Scientia Iranica, Vol. 14, No. 2, pp 126–132
© Sharif University of Technology, April 2007

SCIENTIA
IRANICA

Relaxation Time for Bulk Viscosity of Soft-Sphere and Lennard-Jones Fluids

M. Vahedpour[1], **S. Alavi**[2], **B. Najafi*** and **E. Keshavarzi**[1]

The density and temperature dependence of bulk relaxation time is studied for soft-sphere and Lennard-Jones fluids. For soft-sphere fluid, the bulk relaxation time is determined by numerical solution of the Zwanzig-Mountain equation, using the data of Hansen and Weis for the radial distribution function. The bulk relaxation time for soft sphere fluids decreases monotonically with density and increases with temperature. The bulk relaxation times of Lennard-Jones fluids are determined by numerical integration of the Zwanzig-Mountain equation with the Matteoli-Mansoori radial distribution function. For isotherms up to $T^* < 2.1$, the density dependence of the relaxation time of Lennard-Jones fluids goes through a minimum at a reduced density of approximately 0.85.

INTRODUCTION

Bulk viscosity is related to the irreversible resistance to change in the volume of a fluid upon compression and arises from the unequal partition of energy among translational and internal modes in non-equilibrium states [1]. This transport property has been the object of study in the field of fluid physics and recently in such diverse fields as polymer science, quantum field theory and even medicine [2]. Unfortunately, there is only a single indirect method for measuring bulk viscosity, which is based on acoustic adsorption, and the technique has experimental errors ranging up to 25% [3]. The comparison of theoretical calculations with experimental data is not always possible, since bulk viscosity data are generally scarce.

Stokes [4] realized the existence of bulk viscosity in the context of the propagation of ultrasonic waves through a fluid. He believed the measurement of the density variations required to determine bulk viscosity would be difficult and did not further pursue the characterization of this property. Tisza [5] used a formal theory for a complex bulk viscosity coefficient, which is expressed in terms of the relaxation time and applied ultrasonic wave frequency. His analysis explains the excess ultrasonic absorption and dispersion of sound waves in fluids [5]. Excess ultrasonic absorption is defined in relation to classical absorption, which is due to shear viscosity and thermal conductivity [6].

Bulk viscosity is related to the irreversible resistance to change in volume of a fluid under strain. The resistance to volume change in a nonequilibrium system is above that given by the isentropic bulk modulus of a fluid under hydrostatic pressure.

A study of the bulk modulus can reveal microscopic aspects of intermolecular attractive forces, acoustic phenomena and the dynamical structure factor in fluids. In dilute monoatomic gases and incompressible fluids, the effects of bulk viscosity are small and are usually ignored. In dense fluids undergoing strong compression, bulk viscosity plays an important role in determining shock-wave behavior [7]. For polyatomic fluids, bulk viscosity is associated with the relaxation of intramolecular rotations and vibrations. Intramolecular relaxation is a thermal process, which must be considered, in addition to the structural relaxation in polyatomic liquids. It is difficult to isolate and

---

1. *Department of Chemistry, Isfahan University of Technology, P.O. Box 84154, Isfahan, I.R. Iran.*
2. *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

*. *Corresponding Author, Department of Chemistry, Isfahan University of Technology, P.O. Box 84154, Isfahan, I.R. Iran.*

evaluate the exact role of intrinsic bulk viscosity during an irreversible expansion or compression process, in a manner similar to the shear viscosity, which is linked to a shearing process. This is why the study of monoatomic fluids, which have no internal structure, is particularly interesting in determining the magnitude of the factors affecting bulk viscosity. It was initially thought that monoatomic fluids would not show the type of relaxation associated with bulk viscosity, however, theoretical studies for hard sphere liquids with Enskog's theory [8] and computer simulations [7,9-11] and also recent experimental studies [12-15] confirm the existence of bulk viscosity for monatomic systems.

