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ENTROPY SCALING FOR VISCOSITY OF PURE LENNARD-JONES FLUIDS AND THEIR BINARY MIXTURES

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Abstract. *In this work, entropy scaling approaches for viscosity of pure Lennard-Jones (LJ) fluids and their mixtures have been investigated. To do so, we have used a reliable viscosity database available in the literature for the pure LJ fluids, and performed molecular dynamics simulations to generate a viscosity database over a wide range of thermodynamic conditions for LJ mixture fluids. It has been found that, for the pure LJ fluid, the entropy scaling approaches using macroscopic properties for the reduction of viscosity yield a noticeably better collapse of data in the dense fluid region than the approach using the zero-density viscosity. Then, we have developed viscosity correlations replied on these approaches. It has been obtained that the correlations based on macroscopic properties scaling predict the pure LJ fluid viscosity with an average absolute deviation of about 4% mostly coming from the low-density states, whereas it is of about 8.50% mostly coming from the dense states for the other correlation. Finally, the viscosity correlations combined with a one-fluid approximation have been applied to the LJ mixtures. Interestingly, the correlations based on macroscopic properties scaling are able to provide good estimations for all mixtures studied. However, for the other correlation, the results deteriorate in dense mixtures.*

Keywords: Entropy scaling, viscosity, Lennard-Jones fluid, molecular simulations, equation of state, mixtures.

Classification numbers: 51.20.+d, 51.30.+i, 07.05.Tp, 02.70.Ns, 05.10.Ln.

I. INTRODUCTION

Viscosity of fluid is a key quantity in many fields such as physical engineering and chemical engineering. To estimate this property, an extensive number of methods, both correlative and theoretical, have been developed and reported in the literature [1-3]. However, they are often unreliable when applied to extreme thermodynamic conditions, e.g. high pressures and high temperatures, and mixtures.

Entropy scaling approach, originally suggested by Rosenfeld to deal with dense fluids [4], has recently attracted a lot of attention. This approach is somewhat a hypothesis, as it cannot be derived from a rigorous theory [5]. Still, physical understanding of the approach can be achieved within the framework of hidden scale invariance [5-6]. To extend it to low-density regions, alternative approaches have been proposed [7-10]. Very interestingly, it has been shown that they are able to provide very promising results on pure model and real compounds [8-14]. However, their capability to be extended to mixtures has been less investigated [15-18], which is probably due to the lack of accurate data, e.g. viscosity and excess entropy. Therefore, the applicability to mixtures of these entropy scaling approaches is still questionable. Thus, we propose in this work to systematically study their capability to correlate viscosity of pure and mixture fluids over a wide range of thermodynamic conditions.

Lennard-Jones fluids are not only of great interest in fundamental research, but also in application engineering [19-20]. This is because this model fluid exhibits main physical interaction characteristics found between real molecules [19], i.e. consisting of attractive and repulsive interactions. Therefore, it can be used to consistently describe some real small compounds such as gases [20]. In particular, with recent progresses in the molecular simulations and equations of state [21-24], their thermophysical properties including viscosity and excess entropy can be now accurately estimated over a wide range of thermodynamic conditions. Thus, the Lennard-Jones fluids are fully consistent with the purpose of this work and we have used them to better assess the capability of the excess entropy scaling frameworks.

The article is organized as follows. A brief description on excess entropy approaches is presented in Sec. II. The molecular simulations are detailed in Sec. III. The results obtained from molecular simulations and excess entropy approaches are presented and discussed in Sec. IV. Finally, we summarize the main outcomes of this study to form the conclusion in Sec. V.

