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Triple-Dipole Potentials in Classical Nonpolar Fluids*

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Formulas which express the triple-dipole contribution to the pressure, internal energy, effective pair potential, and density expansion of the radial distribution function appropriate to classical nonpolar fluids are evaluated. A rational approximation to tabulated theoretical values of the radial distribution function for argon based on the Lennard-Jones (12, 6) model is used to facilitate the numerical evaluation of the two- and three-fold integrals involved. The nonadditive contribution to the pressure and internal energy of argon is several percent over the temperature-density range considered which includes the critical region. It is found that the triple-dipole energy cannot account for the observed variation with density of the effective pair potential for argon reported by Mikolaj and Pings.

I. INTRODUCTION

Sinanoğlu[1] and Kestner[2] have shown that three-body forces play an important role in determining the effective London dispersion force between two molecules in a nonpolar medium. Recently Rushbrooke and Silbert,[3] Pings,[4] and Rowlinson[5] have incorporated triplet potentials into the classical theory of nonpolar fluids based on the radial distribution function as determined from an integral equation. In particular, formulas which express the triple-dipole contribution to the pressure, internal energy, and effective pair-potential have been developed.[1,3,6]

Numerical estimates of the nonadditive internal energy in argon as a function of temperature and density have already been made based on the low-density limit of the radial distribution function.[6] Subsequently Barker, Henderson, and Smith[7] have made more accurate assessments of the nonadditive internal energy and pressure of dense gaseous argon using a new perturbation theory[8] of the liquid state together with an accurately determined pair-potential function.[9] Calculated pressures, internal energies, and critical constants for argon are found to be in reasonable agreement with experiment provided that the triple-dipole contributions are included.

The effective pair potential accounts for the many-body effects in a fluid in addition to the isolated or bare two-body potential. By inverting the Percus-Yevick equation and using the experimental structure factor measured by x-ray scattering experiments on argon, Mikolaj and Pings[10] have deduced an effective pair interaction in the vicinity of the critical point. Their results indicate that the effective potential-well depth decreases almost linearly with increasing density. Thus, by zero density extrapolation of the effective pair potential they are able to compute a potential which is in good agreement with currently accepted values for the pair potential of argon. Since it has been shown that the Percus-Yevick equation is sufficiently valid at those densities,[11] perhaps the observed change of depth of the potential can be attributed to many-body forces. Levesque and Verlet[12] have recently taken issue with this viewpoint. They compute the structure factor for both a realistic pair potential (Kihara) and an effective pair potential (Lennard-Jones) applicable to the density range measured by Mikolaj and Pings. The effect arising from the difference between these two potentials is claimed to simulate within an order of magnitude that due to many-body forces. The computed effect is an order of magnitude smaller than the difference between the theoretical and experimental structure factor. Hence, Levesque and Verlet conclude that the x-ray scattering data are not sufficiently accurate to extract quantitative information concerning the interaction energy.

In this paper we evaluate the triple-dipole contributions to the pressure, internal energy, and effective pair potential for argon over a temperature-density range which includes the critical region. To avoid the low-density approximation made in our previous work[6] and to facilitate the numerical evaluation of the two- and three-fold integrals involved, a rational approximation to tabulated theoretical values[13] of the radial distribution function for argon based on the Lennard-Jones (12, 6) model is used. Although no new formulas are derived, we show that the triple-dipole contribution to the pressure and internal energy are simply related and need not be computed separately as done elsewhere.[7] Our evaluation of the effective pair potential leads to a direct determination of its variation in well-depth with density as produced by the triple-dipole potential. In addition to these calculations based on tabulated values of the radial distribution function, the triple-dipole contribution to the density expansion of the radial distribution function is evaluated in first-order for suitable ranges of temperature and interatomic distance.