Theoretically, different approaches, based on statistical methods or molecular simulation schemes, can be used to calculate bulk viscosity [3]. The Enskog theory for hard-spheres overestimates bulk viscosity by a factor of two. Borgelt et al. [16] use a kinetic theory approach for Lennard–Jones systems to calculate bulk viscosity, but, their value is at least 60% higher than exact MD simulation values. The time correlation function formalism, in conjunction with Molecular Dynamics (MD) simulations, is a more common approach to studying the transport and dynamics of fluids [10,11,16]. Meier, Laesecke and Kabelac [11] have recently performed extensive molecular dynamics simulations and determined the bulk viscosity for subcritical and supercritical Lennard-Jones fluids. The time correlation function required for the calculation of bulk viscosity can also be calculated by introducing a memory function [17]. The advantage of this approach is that one can introduce an approximate form of the memory function and still preserve a number of useful properties of the time correlation function [18].

At thermal equilibrium, molecular velocities are distributed according to the Maxwell distribution. In non-equilibrium states, the velocity distribution deviates from the Maxwell distribution, which leads to irreversible transport processes. The H-theorem guarantees that an isolated, many particle system will eventually approach equilibrium, irrespective of its initial state. The typical time-scale for this process is called the relaxation time, which depends on the detailed nature of the interparticle interactions.

In this paper, the density and temperature behavior of the infinite-frequency bulk modulus and bulk relaxation times for Soft-Sphere (SS) and Lennard-Jones (LJ) fluids are investigated. The fundamental ideas are those of Mountain and Zwanzig [19,20] who defined bulk relaxation time as follows:

$$\tau = \frac{\eta_{\mathrm{bulk}}}{K_\infty \quad K_0}, \tag{1}$$

where K_0 and K_∞ are the zero- and infinite-frequency bulk modulus, respectively and τ is the bulk relaxation time. In the authors' previous work [21,22], it was observed that the variation of the shear relaxation time with density for LJ fluid passes through a minimum, which indicates a change in behavior from fluid-like to viscoelastic in the supercritical region [21,22]. A similar behavior is observed in the bulk relaxation time, in particular, the bulk relaxation time - density plot shows a minimum of about 0.85. The physical origins of these behaviors are different.

When a mechanical perturbation is suddenly applied to a fluid, the fluid responds elastically at first, as if it were a solid body. The initial response is determined by the infinite-frequency shear modulus (instantaneous rigidity modulus), G_∞, and the infinite-frequency bulk modulus (compression modulus), K_∞. The infinite-frequency shear modulus is related to the diagonal components of the stress tensor and the infinite-frequency bulk modulus is related to both the diagonal and off-diagonal components of the stress tensor. Zwanzig and Mountain find that G_∞ is very sensitive to the repulsive part of the potential for a LJ fluid [19,20].

In the next section of this paper, the density and temperature dependence of the infinite-frequency bulk modulus for the soft sphere potential are obtained. This is used in Equation 1 to obtain the bulk relaxation time for the soft sphere fluid. In the following sections, first, a similar derivation is carried out for the Lennard-Jones fluid, then, the density and temperature dependence of the bulk viscosity relaxation time for both potentials are discussed.

RELAXATION TIME FOR SOFT-SPHERE FLUIDS

Zwanzig and Mountain derived the relation between the infinite-frequency bulk modulus, K_∞, and the radial distribution function (RDF) for fluids with spherically symmetric potentials [20]:

$$K_\infty = \frac{2}{3}\rho kT + p + \frac{2\pi}{9}\rho^2 \int_0^\infty g(r) r^3 \frac{d}{dr}\left[r\frac{d\Phi}{dr}\right] dr, \tag{2}$$

where $g(r)$, $\Phi(r)$, p and ρ are the radial distribution function, intermolecular pair potential, pressure and density, respectively and kT has its usual meaning. Pressure is also related to the RDF and intermolecular potential through the standard expression;

$$p = \rho kT \quad \frac{2\pi}{3}\rho^2 \int g(r) r^3 \frac{d\Phi}{dr} dr. \tag{3}$$

To calculate K_∞ for any thermodynamic state of a simple fluid, an appropriate mathematical form for

$g(r)$, from molecular dynamics simulations or experimental values of $g(r)$ from neutron diffraction, is required.