II. THEORETICAL BACKGROUND

Entropy scaling approach is based on the idea of expressing a dimensionless/reduced viscosity η^r as a mono-variant function of the reduced excess entropy s_r^{ex} that is defined as:

$$s_r^{ex}(T,\rho) = \frac{s^{ex}(T,\rho)}{k_B} = \frac{s(T,\rho) - s^{id}(T,\rho)}{k_B}, \tag{1}$$

where $s^{ex}(T,\rho)$ is the excess entropy, $s(T,\rho)$ is the total entropy per molecule, $s^{id}(T,\rho)$ is the ideal gas entropy per molecule, and k_B is the Boltzmann constant. In the original approach of Rosenfeld [4], the dimensionless viscosity is given as:

$$\eta_{Ros}^r = \eta \frac{\rho^{-\frac{2}{3}}}{(Mk_BT)^{\frac{1}{2}}}, \tag{2}$$

where η is the viscosity, ρ is the molecular number density, M is the molecular mass, and T the temperature. It is worth noticing that Rosenfeld has employed macroscopic properties, temperature and density, for reduction, which is somewhat similar to the application of the isomorph theory [5]. Interestingly, it has been shown that this assumption often yields a rather-linear relationship between $\ln\eta^r_{Ros}$ and s^{ex}_r in the dense-fluid region for various fluids [9]. So, this framework is an efficient way to develop viscosity correlations of fluids in such region. However, it exhibits an inconsistency in the dilute-gas region due to a divergence of η^r_{Ros} at zero density, i.e. when ? tends to zero. To circumvent this problem, some approaches have been proposed in the literature [7-10].

Novak has proposed to define the dimensionless viscosity as [8]:

$$\eta^r_{Nov} = \frac{\eta}{\eta_0}, \tag{3}$$

where η_0 is the Chapman-Enskog viscosity, i.e. the one at zero density. By doing so, at extremely low-density conditions the dimensionless viscosity converges to one, which enables to fit the viscosity data of fluid in the entire fluid region, i.e. including the dilute gas region. This approach has shown to provide reasonable results for real fluids [8, 11-12, 15]. It has also been applied to LJ fluid and their mixtures, but limited to a small range of thermodynamic conditions [15].

Another approach, proposed by Galliero *et al.* [9], is to apply the Rosenfeld's assumption only to the residual contribution into the viscosity, η_{Res}, defined as:

$$\eta_{Res} = \eta - \eta_0 \tag{4}$$

instead of using the viscosity η, i.e.,

$$\eta^r_{Gal} = \eta_{Res}\frac{\rho^{-\frac{2}{3}}}{(Mk_BT)^{\frac{1}{2}}} = (\eta - \eta_0)\frac{\rho^{-\frac{2}{3}}}{(Mk_BT)^{\frac{1}{2}}}. \tag{5}$$

Using this option, the viscosity in the zero-density limit can be correctly calculated. The approach has been applied to many pure fluids, and has clearly shown an improvement compared to the Rosenfeld's approach [9]. Rather surprisingly, its extensions to mixtures has been less studied, even for simple mixtures of LJ fluids.

More recently, Bell *et al.* have proposed another definition of the dimensionless viscosity [10], thanks to an analysis of the transport properties of dilute gas, as:

$$\eta^r_{Bel} = \eta\frac{\rho^{-\frac{2}{3}}}{(Mk_BT)^{\frac{1}{2}}}(-s^{ex}_r)^{\frac{2}{3}}. \tag{6}$$

This approach retains the use of macroscopic properties to define the dimensionless viscosity as Rosenfeld's assumption, in order to be somewhat consistent with the requirement of application of the isomorph theory [5]. It has been shown that the approach does not only eliminate the divergence at the zero-density limit, but also yield a good one-to-one relationship between η^r_{Bel} and s^{ex}_r over a wide range of thermodynamic conditions for various fluids [10, 13, 14, 16, 18]. However, its application to mixtures of LJ fluids has not yet been largely considered.

Thus, in the present work, the capabilities of these three approaches to correlate the viscosity of LJ fluids have been tested and compared.

III. MOLECULAR SIMULATIONS

III.1. Molecular Modelling

A Lennard-Jones fluid is composed of spherical molecules whose interactions are described by the LJ potential as [25]:

$$u_{LJ}(r_{ij}) = 4\epsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}], \tag{7}$$

where ϵ_{ij} is the potential well depth, σ_{ij} is the collision diameter and r_{ij} the distance between the two spheres.

