij) = \epsilon\{e^{12.5(1-r)}[0.2349 - 4.7735(r-1) - 10.2194(r-1)^2 - 5.2905(r-1)^3]$$

$$-1.0698/(r^6 + 0.01) - 0.1642/(r^8 + 0.01) - 0.0132/(r^{10} + 0.01)\}, \quad r = R/R_m, \qquad (3)$$

in which ϵ and R_m, the depth and separation at the minimum of the potential, are given by ϵ/k = 147.7°K and R_m = 3.756 Å, respectively. This potential was shown to be consistent with available information on pair interactions (second virial coefficients, gas-transport properties, molecular-beam scattering, and known long-range-interaction coefficients) and also gave approximately correct values for third virial coefficients as well as for the lattice spacing and energy of crystalline argon at 0°K, provided that the three-body interaction given by (2) was included (but not otherwise).

We now use the perturbation theory of Barker and Henderson[2] to calculate thermodynamic properties of dense gaseous argon with pair and triplet interactions specified by (1)-(3). In our perturbation theory,[2] the Helmholtz free energy A is

expanded in powers of "inverse steepness" and "depth" parameters α and γ about that of an unperturbed hard-sphere system with the effective hard-sphere diameter, d, chosen to annul the term of order α. The theory is readily extended to cover three-body interactions by including ν as a third perturbation parameter. The result is (when α and γ are set equal to 1 to recover the original potential)

$$A = A_0 + 2\pi N\rho \int_\sigma^\infty g_0(R)u(R)R^2 dR$$

$$-\pi N\beta\rho \frac{(1-\eta)^4}{1+4\eta+4\eta^2} \frac{\partial}{\partial\rho}[\rho\int_\sigma^\infty g_0(R)u(R)R^2 dR]$$

$$+ (\nu N\rho^2/6)\int\int g_0(123)u(123)d\vec{r}_2 d\vec{r}_3, \qquad (4)$$

in which N is the number of molecules in volume

V, ρ is N/V, β is $1/kT$, σ is the value of R for which $u(R) = 0$, η is $\pi\rho d^3/6$, and d is given by

$$d = \int_0^\sigma \{1 - \exp[-\beta u(R)]\} dR. \tag{5}$$

In (4), A_0, $g_0(R)$, and $g_0(123)$ are, respectively, the free energy, the radial-distribution function, and the three-body-distribution function of the hard-sphere system. The term of order α is zero by virtue of (5), the term of order γ^2 is given by our "local compressibility" approximation,[2] while terms of order $\alpha\gamma$, α^2, $\nu\gamma$, $\nu\alpha$, ν^2 and all higher-order terms are neglected. In our calculations, we have used the values of A_0 and $g_0(R)$ given by the Percus-Yevick theory.[6] The last term in (4) represents the effect of the three-body (3b) interactions.

We have evaluated the integral in this term by two methods: first, by Monte Carlo averaging in a system of 108 hard spheres with periodic boundary conditions and, second, by using the superposition approximation $g_0(123) = g_0(12)g_0(23)g_0(13)$ with Percus-Yevick values of $g_0(12)$, etc. Details of the Monte Carlo calculations will be given in a later publication; since the two methods agreed closely (within 1.2% at $\rho d^3 = 0.6$), we use here

the results found with the superposition approximation, which are described to an accuracy of 1 part in 10^5 by the Padé expression

$$\frac{d^9 A^{3b}}{N\nu} = \rho'^2 \frac{2.707\,97 + 1.689\,18\rho' - 0.315\,70\rho'^2}{1 - 0.590\,56\rho' + 0.200\,59\rho'^2}, \tag{6}$$

where $\rho' = \rho d^3$.

From the results (4)-(6) for the free energy, values of pressure and internal energy may be derived by numerical differentiation with respect to density and temperature. Some results of these calculations are shown in Table I with experimental data for gaseous argon. We have used the value $\nu = 73.2$ erg cm^9 due to Leonard[5]; this is very close to the value $\nu = 74.5$ erg cm^9 given by Bell and Kingston.[5] In the table we also list values calculated without three-body contributions for the 6-12 potential:

$$u(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6] \tag{7}$$

with $\epsilon/k = 119.8°$K, $\sigma = 3.405$ Å determined by Michels, Levelt, and DeGraaff[7] from second virial coefficients.

The results calculated from the pair potential

Table I. Thermodynamic properties of Ar. 3b and 2b denote three- and two-body.

