CONTRIBUTION OF THREE-BODY FORCES TO THE THEORY OF LIQUIDS

H. W. Graben

Department of Physics, Clemson University, Clemson, South Carolina 29631

(Received 22 January 1968)

Already theoretical calculations have shown that three-body forces contribute significantly to the cohesive energy of rare-gas solids[1] and to their third virial coefficients.[2] Estimates of the nonadditive effects in liquids are needed.[3] In this Letter a theoretical framework for assessing three-body effects in liquids is presented. Preliminary calculations indicate that the contribution to the excess internal energy of fluids is important and produces better agreement with experiment.

The interaction energy among three atoms is taken to be

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

where w is the nonadditive energy appended to the sum of the 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 liquid are then given by

$$p/kT = \rho - \rho^2/6kT \int g(r)(du/dr)d\tau$$
$$- \rho^3/18kT \int \int g(r_{12}, r_{23}, r_{31})$$
$$\times (\sum_{i>j} r_{ij} \partial w/\partial r_{ij})d\tau_2 d\tau_3, \qquad (2)$$

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

where ρ is the density, N is the number of atoms, and kT is the product of the Boltzmann constant and the absolute temperature. The first two terms on the right-hand side of each equation are the customary expressions[4] derived on the basis of the additivity hypothesis. The third terms are new and represent the effect of w on p and E.

As a starting point, w is treated as a small "perturbation," and its contributions to thermodynamic quantities are calculated with the "unperturbed" radial distribution function.[5] Thus the Kirkwood[6] or superposition approximation is made:

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

where $g(r)$ is the radial distribution function calculated on the basis that $w = 0$. The following argument supports this perturbation procedure: In order that the new term in Eq. (2) give rise to the exact nonadditive contribution to the third virial coefficient, the low-density limit of the triplet distribution function must

529

Table I. Reduced excess internal energies E_2^E/ϵ and E_3^E/ϵ vs v^* and T^*.

v^*	$T^*=1.250$		$T^*=1.667$		$T^*=2.500$		$T^*=5.000$	
	$-E_2^E/\epsilon$	E_3^E/ϵ	$-E_2^E/\epsilon$	E_3^E/ϵ	$-E_2^E/\epsilon$	E_3^E/ϵ	$-E_2^E/\epsilon$	E_3^E/ϵ
3.632	2.035	0.056	1.939	0.047	1.856	0.039	1.787	0.031
2.260	3.192	0.143	3.118	0.121	3.050	0.100	2.990	0.080
1.483	4.974	0.332	4.925	0.280	4.873	0.231	4.822	0.186
1.222	6.232	0.489	6.181	0.413	6.125	0.339	6.066	0.275

be

$$g_0(r_{12}, r_{23}, r_{31}; T)$$

$$= \exp\{-[\sum_{i>j} u(r_{ij}) + w]/kT\}. \quad (5)$$

However, the appearance of w in the Boltzmann factor contributes only (negligible) second- and higher-order terms to the nonadditive third virial coefficient.[2]

In order to give an immediate estimate of the nonadditive contribution to the internal energy, a simple illustrative calculation is given. First the low-density approximation[4] for $g(r, \rho, T)$ is made, viz.

$$g_0(r, T) = \exp[-u(r)/kT]. \quad (6)$$

By using this approximation[7] the third term in Eq. (3) reduces to integrals which have already been evaluated in calculating (to first order) the nonadditive contribution to third virial coefficients,[2]

$$\Delta C = (3kT)^{-1}$$

$$\times \iint \exp[-\sum_{i>j} u(r_{ij})/kT] w \, d\tau_2 d\tau_3. \quad (7)$$

In the case of argon at normal densities,[8] the dominant contribution[9] to w is the Axilrod-Teller-Muto or triple-dipole dispersion energy[10]