The soft potential (SS) is written as:

$$\Phi = 4\varepsilon\left(\frac{\sigma}{r}\right)^{n}, \tag{4}$$

where σ is the effective radius, ε the energy factor and n the power of the potential. Substituting the derivative of Φ, with respect to r, in Equation 2, gives:

$$K_\infty = \frac{5}{2}\rho kT + 4n(n+3)\varepsilon\sigma^2\rho^2\frac{2\pi}{9}\int_0^\infty g(r)\left(\frac{\sigma}{r}\right)^{n-2} dr. \tag{5}$$

Heyes and Aston [23] demonstrate that the integral in Equation 5 and, therefore, K_∞, is infinite for a hard-sphere potential, where $n \to \infty$. However, this integral is finite for soft-sphere repulsive potential with $n = 12$ and can be solved numerically.

For a r^{-n} potential, Hansen [24] and, also, Cape and Woodcock [25] showed that the configurational part of all thermodynamic quantities depends on temperature and density only through a dimensionless combination of these variables in the form of $x = \rho\sigma^3(\varepsilon/kT)^{3/n}$. Thus, the values of a thermodynamic property computed along a single isotherm or isochor are sufficient to determine all thermodynamic states. Hansen and Weis [26] tabulated $g(r)$ for soft-sphere fluids ($n = 12$) as a function of x. One uses these values of $g(r)$ to calculate the configurational part of Equation 5. Using the reduced variables, $K^*_\infty = K_\infty\sigma^3/\varepsilon$, $\rho^* = \rho\sigma^3$ and $T^* = kT/\varepsilon$, one defines;

$$z \equiv \frac{K^*_\infty - \frac{5}{2}\rho^* T^*}{\rho^{*2}}. \tag{6}$$

Using the definition of z from Equation 6 in Equation 5 gives.

$$z = 4n(n+3)\frac{2\pi}{15}\int_0^\infty g(r)\left(\frac{\sigma}{r}\right)^{n-2} d\left(\frac{r}{\sigma}\right). \tag{7}$$

The quantity z scales with x for all the thermodynamic states with no distinction made between gas and liquid phases.

K^*_∞ is determined from numerical integration of Equation 5 for several thermodynamic states, using the SS potential with $n = 12$ and $g(r)$ from [26]. Figure 1 shows K^*_∞ as a function of density for several isotherms. The different isotherms are summarized in a single curve by plotting the same data in the form of z as a function of x, see Figure 2. The dependence of z on x can be expressed in the functional form;

$$z = 25.9039 - 31.361x + 266.898x^2 - 237.46x^3 + 150.874x^4, \tag{8}$$

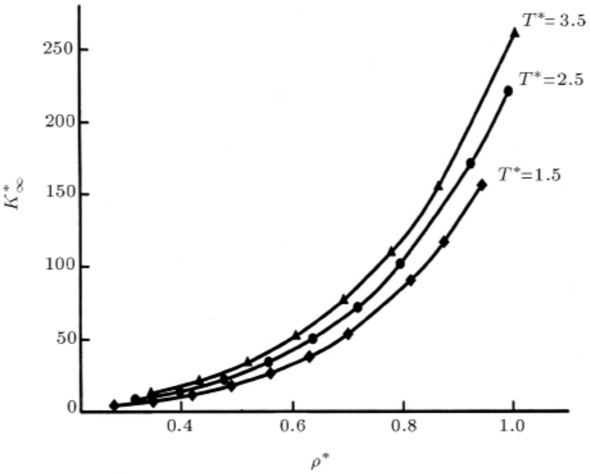

Figure 1. Calculated infinite-frequency reduced bulk modulus K^*_∞, for three isotherms using soft-sphere $n = 12$ potential and the radial distribution function of [26].

