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Abstract

An analytical expression for the shear viscosity of a fluid with particles interacting via pairwise interaction of hard spheres plus an attractive Yukawa potential is presented. The impact of the kinetic pressure has been included following the thermodynamic energy equation and a non-empirical equation of state based on the inverse temperature expansion of the free energy from the mean spherical approximation. Viscosity is computed along the liquid–vapour coexistence curves for different ranges of attractive interactions. The viscosity's dependence on density and temperature up to the critical point has been investigated. The surface tension under similar conditions is also calculated and, therefore, the relation between surface tension and viscosity along the coexistence curve is established. The validity of the Arrhenius type empirical equation depicting the temperature dependence of viscosity in the vicinity and away from the critical point is also examined.

1. Introduction

Viscosity is the manifestation of fluid friction. The presence of a velocity gradient in the fluid amounts to a diffusion of momentum due to transfer of moving molecules from the higher velocity layer to the lower velocity layer, and vice versa. In addition to its key role in grasping the problems of fluid flow, it is also related to the kinetics of reactions and nucleations in material processing.

In the past, considerable effort has been made to derive semi-empirical relations (for reviews see [1, 2]) based on phenomenological parameters. From the theoretical standpoint, expressions for viscosity have been formulated [3] on the basis of equilibrium statistical mechanical theory in terms of the pair distribution function, $g(r)$, and the pair potential, $\phi(r)$. As regards the dynamical approach, the time evolution of the distribution function cannot be precisely described. Consequently, various approximate expressions have been proposed

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based on different concepts. According to Longuet-Higgins and Pople [4], the shear viscosity, η, of a dense hard sphere fluid is given as

$$\eta = \frac{2\sigma}{5}\left(\frac{M}{\pi\beta}\right)^{1/2}\rho\left(\frac{\beta P}{\rho} - 1\right). \tag{1}$$

σ and M are the hard sphere diameter and mass, respectively. ρ represents the number density, $\beta^{-1} = k_B T$ (where k_B is the Boltzmann constant), T is temperature and P is pressure. The main thrust is to improve equation (1) for dense realistic fluids with attractive forces. We follow the approach of Brown and March [5] who suggested that the pressure P in the right-hand side of equation (1) should be replaced by the kinetic pressure, i.e. $T(\partial P/\partial T)$. Then, following the thermodynamic energy equation one can readily improve equation (1) for energetic effects, i.e.

$$P \to T\left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial U}{\partial V}\right)_T, \tag{2}$$

where U stands for energy. Equation (2) paves the way to incorporate the effect of attractive forces on the viscosity.

In this work, we consider a single component fluid with particles interacting via pairwise interaction of hard spheres plus an attractive Yukawa potential. There is ample evidence in the literature [6, 7] that the Yukawa potential is quite suitable to incorporate the long range correlations and provides accurate thermodynamic properties of simple classical fluids. The advantage of using the Yukawa potential is that it provides an analytical expression for the equation of state (EOS), thus disposing of the uncertainties involved with numerical derivatives. This has allowed us to investigate the role of the attractive part of the potential on viscosity along the liquid–vapour (l–v) coexistence curve.

Another advantage is that a reliable analytical EOS for a fluid whose molecules interact via the Yukawa potential with a hard core is available. This is based [8, 9] on the inverse temperature expansion of the free energy from the mean spherical approximation. The equation of state yields an excellent description of the pressure and of the critical point properties when compared with simulation results. The expression of viscosity for the hard core Yukawa fluid in terms of expansion coefficients is given in section 2. Viscosity calculated along the line of the l–v coexistence curve is presented in section 3, where its dependence on density, temperature and long range interaction is discussed. Section 4 describes the calculation of surface tension under similar conditions and, therefore, the relation between surface tension and viscosity along the coexistence curve is examined. The Arrhenius type empirical equation depicting the temperature dependence of viscosity is discussed in section 5. A summary and conclusion follow in section 6.

2. Expression for viscosity for hard core Yukawa fluid

The pair potential of a hard core Yukawa fluid consists of a short range repulsion (normally the hard sphere potential) and a long range attractive Yukawa tail,

$$\phi(r) = \begin{cases} \infty & r \leqslant \sigma \\ -\dfrac{\epsilon\sigma}{r}\exp\left[\lambda\left(\dfrac{r}{\sigma} - 1\right)\right] & r \geqslant \sigma \end{cases} \tag{3}$$

where σ is the hard sphere diameter and ϵ is the depth of the potential. The inverse range parameter λ controls the decay of the attractive potential. With suitably chosen parameters, this form of the potential provides a close fit to the empirical potentials widely used in the

simulation work. Further, it facilitates obtaining an analytical expression for the Helmholtz free energy within the mean spherical approximation.