II. FORMULAS

The interaction energy of three identical atoms is taken to be

$$U_3(r_{12},r_{23},r_{31}) = \sum_{i>j} u(r_{ij}) + w(r_{12},r_{23},r_{31}) , \tag{1}$$

where w is the nonadditive energy appended to the sum of the three pair potentials, and the r_{ij} are the three interatomic distances. The expressions relating the radial distribution function g to the pressure p and internal energy E of a fluid are then given by

$$\beta p/\rho = 1 - (\beta\rho/6) \int g(r) r (du/dr) d\tau - (\beta\rho^2/18) \iint g(r_{12},r_{23},r_{31}) \times \left(\sum_{i>j} r_{ij} \frac{\partial w}{\partial r_{ij}}\right) d\tau_2 d\tau_3 , \tag{2}$$

$$\beta E/N = \tfrac{3}{2} + (\beta\rho/2) \int u(r) g(r) d\tau + (\beta\rho^2/6) \iint w(r_{12},r_{23},r_{31}) \times g(r_{12},r_{23},r_{31}) d\tau_2 d\tau_3 , \tag{3}$$

where ρ is the density, N is the number of atoms, and $\beta^{-1} = kT$, the product of the Boltzmann constant and the absolute temperature.

Although the low-density limit of $g(r_{12},r_{23},r_{31})$ is known,[3,6] current theories do not provide a prescription for calculating it. In order to proceed further the Kirkwood[14] or superposition approximation is made:

$$g(r_{12},r_{23},r_{31}) = g(r_{12}) g(r_{23}) g(r_{31}), \tag{4}$$

where $g(r)$ is the radial distribution function calculated on the basis that $w = 0$. This assumption enables us to evaluate the formulas to first-order in w in a perturbative sense.[6]

Sinanoğlu[1] considers an effective pair potential obtained from the relation

$$u^{\text{eff}}(r_{12}) = u(r_{12}) + (\rho/3) \int w(r_{12},r_{23},r_{31}) \times g(r_{23}) g(r_{31}) d\tau_3 . \tag{5}$$

This effective pair potential represents a merger of the second and third terms in Eq. (3).

Next we write the density expansion of the radial distribution function in the form:

$$g(r,\rho,T) \exp[\beta u(r)] = \sum_{i=0} g_i(r) \rho^i = g_0(r) + [g_1^{(\text{A})}(r) + g_1^{(\text{NA})}(r)]\rho + \cdots , \tag{6}$$

where $g_1(r)$ has been split into an additive part $g_1^{(\text{A})}$ and a nonadditive term $g_1^{(\text{NA})}$. It is well known that $g_0 = 1$, and

$$g_1^{(\text{A})}(r_{12}) = \int f(r_{23}) f(r_{31}) d\tau_3 , \tag{7}$$

where $f(r) = \exp[-\beta u(r)] - 1$. Pings[4] has shown that

$$g_1^{(\text{NA})}(r_{12}) = \int \exp\{-\beta[u(r_{23}) + u(r_{31})]\} \times [\exp(-\beta w) - 1] d\tau_3 . \tag{8}$$

In the next section we evaluate the above terms which contain w.

III. CALCULATIONS

To be explicit we select for the pair potential the Lennard-Jones (12, 6) model, viz.,

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] , \tag{9}$$

where $-\epsilon$ is the potential minimum and σ is the slow-collision diameter. At nonoverlap distances the appropriate expression for w is the Axilrod-Teller-Muto[15] or triple-dipole potential

$$w = 3\alpha\epsilon\sigma^6 (r_{12}, r_{23}, r_{31})^{-3} \Gamma(\theta_1,\theta_2,\theta_3) \tag{10}$$

where $\Gamma = (1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)$, θ_i are the interior angles of the three-atom triangle, and α is the polarizability of the atom.