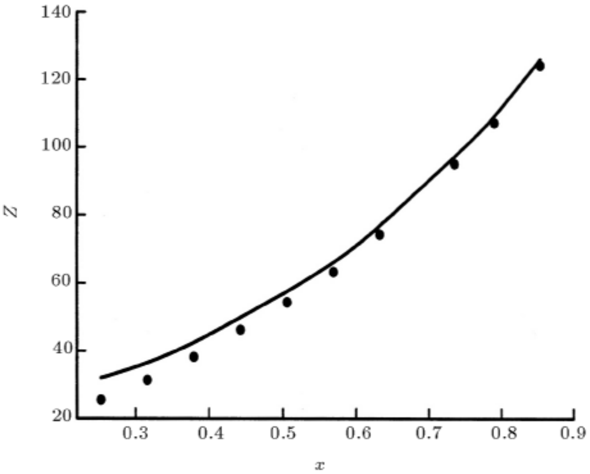

Figure 2. The z variable from Equation 6 plotted as a function of $x = \rho\sigma^3(\varepsilon/kT)^{3/n}$ for all thermodynamic states and compared with molecular dynamics simulations (●) of Heyes [28] for this variable.

which is valid in the range of $0.253 < x < 0.854$, since the data for $g(r)$ of [26] are given for this range. The maximum error in this correlation is 0.85% and the mean error 0.36%. With this functional form, K^*_∞ can be calculated for different values of ρ^* and T^*.

To calculate the bulk relaxation time from Equation 1, the adiabatic (zero-frequency) bulk modulus, K_0, is required. This quantity is defined as:

$$K_0 = \rho\left(\frac{\partial p}{\partial \rho}\right)_s = \rho\gamma\left(\frac{\partial p}{\partial \rho}\right)_T, \tag{9}$$

where $\gamma = C_p/C_v$ is the heat capacity ratio. The adiabatic bulk modulus is determined from the equation of state of the SS fluid, which has been reported in [27] as a function of x;

$$\frac{P^*}{\rho^* T^*} = 1 + 3.62959x + 2.08883x^2 + 0.7575x^3 + 0.17676x^4. \tag{10}$$

The heat capacity ratio can be determined from the thermodynamic relation:

$$\gamma = 1 + \frac{T}{C_v \rho^2} \frac{\left(\frac{\partial p}{\partial T}\right)_\rho^2}{\left(\frac{\partial p}{\partial \rho}\right)_T}, \tag{11}$$

where C_v is the constant volume heat capacity obtained from Equation 17 of [27] which is reproduced in Appendix A. Using Equations 10 and 11, K_0 can be calculated from Equation 9.

Using numerical integration of Equation 5 for K^*_∞ and Equation 9 for K_0, along with the Hoover - Ladd - Hickman and Holian [7] expression for the reduced bulk viscosity, η^*_{bulk}, of a soft sphere fluid, which is reproduced in Appendix A (Equation 13 of [7]), the bulk relaxation time, τ^*_{bulk}, defined as:

$$\tau^*_{\text{bulk}} = \frac{\tau_{\text{bulk}}}{\sigma(m/\varepsilon)^{1/2}}, \tag{12}$$

is determined. Several calculated reduced bulk relaxation times for a SS fluid are shown in Figure 3. Over the temperature range given in this figure, the relaxation time isotherms for the purely repulsive soft-sphere potential decrease monotonically with density after passing a maximum that is caused by the bulk viscosity value.

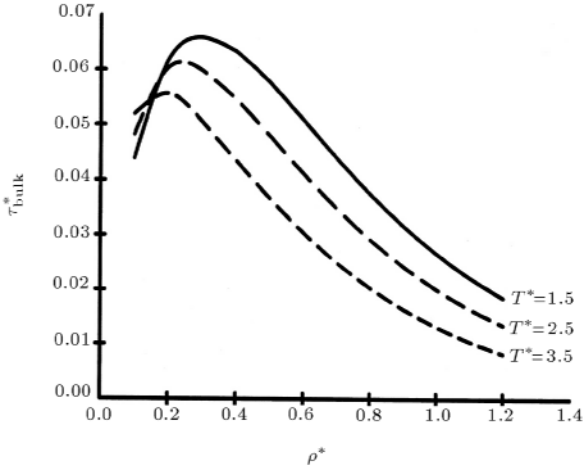

Figure 3. The reduced bulk relaxation time, τ^*_{bulk}, for a SS fluid as a function of the reduced density, ρ^*, for several isotherms.

RELAXATION TIME FOR LENNARD-JONES FLUIDS

There are only a few semi-empirical and analytical expressions for the bulk viscosity for LJ fluids and also little data and no unique formula for the prediction of the relaxation time [28]. To obtain the bulk relaxation time for the LJ fluid, one needs to calculate infinite- and zero-frequency bulk moduli and the bulk viscosity.