Binary mixtures used in this work consist of species differing in terms of either the potential well depth or the collision diameter, while the molecular masses are the same. More precisely, two binary mixtures have been considered: Mixture I: $\epsilon_{22} = 2\epsilon_{11}$ and $\sigma_{22} = \sigma_{11}$, and mixture II: $\epsilon_{22} = \epsilon_{11}$ and $\sigma_{22} = 1.25\sigma_{11}$. Interaction parameters between unlike molecules have been determined by the classical Lorentz-Berthelot combining rules:

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2} \tag{8}$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}. \tag{9}$$

We have investigated the binary mixtures at different molar fractions of species 1, x_1, uniformly varying from 0.00 to 1.00 with steps of 0.05. Thermodynamic conditions have been chosen to represent different component phase behaviors of binary mixtures: gas-gas, liquid-liquid and liquid-gas, detailed in Tables 1 and 2. It is worth mentioning that all thermodynamic states of mixtures studied are stable. This is because either its temperature is greater than the critical temperatures of components, i.e. for gas-gas mixtures, or its pressure at lower temperatures, i.e. for liquid-gas and liquid-liquid mixtures, is greater than the saturation pressures of components. In the following sections, we express thermophysical variables in the dimensionless LJ units, noted with a star as superscript, by using the molecular parameters of component 1 for the reduction [19].

Table 1. Thermodynamic conditions and corresponding component phase behavior of binary mixture I used in this work.

	T^*=1.50	T^*=3.00
P^*=1.635	Liquid-Gas	
P^*=0.502		Gas-Gas (Low density)
P^*=1.662		Gas-Gas (Moderate density)
P^*=7.904		Gas-Gas (High density)

III.2. Numerical details

To calculate the thermodynamics properties, Monte Carlo molecular simulations in the isothermal-isobaric ensemble (NPT) [15] have been performed using an in-house code. Simulation boxes are cubic and contain at least 500 LJ molecules. Periodic boundary conditions (PBC) are applied in three directions. The LJ potential is computed by truncating the interaction at a cut-off radius of $4\sigma_{ij}$, and the long range corrections (LRC) are included. In the simulations, two MC moves are implemented: volume change and molecular translation.

Table 2. Thermodynamic conditions and corresponding component phase behavior of binary mixture II used in this work.

	T*=1.00	T*=2.00
P*=0.787	Liquid-Liquid	
P*=0.227		Gas-Gas (Low density)
P*=0.746		Gas-Gas (Moderate density)
P*=3.763		Gas-Gas (High density)