Let us write Eqs. (2) and (3) in the abbreviated forms

$$\beta p/\rho = (\beta p/\rho)^{(\text{A})} + (\beta p/\rho)^{(\text{NA})}, \tag{2$'$}$$

$$\beta E/N = (\beta E/N)^{(\text{A})} + (\beta E/N)^{(\text{NA})} , \tag{3$'$}$$

where the terms with superscript (NA) represent the nonadditive parts. Applying Euler's theorem we see that

$$\sum_{i>j} r_{ij} \frac{\partial w}{\partial r_{ij}} = -9w , \tag{11}$$

for w given by Eq. (10). Hence,

$$(\beta p/\rho)^{(\text{NA})} = 3(\beta E/N)^{(\text{NA})} . \tag{12}$$

We introduce the following dimensionless quantities:

$$T^* = kT/\epsilon, \quad n^* = \rho\sigma^3, \quad \alpha^* = \alpha/\sigma^3, \quad u^* = u/\epsilon, \quad g(x) = g(r)/\sigma^3, \quad x = r_{12}/\sigma, \quad y = r_{23}/\sigma, \quad z = r_{31}/\sigma . \tag{13}$$

Then we can write

$$\left(\frac{\beta E}{N}\right)^{(\text{NA})} = \frac{4\pi^2\alpha^* n^{*2}}{T^*} \int_0^\infty dx \int_0^\infty dy \int_{|x-y|}^{x+y} dz \times \Gamma g(x) g(y) g(z) (xyz)^{-2} , \tag{14}$$

$$u^{*\,\mathrm{eff}}(x)=u^*(x)+\frac{2\pi\alpha^* n^*}{x^4}\int_0^\infty dy\int_{|x-y|}^{x+y}dz \times\Gamma g(y)g(z)(yz)^{-2}\,. \qquad (15)$$

Throop and Bearman[13] have calculated $g(r)$ from the Percus-Yevick equation using the Lennard-Jones (12, 6) model. We have adequately fitted their tabulated values of $g(r, \rho, T)$ to an expression of the form:

$$g(x, n^*, T^*)=\exp[-u^*(x)/T^*] \times\left(1.0+\sum_{i=1}^{m} a_i(n^*, T^*)/x^i\right)\,, \qquad (16)$$

where the a_i are a set of m coefficients selected for each pair of n^* and T^* values. In Fig. 1 a comparison of our rational approximation to tabulated values of $g(x)$ is made for $T^*=1.2$, $n^*=0.60$, and $m=12$. The solid curve represents the rational approximation to the tabulated values indicated by the points. The dashed curve, which is to be used in a later discussion, is a plot of $\exp[-u^*(x)/T^*]$ versus x for $T^*=1.2$. The theoretical critical constants for the Lennard-Jones (12, 6) model should lie within the range[16] $T_c^*=1.32$, $n_c^*=0.32$ to $T_c^*=1.36$, $n_c^*=0.36$. Using this rational approximation for $g(r)$, we have evaluated the triple integrals in Eq. (14) numerically. In Table I the results, with α^* (argon) $=0.04$, are displayed. These results are discussed later. Values of $(\beta p/\rho)^{(\mathrm{A})}$ and $(\beta E/N)^{(\mathrm{A})}$ are given in Table IIb and Table IIc of Ref. 13.

The density dependence of the effective pair potential as given by Eq. (15) is of particular interest in view of the aforementioned variance between the work of Mikolaj and Pings and that of Levesque and Verlet. For reasons to be discussed later we find that the values of the double integrals in Eq. (15) are relatively insensitive to variations in n^* for fixed values of T^*. Hence, the density dependence of the ratio of the effective well depth and ϵ is primarily determined by the linear factor preceding the integrals. If we set $x=2^{1/6}$ and $T^*=1.2$ in Eq. (15), we obtain for argon the results[17]

$$\epsilon^{\mathrm{eff}}/\epsilon=1-0.072\rho, \quad \text{for } n^*=0.10 \qquad (17a)$$

$$\epsilon^{\mathrm{eff}}/\epsilon=1-0.051\rho, \quad \text{for } n^*=0.60 \qquad (17b)$$

with ρ in g/cm³. From their measurements made at temperatures in the vicinity of $T^*=1.2$ and densities encompassed by the range given above, Mikolaj and Pings find this ratio to be $(1-0.394\rho)$. Thus we see that the "measured" coefficient is an order of magnitude larger than that predicated by the triple-dipole effect. We conclude from this comparison that the observed variation with density of the effective pair potential cannot be attributed to the triple-dipole effect.