$$w_D = \tfrac{3}{4}\alpha\mu(r_{12}, r_{23}, r_{31})^{-3}$$

$$\times(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3), \quad (8)$$

where θ_i are the interior angles of the three-atom triangle, α is the polarizability of the atom, and μ is the coefficient of the Wang-London dispersion energy $(-\mu/r^6)$. Equation (7) has been evaluated[11] analytically for $w = w_D$, using the modified Lennard-Jones (12, 6) model for the pair potential as done by Kirkwood, Lewinson, and Alder (KLA).[12] The result[13]

for this nonadditive excess internal energy is

$$E_3^E/\epsilon = (5\pi^2 \alpha^*/6v^{*2})(1 + 1.0642/T^*$$

$$+ 0.8772/T^{*2} - 0.3774/T^{*3} + \cdots), \quad (9)$$

where $\alpha^* = \alpha/\sigma^3$ is the reduced polarizability, $T^* = kT/\epsilon$, and $v^* = v/\sigma^3$; σ is the slow collision diameter and $-\epsilon$ is the potential minimum in the modified Lennard-Jones model used by KLA. Values of the critical constants given by KLA for the modified Lennard-Jones model are $T_c^* = 1.433$ and $v_c^* = 2.585$. In Table I these results, with $\alpha^*(\text{argon}) = 0.04$, are compared with values of the additive excess internal energy E_2^E/ϵ computed by KLA. For argon their values of E_2^E/ϵ are more negative by several percent than experimental values. Recent calculations[14] for argon based on the Lennard-Jones potential have reduced this discrepancy to a few percent. The important conclusion is that the nonadditive contribution to the internal energy of fluids at ordinary pressures is of the order of a few percent and has the right sign to yield better agreement with experiment.

In summary, the new terms in Eqs. (2) and (3), handled by the perturbation procedure described, should serve as a starting point for studying three-body effects in liquids. Numerical integrations of these terms using tabulated values of $g(r)$ are in progress. The influence of w on $g(r)$ to first order in a perturbative sense is also being examined. Of particular interest are the nonadditive effects in determining $u(r)$ from the "experimental" integral equation at low densities.[15]

―――――――――

[1]B. M. Axilrod, J. Chem. Phys. 19, 724 (1951); W. L. Bade and John G. Kirkwood, J. Chem. Phys. 27, 1284 (1957); L. Jansen, Phys. Rev. 135, A1292 (1964).

[2]S. Koba, S. Kaneko, and T. Kihara, J. Phys. Soc. Japan 11, 1050 (1956); for additional reference, see H. W. Graben, R. D. Present, and R. D. McCulloch, Phys. Rev. 144, 140 (1966).

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

[4]See, e.g., Terrell L. Hill, Statistical Thermodynamics (Addison-Wesley Publishing Company, Inc., Reading Mass., 1960), Chap. 17.

[5]In calculating nonadditive effects in solids, an analogous procedure is followed. First a discrete sum over pair interactions is computed and the parameters for the chosen two-body potential model are selected. Assuming that three-body forces do not alter the lattice structure, a discrete sum over three-body energies is then added to obtain the total potential energy.

[6]J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935); J. G. Kirkwood, Eugene K. Maun, and Berni J. Alder, J. Chem. Phys. 18, 1040 (1950). These authors point out that this approximation is analogous to the Hartree approximation in quantum mechanics.

[7]It would certainly be invalid to make this approximation in the first integral in Eq. (3), but use of the approximation in the nonadditive "correction" term is less serious, particularly if applications are restricted to not-too-dense fluids. The error incurred is a correction on a correction term.

[8]Marvin Ross and Berni Alder, J. Chem. Phys. 46, 4203 (1967). For liquid argon compressed twofold, the nonadditivity effect in the potential is about 30%.

[9]R. D. Present, J. Chem. Phys. 47, 1793 (1967); R. Bullough, H. R. Glyde, and J. A. Venables, Phys. Rev. Letters 17, 249 (1966).