In recent works by Henderson *et al* [8] and Duh and Y-Téran [9], an explicit analytical formula for the free energy, F, of a hard core Yukawa fluid is given as a series expansion up to five terms,

$$\beta F = \beta F_0 - \frac{1}{2} \sum_{n=1}^{5} \frac{V_n}{nT^n}. \tag{4}$$

The corresponding pressure equation becomes

$$\frac{\beta P}{\rho} = \frac{\beta P_0}{\rho} - \frac{y}{2} \sum_{n=1}^{5} \frac{1}{nT^n} \frac{\partial V_n}{\partial y}, \tag{5}$$

where y is the packing fraction. V_n are the expansion coefficients whose explicit expressions can be found in [9].

F_0 and P_0 are, respectively, the free energy and pressure of the hard sphere reference system. Baus and Colot [10] used the virial series expansion for the EOS and rescaled to obtain a general form for the hard sphere fluid, given as

$$\frac{\beta P_0}{\rho} = \frac{1 + y + y^2 - ay^3 - by^4}{(1 - y)^3}, \tag{6}$$

where a and b are scaling parameters. It can be seen that some of the famous theoretical expressions, like Percus–Yevick ($a = b = 0$) and Carnahan–Starling ($a = 1, b = 0$) equations, are obtained readily from equation (6). In the present work we take $a = b = 2/3$ because it gives better agreement when compared to the very precise (MC-MD) simulation results of Erpenbeck and Wood [11].

The free energy, F_0, corresponding to pressure equation (6) has been obtained here by solving the integral equation

$$\beta F_0 = \beta F_{\text{ideal}} + \int \left(\frac{\beta P_0}{\rho} \right) \frac{\mathrm{d}y}{y}, \tag{7}$$

where F_{ideal} is the free energy of an ideal gas. On substituting equation (6) into (7) we obtain

$$\beta F_0 = -1 - \frac{3}{2} \ln T^* + \ln \rho^* + (a - 3b - 1) \ln(1 - y^*)$$
$$+ \frac{(6 + 2a + 6b)y^* - (3 + 3a + 9b)y^{*2} + 2by^{*3}}{2(1 - y^*)^2}. \tag{8}$$

T^*, ρ^* and y^* are expressed in reduced units,

$$T^* = \frac{k_B T}{\epsilon}, \qquad \rho^* = \rho\sigma^3, \qquad y^* = \frac{\pi}{6}\rho^*\sigma^{*3}. \tag{9}$$

Having defined all the terms in the free energy expression (4) for a hard core Yukawa fluid, the internal energy, U, can be obtained via the standard thermodynamic relation

$$U = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right)_\rho. \tag{10}$$

On using equations (4) and (10) in (1) and (2), we obtain the expression for the viscosity of a hard core Yukawa fluid,

$$\eta^* = \frac{2}{5} \left(\frac{T^*}{\pi} \right)^2 \rho^* \left[\frac{\beta P_0}{\rho^*} - 1 + \frac{y}{2} \sum_{n=1}^{5} \frac{1}{nT^{*n}} \frac{\partial V_n}{\partial y} \left(1 - \frac{1}{n} \right) \right] \tag{11}$$

with

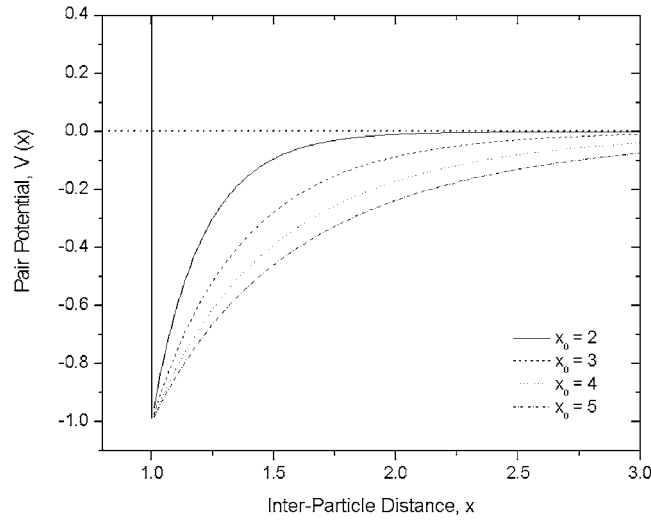$$\eta^* = \frac{\eta\sigma^2}{(M\epsilon)^{1/2}}. \tag{12}$$

Figure 1. Hard core Yukawa potential with various values of the interaction range, x_0.