TABLE I. Values of $(\beta E/N)^{(NA)}$ with $\alpha^*=0.04$.

n^*	$T^*=1.2$	$T^*=1.3$	$T^*=1.4$	$T^*=1.5$
0.10	0.0095	0.0075	0.0063	0.0055
0.25			0.0345	0.0301
0.30				0.0413
0.40			0.0759	0.0701
0.45			0.0946	0.0875
0.55	0.1696	0.1548	0.1420	0.1317
0.60	0.2044	0.1868	0.1729	0.1607

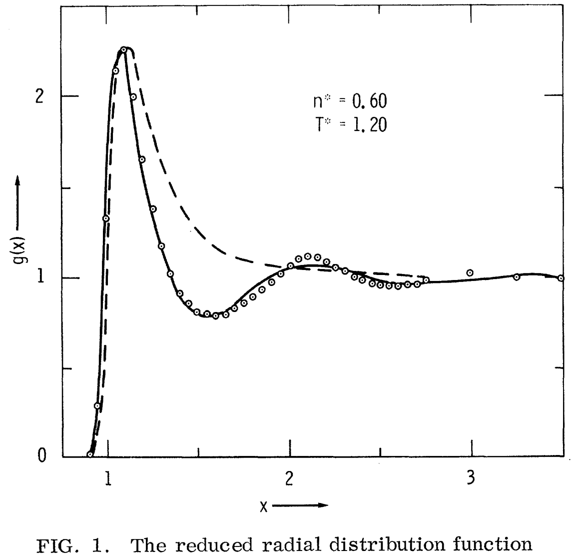

FIG. 1. The reduced radial distribution function $g(x)$ versus the reduced interatomic distance.

We turn now to the assessment of the lowest-order triple-dipole effect on the pair radial distribution function. For small values of α^*/T^*, we may replace the factor $[\exp(-\beta w)-1]$ in Eq. (8) by $(-\beta w)$.[18] Then in terms of reduced quantities we have

$$g_1^{(\mathrm{NA})}(x)=-(3\alpha^*/T^*)I(x, T^*)\,, \qquad (18)$$

where

$$I(x, T^*)=2\pi x^{-4}\int_0^\infty dy\int_{|x-y|}^{x+y}dz \times\Gamma\exp\{-[u^*(y)+u^*(z)]/T^*\}(yz)^{-2}. \qquad (19)$$

A few computed values of $I(x, T^*)$ are presented in Table II. Henderson[19] has computed $g_1^{(\mathrm{A})}(x)$ for the Lennard-Jones 12-6 model. Figure 2 illustrates the significance of $g_1^{(\mathrm{NA})}(x)$ in relation to $g_1^{(\mathrm{A})}(x)$ for $T^*=1.4$ and $\alpha^*=0.04$. A comparison of the two curves in Fig. 2 indicates that the triple-dipole interaction has little effect on the fluid structure beyond about two atomic diameters. Inside this region the triple-dipole effect is to expand the local structure because this

TABLE II. Values of $I(x, T^*)$.

x	$T^*=1.0$	$T^*=1.2$	$T^*=1.4$	$T^*=1.5$	$T^*=1.6$	$T^*=2.0$
0.9	6.5551	5.2704	4.5408	4.2860	4.0787	3.5362
1.0	4.8576	3.9346	3.4084	3.2243	3.0743	2.6810
1.1	3.6693	2.9921	2.6050	2.4694	2.3590	2.0697
1.2	2.8083	2.3037	2.0143	1.9127	1.8298	1.6123
1.3	2.1662	1.7871	1.5689	1.4921	1.4294	1.2644
1.4	1.6756	1.3902	1.2254	1.1672	1.1197	0.9944
1.5	1.2927	1.0787	0.9545	0.9105	0.8745	0.7790
1.6	0.9883	0.8301	0.7378	0.7050	0.6781	0.6065
1.7	0.7424	0.6285	0.5614	0.5374	0.5177	0.4649
1.8	0.5410	0.4627	0.4160	0.3992	0.3853	0.3478
1.9	0.3740	0.3248	0.2949	0.2839	0.2748	0.2498
2.0	0.2360	0.2114	0.1959	0.1901	0.1852	0.1716

nonadditive energy is positive for most triangular configurations.[20] The small magnitude of this contribution justifies using a perturbation procedure in calculating the triple-dipole effects on fluid properties.