[10]B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943); Y. Muto, Proc. Phys. Math. Soc. Japan 17, 629 (1943); Y. Midzuno and T. Kihara, J. Phys. Soc. Japan 11, 1045 (1956); R. J. Bell and A. E. Kingston, Proc. Phys. Soc. (London) 88, 901 (1966).

[11]R. H. Fowler and H. W. Graben, to be published.

[12]John G. Kirkwood, Victor A. Lewinson, and Berni J. Alder, J. Chem. Phys. 20, 929 (1952); see also Terrell L. Hill, Statistical Mechanics (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

[13]If the theoretical value of μ is used instead of the experimental value, Eq. (8) should be multiplied by μ_{th}/μ_{ex}. For argon this ratio is about one-half. Here an order of magnitude rather than significant figures is wanted.

[14]J. De Boer, J. M. J. Van Leeuwen, and J. Groenveld, Physica 30, 2265 (1964); G. J. Throop and R. J. Bearman, Physics 32, 1298 (1966); Loup Verlet, Phys. Rev. 159, 98 (1967).

[15]P. G. Mikolaj and C. J. Pings, Phys. Rev. Letters 16, 4 (1966).

MASS-CURRENT FLUCTUATIONS IN LIQUID LEAD*

P. D. Randolph

Idaho Nuclear Corporation, Idaho Falls, Idaho

(Received 22 January 1968)

In a recent Letter[1] Rahman has pointed out that for a many-body system, the function $E(\kappa, \omega) \equiv \omega^2 S(\kappa, \omega)$ is the spectral function of the autocorrelation function of the fluctuations in the mass-current density for the system, i.e.,

$$C(\kappa, t) \equiv \langle J_{\kappa}(0) J_{-\kappa}(t) \rangle = \int_{-\infty}^{\infty} e^{i\omega t} \omega^2 S(\kappa, \omega) d\omega.$$

Here $S(\kappa, \omega)$ is the scattering law for the system and is directly observable in slow-neutron inelastic-scattering experiments. $J_{\kappa}(t)$ is the Fourier component in the direction $\hat{\kappa}$ of the linearized mass-current density of wave vector $\hat{\kappa}$ at time t. Rahman[1] has clearly pointed out that $E(\kappa, \omega)$ possesses a maximum at a nonzero value of ω for all systems (even a classical dilute gas) so that $C(\kappa, t)$ will always show some kind of damped oscillatory time dependence. In particular, for instance, it can be shown that in ideal classical fluids [for which $S(\kappa, \omega) = S(\kappa, -\omega)$], the integral $\int_0^{\infty} C(\kappa, t) dt = 0$, and $C(\kappa, 0)$ is a maximum. This implies that $C(\kappa, t)$ must cross the positive t axis at least once and vanish for large t. Thus $C(\kappa, t)$ cannot be adequately described by a simple relaxation model of the form $C(\kappa) e^{-t/\tau}$. Since the current density fluctuations in a liquid are of interest in attempting to understand the liquid state, $C(\kappa, t)$ is worthy of investigation.

The simplest things obtainable that characterize $C(\kappa, t)$ are the value of ω at which $\omega^2 S(\kappa, \omega)$ has its maximum and the κ dependence of this value, which we call $\Omega(\kappa)$. Using a computer and the method of molecular dynamics, Rahman obtained $\Omega(\kappa)$ for liquid argon in the κ range around the first diffraction maximum. The curve showed a well-defined minimum at the κ value of the diffraction peak and a broad maximum below this.

The purpose of this Letter is to present experimentally obtained $\Omega(\kappa)$ values for liquid lead at 352°C. These confirm Rahman's computer-based results. In addition they extend to a larger value of κ. The measurements of $\Omega(\kappa)$ for liquid lead were obtained from slow-neutron inelastic-scattering measurements of $S(\kappa, \omega)$. A detailed report of this experiment has been given.[2] In brief, the experiment was