To determine the infinite frequency bulk modulus, K^*_∞, the integral in Equation 2 is evaluated numerically for the LJ potential using a simple expression for the radial distribution function of pure fluids, given by Matteoli and Mansoori [29]. Their expression is:

$$g(R) = 1 + R^{-m}[g(d) - 1 - \lambda] + [(R - 1 + \lambda)/R]\exp[-\alpha(R-1)]\cos[\beta(R-1)],$$
$$m \geq 1,\ R \geq 1,$$
$$g(R) = g(d)\exp[-\theta(R-1)^2], \qquad R < 1, \tag{13}$$

where $R = r/d$ is a reduced intermolecular distance, d is the location of the maximum of the first peak in the radial distribution function and $h = d/\sigma$, m, λ, α, β, θ and $g(d)$ are adjustable parameters. This expression is valid in the range of $0.3 < \rho^* < 0.95$ and $0.6 < T^* < 3.7$, when $m \geq 1$ and, therefore, K^*_∞ can be calculated in this region. In Figure 4, the LJ, K^*_∞, obtained from numerical solution of Equation 2 is compared with LJ Molecular Dynamics (MD) results [28] for two isotherms. The agreement between the two sets is acceptable.

The adiabatic bulk modulus is calculated from

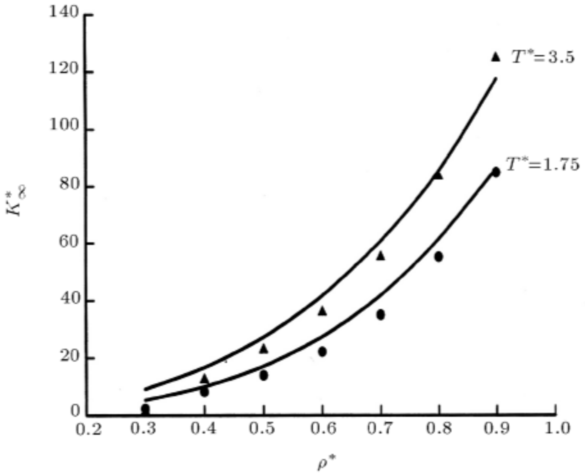

Figure 4. Comparison of the reduced density dependence of the reduced infinite-frequency bulk modulus, K^*_∞, using numerical solution of Equation 2 (   ) and MD results [28] for $T^* = 3.5$ (▲) and $T^* = 1.75$ (●) isotherms.

Equation 9 and the equation of state of the LJ potential [30], which is reproduced in Appendix B.

Calculation of the bulk relaxation time for LJ fluids requires the bulk viscosity, in addition to the infinite-frequency bulk modulus and the adiabatic bulk modulus. The molecular dynamics results of Meier et al. were used for the bulk viscosity [11]. These very accurate results were determined in a wide range of fluid states performed at 351 state points along 16 isotherms.

Figure 5 shows that the bulk relaxation time of six isotherms ($T^* = 1.35 \quad 3.0$) have minima at certain densities. This figure shows a minimum at reduce density approximately 0.85 after passing a maximum. The bulk relaxation time isotherms approach zero at the zero density limit, because the bulk viscosity isotherms are zero in the ideal gas limit.

DISCUSSION

For soft-spheres, the integral for the infinite frequency of bulk modulus, K^*_∞, in Equation 2 is solved numerically. Using this infinite-frequency bulk modulus, the adiabatic bulk modulus from the equation of state of Hoover et al. [27], the bulk viscosity expression of Hoover et al. [7] and the density and temperature behavior of the bulk relaxation time was calculated and shown in Figure 3. The soft-sphere relaxation time decreases monotonically as the density of the fluid is increased. At each density the isotherms with larger temperatures have greater relaxation times.

The infinite-frequency bulk modulus can be determined numerically for the LJ potential, using the Matteoli - Mansoori RDF [29]. The LJ adiabatic (zero-frequency) bulk modulus is obtained using LJ equation of state [30]. Using Equation 2 and the data of Meier et al. for the bulk viscosity from MD calculations (Figure 5), the temperature and density dependence of the bulk viscosity relaxation time of LJ fluids were determined. The isotherms have shallow minima at reduced densities of approximately 0.85.