3. Viscosity along the line of the coexistence curves

Here we study the dependence of viscosity on liquid density and temperature along the l–v coexistence curves for different sets of long range interactions. These curves are obtained by solving numerically the simultaneous equations

$$P(\rho_l^*, T^*) = P(\rho_v^*, T^*)$$
$$\mu(\rho_l^*, T^*) = \mu(\rho_v^*, T^*). \tag{13}$$

The pressure, P, can be obtained from equation (5). The chemical potential, μ, is related to F and P by

$$\beta\mu = \beta F - \frac{\beta P}{\rho}. \tag{14}$$

To show the impact of the potential range parameter, λ, we have used the scaled parameter, x_0, introduced by Tejero *et al* [12],

$$\lambda = \frac{\ln(100/x_0)}{x_0 - 1}, \tag{15}$$

where x_0 is defined as the range of attractive potential at which $\phi(x_0) = -0.01\epsilon$ (cf equation (3)). The Yukawa potential with various values of the range parameter x_0 is shown in figure 1. It is evident that by changing x_0 the Yukawa potential can be used to model many different forms of long range interactions. It is now used via equations (13), (14) and (4) to calculate the l–v coexistence curves. The calculated results for different values of x_0 are plotted in figure 2. The shape of the curves, critical temperature (T_c) and critical density (ρ_c) depend strongly on the range of the attractive potential. T_c increases while ρ_c decreases with increasing range of the attractive potential.

These results are then used in equation (11) to investigate the impact of long attractive interaction on viscosity. The attractive Yukawa potential enters the calculation through the expansion coefficients V_n which are functions of λ and, hence, x_0 (we may recall that the larger values of x_0 account for long range attractions). The calculated η^* as a function of reduced liquid density (ρ_l^*/ρ_c^*) are plotted in figures 3(a) and (b). For a better visualization of
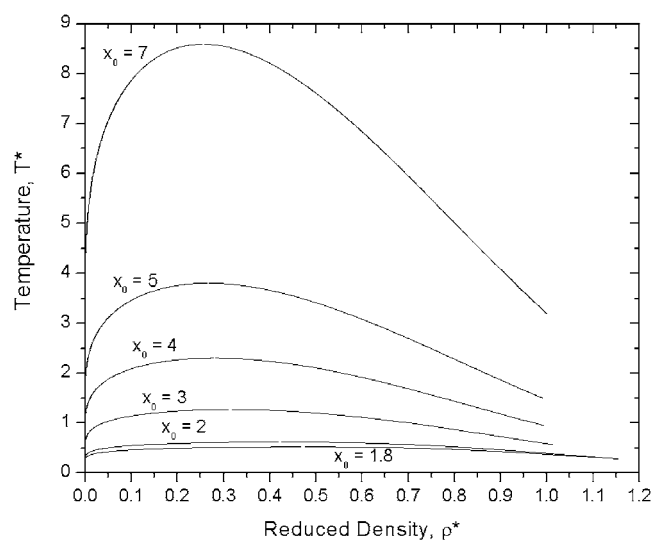
Figure 2. l–v coexistence curves for hard core Yukawa fluid for different values of interaction range, x_0.

the dependence of viscosity on density and x_0, one should refer to the l–v coexistence curves of figure 2. It is evident that x_0 affects the l–v coexistence phase densities considerably. Higher x_0 (say >3) refers to a smaller range of density for the l–v coexistence region in contrast to lower x_0. As x_0 decreases (say to <3), the curves flatten and the l–v coexistence density region increases considerably. The asymmetry of the curves shifts towards the liquid phase and, hence, the liquid phase density increases sharply with decreasing x_0. For clarity, the effect of the two different regions of x_0 ($x_0 \geqslant 4$ and $x_0 \leqslant 3$) on viscosity is shown in figures 3(a) and (b) separately. The sharp gradient of viscosity in figure 3(a) for smaller x_0 is a manifestation that the fluid phase is approaching solidification. Further, figure 3 indicates that as the density tends to its critical value ($\rho_l^* \to \rho_c^*$), the viscosity approaches a minimal value where the effect of x_0 is comparatively small.