We would like to point out that additional low-density values of $(\beta E/N)^{(\mathrm{NA})}$ and u^{eff} can be obtained from other computations. If we use the low-density limit for $g(r)$, i.e.,

$$g(r) = \exp[-\beta u(r)], \tag{20}$$

then, as previously pointed out,[6] Eq. (14) becomes

$$(\beta E/N)^{(\mathrm{NA})} = (\rho^2/2)\Delta C , \tag{21}$$

where ΔC is the nonadditive third virial coefficient. Kihara, Koba and Kaneka, and Sherwood and Prausnitz have evaluated ΔC using Eqs. (9) and (10).[18] Using the low-density limit for the radial distribution function appearing in Eq. (5) leads to[3]

$$u^{*\mathrm{eff}}(x) = u^*(x) + \alpha^* n^* I(x, T^*) , \tag{22}$$

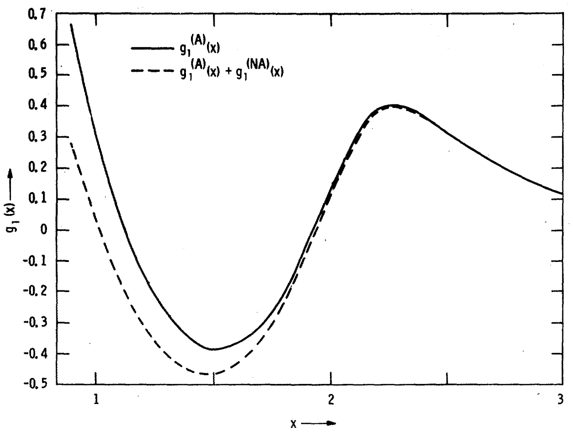

FIG. 2. Calculated values of $g_1(x)$ for $T^*=1.4$ and $\alpha^*=0.04$.

where $I(x, T^*)$ is given by Eq. (19).

IV. DISCUSSION

Any quantitative conclusion drawn from the foregoing calculations rests primarily upon the reliability of Eq. (10) particularly in the vicinity of the pair-potential minimum. Presently no simple expression for the three-body overlap energy is available.[21] However, since each formula considered has a factor which rapidly reduces its integrand toward zero for any $r_{ij} < \sigma$, the dominant three-body contribution in fluids should be the triple-dipole energy.[22]

The coefficient ν of the triple-dipole term[23] is accurately approximated by the relation[24] $\nu = \frac{3}{4}\alpha\mu$, where μ is the coefficient of the London dispersion energy $-\mu/r^6$. For the Lennard-Jones model $\nu = 3\alpha\epsilon\sigma^6$, which is the coefficient used in Eq. (10). If the theoretical value of μ is used instead of the experimental value as done here, all (linear) terms in w should be multiplied by $\mu_{\mathrm{th}}/\mu_{\mathrm{ex}}$. For argon this ratio is about one-half. Thus, the numerical results presented here could be overestimations of the triple-dipole effects by a factor of two. It would be preferable to use a pair-potential model which has a long-range interaction coefficient that agrees with the theoretical value.[9] Moreover, the Lennard-Jones 12-6 model simulates an effective pair potential for dense argon, already taking account of the nonadditive interactions.[12, 25] For these reasons no comparison of calculated values of p and E with experimental data is made. In making exploratory calculations at this level, we are primarily concerned with the order-of-magnitude contribution of the triple-dipole energy to fluid properties. Although the quantitative results presented in Table I may be in doubt by a factor of two, it is evident that the triple-dipole contribution to the internal energy and pressure is significant and continues to increase with increasing density below the coexistence curve.