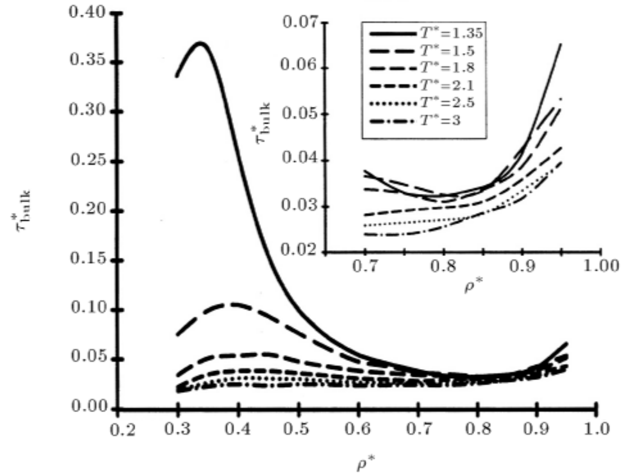

Figure 5. Reduced bulk relaxation time, τ^*, for a Lennard-Jones fluid as a function of the reduced density for six isotherms. The bulk viscosity values required to calculate τ^* were determined from MD simulations.

The behavior of the bulk relaxation time for both SS and LJ fluids are dominated by the behavior of the bulk viscosity. In both these cases, the $K_\infty \quad K_0$ term, in denominator of Equation 1 varies monotonically with the density and temperature regions of interest. The "critical enhancement" of the bulk modulus for supercritical isotherms is seen in the calculations of Meier et al. (Figure 6 of [11]). For higher temperature isotherms, the magnitude of the enhancement becomes smaller and effectively vanishes for isotherms with $T^* > 2.1$. This leads to the disappearance of the minima in the bulk relaxation time for high temperature isotherms with $T^* > 2.1$ (see Figure 5). Thermal conductivity also shows a critical enhancement in the same region and the physical origin of both phenomena is related to critical clustering [31].

The shear viscosity relaxation time isotherms up to $T^* \approx 2.1$ show a minimum at the reduced density of $\rho^* \approx 0.7$ [21,22]. The physical origin of the minimum in the shear and bulk relaxation times is not directly related.

ACKNOWLEDGMENT

The authors wish to acknowledge the research council of Isfahan University of Technology for financial support (Grant No. 1CHA811).

REFERENCES

1. Ferziger, J.H. and Kaper, H.G., *Mathematical Theory of Transport Processes in Gases*, North-Holland, Amsterdam (1972).
2. Bertolini, D. and Tani, A., *J. Chem. Phys.*, **115**, p 6285 (2001).
3. Rah, K. and Eu, B.C., *J. Chem. Phys.*, **114**, p 10436 (2001).
4. Stokes, G., *Trans. Cambrige Phil. Soc.*, **8**, p 287 (1845).
5. Tisza, L., *Phys. Rev.*, **61**, p 531 (1942).
6. Narasimhum, A.V., *Can. J. Phys.*, **45**, p 3923 (1967).
7. Hoover, W.G., Ladd, A.J.C., Hickmen, R.B. and Holian, B.L., *Phys. Rev.*, **21A**, p 1756 (1980).
8. Hirschfelder, J.O., Curtiss, C.F. and Bird, R.B., *Molecular Theory of Gases and Liquids*, Wiley, New York, USA (1954).