The temperature dependence (T^*/T_c^*) of viscosity is shown in figure 4. Viscosity decreases with increasing temperature. The effect of long range interaction on viscosity is higher at lower temperature ($T^* < T_c^*$). As one approaches the critical temperature ($T^* \to T_c^*$), η^* falls to its minimum value. It is interesting to observe that the long range interactions do not affect the viscosity appreciably near T_c^*.

The results of viscosity calculated at a given isotherm are shown in figure 5 for $x_0 = 3$. For isotherms $T^* > T_c^*$, η^* increases with density. On the other hand, for isotherms $T^* < T_c^*$, the dependence of η^* exhibits mixed behaviours. For the vapour-rich phase (small ρ^*), η^* first increases with ρ^*. For l–v mixed phases (metastable state), η^* becomes negative, which has no physical meaning. As density $\rho^* \to \rho_l^*$, η^* once again increases with the liquid phase density.

4. Ratio of viscosity and surface tension

The statistical mechanical approach of Fowler [13] allows us to express the surface tension, γ, in terms of the radial distribution function $g(r)$ and the pair potential $\phi(r)$ as

$$\gamma = \frac{\pi}{8}\rho^2 \int_0^\infty r^4 \frac{\partial \phi(r)}{\partial r} g(r) \, dr. \tag{16}$$
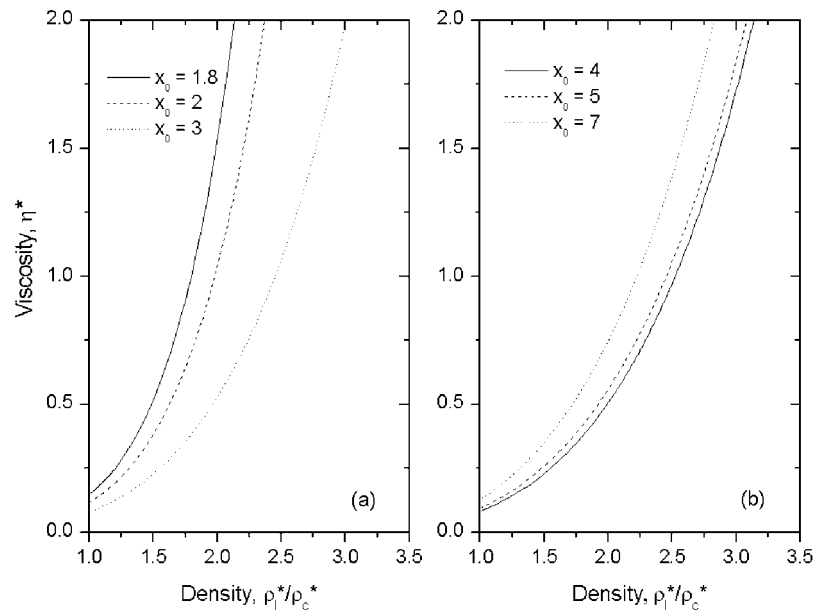
Figure 3. Viscosity, η^*, against reduced density, ρ_l^*/ρ_c^*. ρ_l^* is the liquid density along the coexistence curve and ρ_c^* is the critical density for a given x_0. (a) $x_0 \leqslant 3$. (b) $x_0 \geqslant 4$.
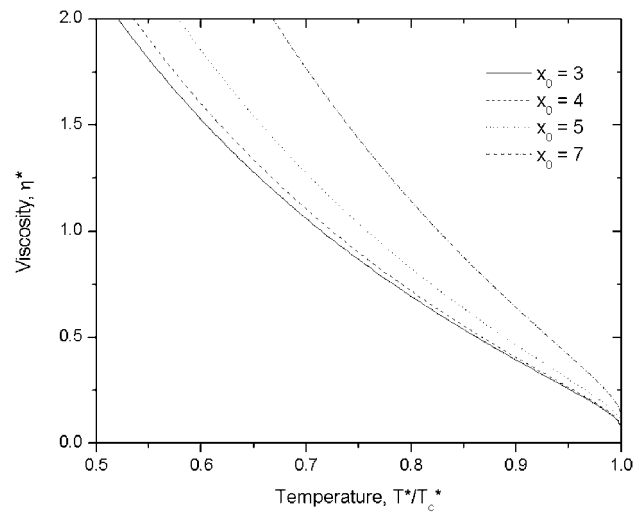

Figure 4. Viscosity, η^*, against reduced temperature, T^*/T_c^*. T^* is the temperature corresponding to liquid density along the coexistence curve and T_c^* is the critical temperature for a given x_0.