ρ(mole-cm^{-3})	pV/NkT				U$_i$/NkT			
	Expt	Eq.(2) 3b	Eqs(3)and(2) 2b + 3b	6:12 2b	Expt	Eq.(2) 3b	Eqs(3)and(2) 2b + 3b	6:12 2b
				T = 150°C				
0.0178	1.438	0.043	1.410	1.452	-0.641	0.017	-0.619	-0.660
0.0214	1.699	0.067	1.662	1.732	-0.755	0.026	-0.727	-0.778
0.0250	2.071	0.100	2.020	2.132	-0.858	0.038	-0.821	-0.883
0.0286	-	0.191	2.564	2.690	-0.942	0.053	-0.897	-0.968
				T = 0°C				
0.0178	1.087	0.065	1.067	1.083	-1.108	0.026	-1.096	-1.145
0.0214	1.295	0.102	1.277	1.315	-1.316	0.040	-1.298	-1.361
0.0250	1.639	0.151	1.616	1.691	-1.517	0.058	-1.487	-1.564
0.0286	2.174	0.214	2.131	2.264	-1.703	0.082	-1.654	-1.746
				T = -122.5°C				
0.0178	0.233	0.114	0.166	0.127	-2.357	0.046	-2.266	-2.314
0.0214	0.240	0.181	0.236	0.200	-2.721	0.072	-2.678	-2.751
0.0250	0.405	0.268	0.471	0.455	-3.120	0.105	-3.073	-3.175
0.0286	0.837	0.380	0.944	0.973	-3.536	0.147	-3.444	-3.577

Table II. Critical constants of Ar.

	Exptl	Eq. (3) two body	Eqs. (3) and (2) two body and three body	6:12 potential two body
T_c (°K)	150.87	168	159	162
p_c (atm)	48.43	66	57	57
ρ_c (mole cm^{-3})	0.0134	0.014	0.013	0.013

(1) with the three-body contribution (2) included agree reasonably well with the experimental values, and the same is true for the 6-12 results computed without the three-body contribution. As far as pV/NkT is concerned, the 6-12 values are already a little high at high densities, and addition of a three-body contribution [which would differ little from the values in the table, although these were computed for the pair potential (3)] would make the agreement significantly worse. This is also apparent from the liquid-phase Monte Carlo calculations made by McDonald and Singer[8] and is in accord with the view[1,8] that the 6-12 potential is a good effective pair potential for dense argon, already taking account of the three-body interactions.

Calculated and experimental[9] critical constants are shown in Table II. Potential (1) without three-body interactions gives a critical temperature which is much too high, but with three-body interactions, the value of T_c is somewhat better than that given by the 6-12 potential. It would appear from Table II that the 6-12 potential with the three-body term added would give a good estimate of the critical point. We believe that this is because of accidental cancellation of errors, since adding the positive three-body term would give pressures appreciably higher than experimental at high densities,[8] and would also lead to a discrepancy of about 7% in the calculated cohesive energy of crystalline argon at 0°K. The remaining error in the estimate of T_c given by (1) and (2) is probably due to the neglect of higher-order terms in the perturbation theory (and perhaps partly due to the neglect of quantum effects).

Classical behavior, pairwise additivity of potentials, and similarity of pair potentials are sufficient conditions for the principle of corresponding states; however, they are by no means necessary conditions. Thus, two substances with precisely similar pair interactions and with three-body interactions given by (2) would follow corresponding states exactly if the respective values of $v^* = v/\epsilon\sigma^9$ were equal. Table III shows values of v^* for inert gases given by Chell and Zucker.[10] On the basis of these values, one expects Kr-Xe to follow corresponding states more closely than Ar-Kr or Ar-Ar, and just this behavior is shown by the precise sound-velocity measurements made by Aziz, Bowman, and Lim.[11]

[1]J. A. Barker and A. Pompe, to be published.

[2]J. A. Barker and D. Henderson, J. Chem. Phys. 47, 2856, 4714 (1967); in Proceedings of the Fourth Symposium on Thermophysical Properties, edited by J. R. Moszynski (American Society for Mechnanical Engineers, New York, 1968), p. 30.

[3]H. W. Graben, Phys. Rev. Letters 20, 529 (1968).

[4]R. D. Present, J. Chem. Phys. 47, 1793 (1967).

[5]R. J. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 88, 901 (1966); P. J. Leonard, personal communication.

[6]M. S. Wertheim, Phys. Rev. Letters 10, 321 (1963), and J. Math. Phys. 5, 643 (1964); E. Thiele, J. Chem. Phys. 39, 474 (1963); G. J. Throop and R. J. Bearman, J. Chem. Phys. 42, 2408 (1965).

[7]A. Michels, Hub. Wijker, and Hk. Wijker, Physica 15, 627 (1949).

[8]I. R. McDonald and K. Singer, Discussions Faraday Soc. 43, 40 (1967).

[9]A. Michels, J. M. H. Levelt, and W. DeGraaff, Physica 24, 659 (1958).

[10]G. G. Chell and I. J. Zucker, Proc. Phys. Soc. (London) 1, 35 (1968).

[11]R. A. Aziz, D. H. Bowman, and C. C. Lim, Can. J. Chem. 45, 2079 (1967).

Table III. Values of $v^* = v/\epsilon\sigma^9$ from Chell and Zucker.[a]

	Ne	Ar	Kr	Xe
v^*	0.035	0.075	0.090	0.099

[a]Ref. 10.