9. Alder, B.J., Gass, D.M. and Wainwright, T.E., *J. Chem. Phys.*, **53**, p 3813 (1970); Hoover, W.G., Evans, D.J., Hickman, R.B., Ladd, A.J.C., Ashurst, W.T. and Moran, B., *Phys. Rev.*, **22A**, p 1690 (1980).
10. Levesque, D., Verlet, L. and Kurkijarvi, J., *Phys. Rev.*, **7A**, p 1690 (1973).
11. Meier, K., Laesecke, A. and Kabelac, S., *J. Chem. Phys.*, **122**, p 014513 (2005).
12. Malbrunot, P., Boyer, A., Charles, E. and Abishi, H., *Phys. Rev.*, **27A**, p 1523 (1983).
13. Baharudin, B.Y., Jackson, D.A., Schoen, P.E. and Rouch, J., *Phys. Lett.*, **51A**, p 409 (1975).
14. Naugle, D.G., Lunsford, J.H. and Singer, J.R., *J. Chem. Phys.*, **45**, p 4669 (1966).
15. Cowan, J.A. and Ball, R.N., *Can. J. Phys*, **50**, p 1881 (1972); Cowan, J.A. and Ball, R.N., *Ibid*, **58**, p 74 (1980).
16. Brogelt, P., Hoheisel, C. and Stell, G., *Phys. Rev.*, **42A**, p 789 (1990).
17. Martin, P.C. and Yip, S., *Phys. Rev.*, **170**, p 151 (1968).
18. Tankeshwar, K., Pathak, K.N. and Ranganathan, S., *J. Phys. Condened Matter*, **8**, p 10847 (1996).
19. Copley, J.R.D. and Lovesey, S.W., *Rep. Prog. Phys.*, **38**, p 461 (1975).
20. Zwanzig, R. and Mountain, R.D., *J. Chem. Phys.*, **43**, p 4464 (1965); Mountain, R.D. and Zwanzig, R., *Ibid*, **44**, p 2777 (1966); Mountain, R.D., *Ibid*, **48**, p 2189 (1968).
21. Keshavarzi, E., Vahedpour, M., Alavi, S. and Najafi, B., *Inter. J. Thermophys*, **25**, p 1747 (2004).
22. Bamdad, M., Alavi, S., Najafi, B. and Keshavarzi, E., *Can. J. Chem.*, **83**, p 236 (2005).
23. Heyes, D.M. and Aston, P.J., *J. Chem. Phys.*, **100**, p 2149 (1994); Heyes, D.M., *Ibid.*, **107**, p 1963 (1997).
24. Hansen, J.P., *Phys. Rev.*, **2A**, p 221 (1970).
25. Cape, J.N. and Woodcock, L.V., *J. Chem. Phys.*, **72**, p 976 (1980).
26. Hansen, J.P. and Weis, J.J., *Mol. Phys.*, **23**, p 853 (1972).
27. Hoover, W.G., Ross, M., Johnson, K.W., Henderson, D., Barker, J.A. and Brown, B.C., *J. Chem. Phys.*, **52**, p 4931 (1970).
28. Heyes, D.M., *J. Chem. Soc. Faraday Trans. 2*, **80**, p 1363 (1984); *Ibid. Physica*, **146A**, p 341 (1987).
29. Matteoli, E. and Mansoori, G.A., *J. Chem. Phys.*, **103**, p 4672 (1995).
30. Mecke, M., Muller, A., Winkelmann, J. and Vrabec, J., *J. Fischer, R. Span, and W. Wagner. Int. J. Thermophys*, **17**, p 391 (1996).
31. Michels, A., Sengers, J.V. and van der Gulik, P.S., *Physica*, **28**, p 1216 (1962); Tiesinga, B.W., Sakonidou, E.P. and van der Berg, H.R., *J. Luettmer Strathmann* and Sengers, J.V., *J. Chem. Phys.*, **101**, p 6944 (1994); Bailey, B.J. and Kellner, K., *Brit. J. Appl. Phys.*, **18**, p 1645 (1967); *Ibid. Physica*, **39**, p 444 (1968).

APPENDIX A

For soft-sphere fluids, the specific heat can be estimated from the following equation (Equation 17 of [27]):

$$\left(\frac{C_v}{Nk}\right)=\frac{3}{2}+\frac{P^*V}{4NkT}\quad\frac{1}{16}\left(\frac{\partial(P^*V/NkT)}{\partial\ln\rho}\right)_T,$$

where $P^*=P \quad P_{\text{static}} \quad P_{\text{ideal}}$.