Ali *et al* [14] have solved the above equation analytically for the Yukawa potential resulting in

$$\gamma^* = \frac{\pi \rho^{*2}}{8}[\lambda G''(\lambda) - G'(\lambda)]. \tag{17}$$

Here, $G(\lambda)$ is the Laplace transform of $g(r)$, i.e.

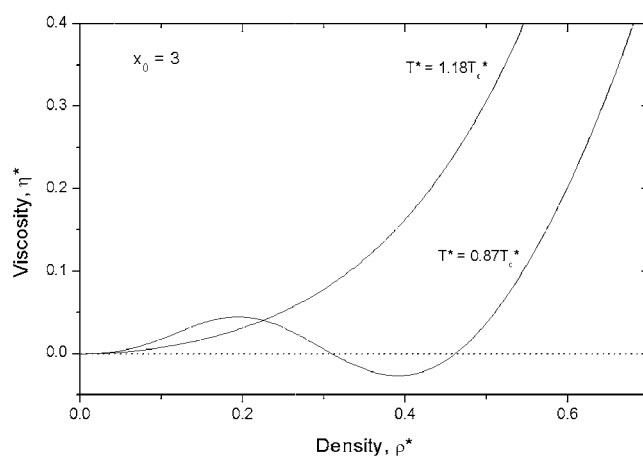$$G(\lambda) = \int_0^\infty x g(x) e^{-\lambda x} \, dx \tag{18}$$

Figure 5. Viscosity, η^*, versus density for isotherms at $T^* = 0.87T_c^*$ and $1.17T_c^*$ for $x_0 = 3$.

with

$$x = \frac{r}{\sigma} \qquad \text{and} \qquad \gamma^* = \frac{\gamma\sigma^3}{\epsilon}. \tag{19}$$

$G'(\lambda)$ and $G''(\lambda)$ in equation (17) are the first and second derivatives, respectively, of $G(\lambda)$ with respect to λ. We may recall that the viscosity expression of Born and Green [3] also involves a similar integrand as in equation (16). Therefore, viscosity and surface tension expressions are intimately related. Following March [15], one can readily eliminate the integral to show that

$$\frac{\gamma^*}{\eta^*} = \text{constant} \sqrt{\frac{T^*}{T_c^*}}. \tag{20}$$

In order to examine the validity of equation (20), we have plotted (figure 6) γ^*/η^* as a function of $(T^*/T_c^*)^{1/2}$ for different values of x_0. γ^* has been calculated from equation (17) for different values of T^*. All other inputs are common for the calculations of γ^* and η^*. It can be readily seen from figure 6 that γ^*/η^* remains pretty constant as a function of $(T^*/T_c^*)^{1/2}$. Variation is observed for smaller values of x_0 in the region $T^* < T_c^*$, which appears due to the flat nature of the l–v coexistence curve (figure 2). The value of the constant depends strongly on x_0. Larger x_0 gives greater values of the ratio γ^*/η^*. March [15] has interpreted this ratio as an outcome of the thermal velocity of the atoms.

5. Arrhenius type relationship along the coexistence curves

It has always been of considerable significance to examine the empirical equation depicting the temperature dependence of viscosity. Befitting our approach, we have examined the empirical dependence of viscosity on temperature along the l–v coexistence curves. The plot of $\ln\eta^*$ as a function of T_c^*/T^* is shown in figure 7 for different values of x_0. It exhibits a linear relationship over a wide range of temperature. However, in a narrow band of temperature near $T^* \approx T_c^*$, it differs from straight line behaviour. Deviation from linearity has also been noticed by Singh and Sommer [16] for demixing liquid alloys as $T^* \to T_c^*$.