The density dependence of the integrand in Eq. (15) enters through the radial distribution function only. Since the triple-dipole energy varies inversely with the ninth power of interatomic distances, its effects are relatively short-ranged (as indicated in Fig. 2). Hence the bulk of the double integral's value in Eq. (15) is obtained for distances between one and two atomic diameters. A comparison of the solid curve and dashed curve in Fig. 1 shows that within this range the low-density limit of $g(x)$ is slightly larger than the radial distribution function itself for a common value of the temperature. This explains why the density coefficient in Eq. (17a) slightly exceeds the one in Eq. (17b) – a result which might have been unexpected at first glance. Moreover, since the two curves in Fig. 1 differ by very little, particularly in the vicinity of their peaks, it is clear that the density dependence of the effective pair potential is almost linear.

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[1] Oktay Sinanoğlu, Chem. Phys. Letters 1, 340 (1967); Advan. Chem. Phys. 12, 283 (1967).

[2] Neil R. Kestner and Oktay Sinanoğlu, J. Chem. Phys. 38, 1730 (1963).

[3] G. S. Rushbrooke and M. Silbert, Mol. Phys. 12, 505 (1967).

[4] C. J. Pings, Mol. Phys. 12, 501 (1967).

[5] J. S. Rowlinson, Mol. Phys. 12, 513 (1967).

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

[7] J. A. Barker, D. Henderson, and W. R. Smith, Phys. Rev. Letters 21, 134 (1968).

[8] J. A. Barker and D. Henderson, J. Chem. Phys. 47, 2856, 4714 (1967).

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

[10] P. G. Mikolaj and C. J. Pings, Phys. Rev. Letters 16, 4 (1966); J. Chem. Phys. 46, 1401, 1412 (1967).

[11] L. Verlet, Phys. Rev. 165, 201 (1968).

[12] Dominique Levesque and Loup Verlet, Phys. Rev. Letters 20, 905 (1968).

[13] G. J. Throop and R. J. Bearman, Physica 32, 1298 (1966).

[14] J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

[15] B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943); Y. Muto, Proc. Phys. Math. Soc. Japan 17, 629 (1943).

[16] Loup Verlet, Phys. Rev. 159, 98 (1967).

[17] We have used the parameter values: $\sigma = 3.409$ Å and $\epsilon/k = 119.5°$K.

[18] S. Koba, S. Kaneko, and T. Kihara, J. Phys. Soc. Japan 11, 1050 (1956); A. E. Sherwood and J. Prausnitz, J. Chem. Phys. 41, 413, 429 (1964).

[19] Douglas Henderson, Mol. Phys. 10, 73 (1965).

[20] Similarly, in solid argon the triple-dipole contribution to the cohesive energy is positive and has the effect of enlarging the theoretical lattice constant [Wolfgang Götze and Hartwig Schmidt, Z. Physik 192, 408 (1966)].

[21] L Jansen, Phys. Rev. 135, A1292 (1964).

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

[23] R. J. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 88, 901 (1966).

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

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

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High Speed Vortices in Helium

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It is demonstrated that the energy of a vortex in He II should be increased when it is very near a boundary. This assumption is used to derive expressions for the critical velocity and supercritical flow in the bulk liquid and the film. The creation and annihilation of vortices is also discussed.

A. INTRODUCTION

It is now well established that vortices exist in superfluid He II with quantized circulation[1-3]

$$\kappa = \oint \vec{v} \cdot d\vec{l} = n(h/M) \simeq n \times 10^{-3}\,\mathrm{cm}^2/\mathrm{sec}.$$

Conventional treatments of the properties of helium use the classical vortex theory with quantization and appropriate images to produce the correct boundary conditions. Refinements have been made with quantum mechanical analysis,[4,5] but these result in little substantial change. In general these