The Enskog theory expression for bulk viscosity is given in Equation 21 of [27]. For soft sphere interacting potential, the Hoover, Ladd, Hickman and Holian [7] expression for the bulk viscosity is obtained by substituting the following expressions in the bulk viscosity formula:

$$\eta=1.002b\rho y\eta_0,$$

where:

$$b_0\rho=2.7222x,\qquad x=\left(\frac{N\sigma^3}{\sqrt{2}V}\right)\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{4}},$$

$$y=2.722x+3.791x^2+2.495x^3\quad 1.131x^5,$$

and:

$$\eta_0=0.171(m\varepsilon)^{\frac{1}{2}}(kT/\varepsilon)^{\frac{2}{3}}/\sigma^2.$$

APPENDIX B

The equation of state of Mecke et al. [30] for LJ fluid is based on the Helmholtz free energy, F, in the form of a generalized van der Waals equation, $F = F_H + F_A$, where F_H accounts for hard body interactions and F_A for attractive dispersion forces. For a system of hard spheres with a packing fraction, ξ, the residual Helmholtz energy, F_H, is given, according to the Carnahan and Starling expression [30], as:

$$\frac{F_H}{RT}=\frac{(4\xi\quad 3\xi^2)}{(1\quad \xi)^2},$$

where:

$$\xi=0.1617(\rho^*/\rho_c^*)[0.689+0.311(T^*/T_c^*)^{0.3674}]^{\quad 1},$$

where ρ_c^* and T_c^* are the critical density and temperature, which equal 0.3107 and 1.328, respectively.

For F_A, the following equation is suggested by Mecke et al. [30]:

$$F_A/RT=\sum_i c_i(T^*/T_c^*)^{m_i}(\rho^*/\rho_c^*)^{n_i}\exp[p_i(\rho^*/\rho_c^*)^{q_i}],$$

where the exponents m_i, n_i, p_i and q_i, as well as coefficients c_i, are determined by the optimization procedure of Setzmann and Wagner and are listed in Table B1.

Table B1. Coefficient c_i and powers, m_i, n_i, p_i and q_i, for the attractive part residual Helmholtz free energy.

c_j	m	n	p	q
$0.33619760720 \times 10^{5}$	-2.0	9	0	0
$0.14707220591 \times 10^{1}$	-1.0	1	0	0
-0.11972121043	-1.0	2	0	0
$0.11350363539 \times 10^{4}$	-1.0	9	0	0
$0.26778688896 \times 10^{4}$	-0.5	8	0	0
$0.12755936511 \times 10^{5}$	-0.5	10	0	0
$0.40088615477 \times 10^{2}$	0.5	1	0	0
$0.52305580273 \times 10^{5}$	0.5	7	0	0
$0.10214454556 \times 10^{7}$	1.0	10	0	0
$0.14526799362 \times 10^{1}$	-5.0	1	-1	1
$0.64975356409 \times 10^{1}$	-4.0	1	-1	1
$0.60304755494 \times 10^{1}$	-2.0	1	-1	1
-0.14925537332	-2.0	2	-1	1
$0.31664355686 \times 10^{3}$	-2.0	8	-1	1
$0.28312781935 \times 10^{1}$	-1.0	1	-1	1
$0.13039603845 \times 10^{3}$	-1.0	10	-1	1
$0.10121435381 \times 10^{1}$	0.0	4	-1	1
$0.15425936014 \times 10^{4}$	0.0	9	-1	1
$0.61568007279 \times 10^{1}$	-5.0	2	-1	2
$0.76001994423 \times 10^{2}$	-4.0	5	-1	2
-0.18906040708	-3.0	1	-1	2
0.33141311846	-2.0	2	-1	2
-0.25229604842	-2.0	3	-1	2
0.13145401812	-2.0	4	-1	2
$0.48672350917 \times 10^{1}$	-1.0	2	-1	2
$0.14756043863 \times 10^{2}$	-10.0	3	-1	3
$0.85996667747 \times 10^{2}$	-6.0	4	-1	3
$0.33880247915 \times 10^{1}$	-4.0	2	-1	3
$0.69427495094 \times 10^{2}$	0.0	2	-1	3
$0.22271531045 \times 10^{7}$	-24.0	5	-1	4
$0.22656880018 \times 10^{3}$	-10.0	2	-1	4
$0.24056013779 \times 10^{2}$	-2.0	10	-1	4