Viscosity decreases as $T^* \to T_c^*$, but there is little dependence on x_0 near T_c^*. All the curves tend to merge to a small value of η^* at $T^* = T_c^*$. The linear relationship between $\ln\eta^*$
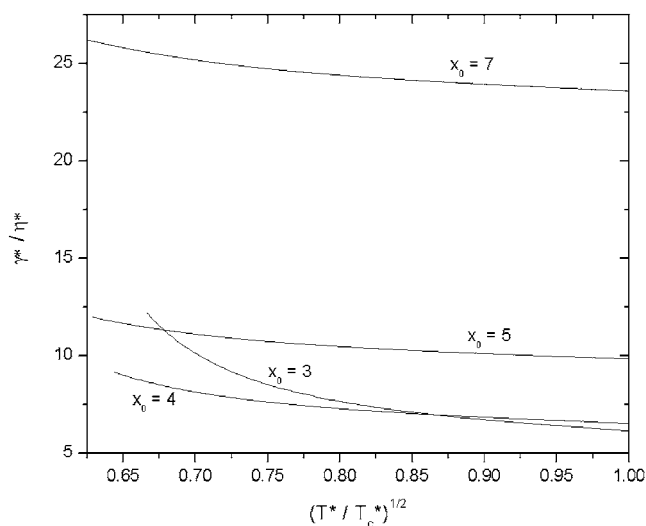
Figure 6. Ratio (γ^*/η^*) of the surface tension γ^* and viscosity η^* versus $(T^*/T_c^*)^{1/2}$ for different x_0.
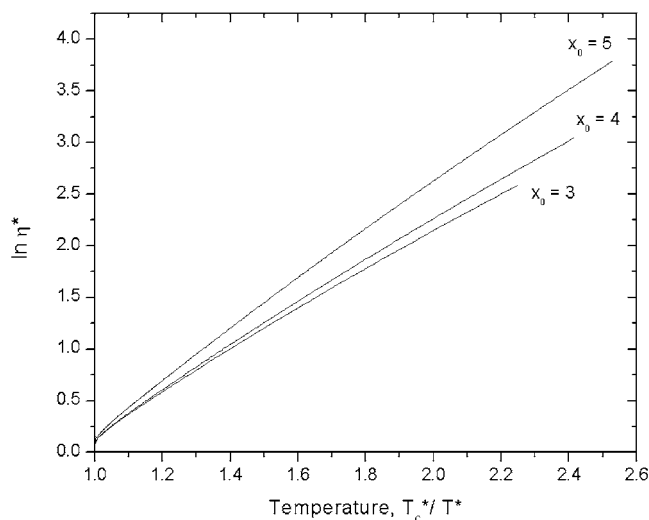

Figure 7. $\ln \eta^*$ versus temperature, T_c^*/T^*, for different x_0.

and T_c^*/T^* can safely be approximated to an Arrhenius type relation, i.e.

$$\eta^* = A \exp\left(B \frac{T_c^*}{T^*}\right), \tag{21}$$

where A and B are constants. An equation like (21) has been very successful in explaining the temperature dependence of viscosity for both classical and metallic liquids. Often B is interpreted as activation energy which in our approach depends on x_0, a measure of the inter-particle correlations. It is evident from figure 7 that the empirical relation (21) works very well below $T^* < T_c^*$, along the l–v coexistence curve. Near T_c^*, the Arrhenius type relationship breaks down.

6. Summary and conclusion

High temperature expansion of the Helmholtz free energy and an improved version of the EOS are used to obtain an analytical expression for the viscosity of the hard core Yukawa fluid. Viscosity is calculated along the l–v coexistence curves and its dependence on density and temperature is discussed up to the critical point. The effect of the long ranged attractive interactions on viscosity is quite significant at higher densities. As density and temperature tend to the critical values ($\rho_l^* \rightarrow \rho_c^*$, $T^* \rightarrow T_c^*$), the viscosity decreases and approaches a minimum value where the effect of the long range interactions is also small. Within our formalism, it has become possible to calculate the ratio of viscosity to surface tension along the l–v coexistence curve. Our results indicate that the ratio of γ^*/η^* remains pretty constant as a function of $(T^*/T_c^*)^{1/2}$, with some variation for low x_0 values. As for the empirical relationship between viscosity and temperature, this work suggests that the Arrhenius type relation works very well for $T^* < T_c^*$, while it breaks down as one approaches T_c^*.

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