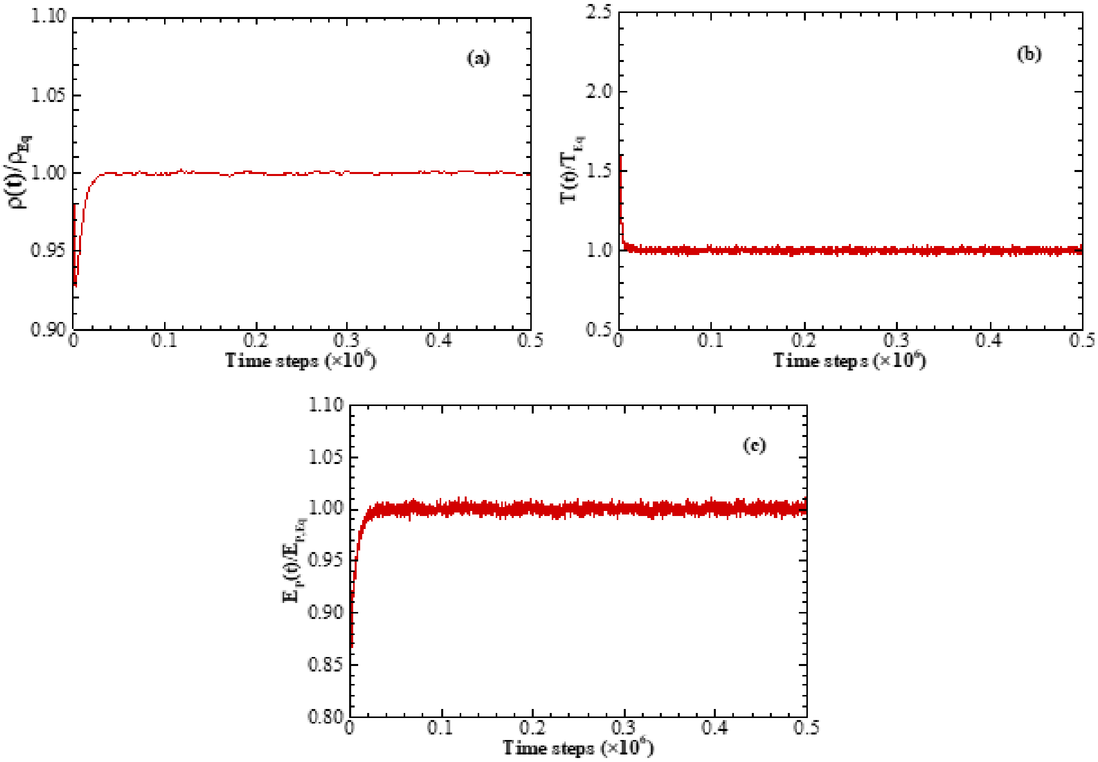

Fig. 1. Evolution of thermodynamic properties scaled by their corresponding equilibrium values for a highly asymmetric mixture, i.e. a liquid-gas mixture at (x_1=0.5, P*=1.635, T* =1.50), obtained from MD simulations in NPT ensemble. (a) Density. (b) Temperature. (c) Potential energy.

All MC simulations are carried out in two steps. First, the simulation systems were equilibrated during a run of 10×10^6 MC moves. During this step, maximum amplitudes of the MC moves were adjusted so that the acceptance rates are about 50%. Then, the data production was performed during 50×10^6 MC moves to compute the thermodynamics properties. To determine the chemical potential that is required to calculate the excess entropy, we have employed the Widom insertion method, with at least 1×10^8 trial insertions [26-27].

Viscosity was computed by performing molecular dynamics (MD) simulations [15] using an in-house code. All MD simulations consist of three steps. In the first step, the simulation systems were equilibrated during a run of 1×10^6 timesteps, see Fig. 1. Then, a reverse non-equilibrium molecular dynamics (RNEMD) algorithm, proposed by F. Müller-Plathe [28-29], has been employed to shear the fluid. The second step to reach the steady state was carried out during 5×10^6 timesteps. In the last step, a run of 30×10^6 timesteps was used for the samplings.

Simulation boxes, containing 3000 molecules, were set up such that $L_z = 2L_x = 2L_y$. The PBC were applied in all directions [15]. The cut-off radius of $3\sigma_{ij}$ was employed to compute the LJ interaction. The equations of motion were computed by employing the velocity Verlet algorithm with timestep $\delta t = 0.002$ [30]. To maintain the temperature, the Berendsen algorithm [31] was applied to all directions of velocity during the equilibrium MD simulations, whereas it was applied to only the two directions perpendicular to the shear direction during the NEMD simulations to remove the effect of streaming velocity.

In all MC and MD simulations, a sub-block method was employed to estimate error bars. It has been obtained that the error bars of excess entropy and viscosity are often smaller than 0.5% and 3%, respectively. For clarity, the error bars are not shown in following figures.

IV. RESULTS AND DISCUSSIONS

IV.1. Computations of excess entropy

In this work, we have employed a LJ equation of state (EoS) developed by Thol *et al* [24] to compute excess entropy of pure LJ fluids. This EoS was also extended to deal with mixtures thanks to a mixing rule based on the van der Waals one-fluid (vdw1) theory [32, 33], so-called as a vdw1 mixing rule.

The LJ EoS equation is written in terms of the reduced Helmholtz free energy $\alpha = \frac{a}{k_B T}$ with a is the Helmholtz free energy per molecule [24]. More precisely, it is decomposed into ideal-gas and residual contributions, α^0 and α^r, that are as functions of the inverse temperature and density, $\tau = \frac{T_c}{T}$ and $\delta = \frac{\rho}{\rho_c}$ with T_c and ρ_c being the critical temperature and density respectively, as:

$$\alpha(\tau,\delta) = \alpha^0(\tau,\delta) + \alpha^r(\tau,\delta) \tag{10}$$

where the contributions are given by:

$$\alpha^0(\tau,\delta) = \ln\delta + 1.5\ln\tau + c_1\tau + c_2, \tag{11}$$

$$\alpha^r(\tau,\delta) = \sum_{i=1}^{6} n_i\delta^{d_i}\tau^{t_i} + \sum_{i=7}^{12} n_i\delta^{d_i}\tau^{t_i}\exp(-\delta^{l_i}) + \sum_{i=7}^{12} n_i\delta^{d_i}\tau^{t_i}\exp(-\xi_i(\delta-\chi_i)^2 - \beta_i(\tau-\gamma_i)^2) \tag{12}$$

where c_i, n_i, d_i, t_i, l_i,ξ_i, χ_i, β_i and γ_i are coefficients, given in [24]. With this formalism, the excess entropy can be computed from:

$$\frac{s^{ex}}{k_B} = \tau(\frac{\partial\alpha^r}{\partial\tau})_\delta - \alpha^r \tag{13}$$

Mixtures are treated as a pure fluid by using the vdw1 mixing rules [32, 33], as:

$$\rho_{c,m}^{-3} = \sum_i \sum_j x_i x_j \rho_{c,ij}^{-3}, \tag{14}$$

$$T_{c,m}\rho_{c,m}^{-3} = \sum_i \sum_j x_i x_j T_{c,ij}\rho_{c,ij}^{-3} \tag{15}$$

$\rho_{c,ij}$ and $T_{c,ij}$ corresponding to the Lorentz-Berthelot combining rules given by:

$$\rho_{c,ij}^{-\frac{1}{3}} = \frac{\rho_{c,ii}^{-\frac{1}{3}} + \rho_{c,jj}^{-\frac{1}{3}}}{2}, \tag{16}$$

$$T_{c,ij} = \sqrt{T_{c,ii}T_{c,jj}}. \tag{17}$$

As the excess entropy is the key quantity for the entropy scaling approaches, we have verified the capability of the LJ-EoS to provide this quantity. To do so, molecular simulations have been performed to compute the excess entropy per molecule for a given state by using the following classical thermodynamic relation [34]:

$$s^{ex} = \frac{[u^{res} + \frac{p^{res}}{\rho} - \mu^{res}]}{T}, \tag{18}$$

where u^{res} is the residual potential energy per molecule, p^{res} is the residual pressure, and μ^{res} is the residual chemical potential per molecule. The residual thermodynamic quantities are calculated as the total thermodynamic quantities minus the ideal gas thermodynamic quantities at the same temperature and density.

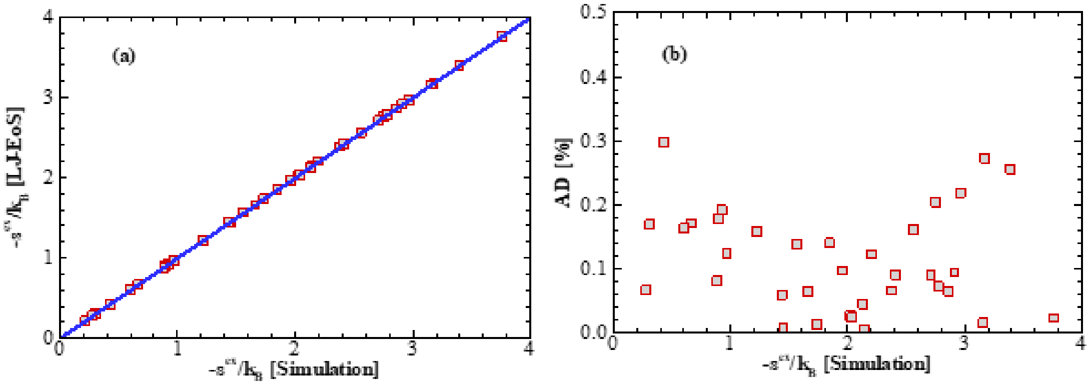

Fig. 2. Comparison between minus reduced excess entropy of pure LJ fluid obtained from the molecular simulations and LJ-EoS. (a) Simulation data versus LJ-EoS data. (b) Absolute deviation versus minus reduced excess entropy. Line corresponds to the identity function, i.e. $(-s_r^{ex})_{Simulation} = (-s_r^{ex})_{LJ-EoS}$.

Figure 2 shows a comparison between the minus reduced excess entropy obtained from molecular simulations and the LJ EoS for the pure LJ fluids. Results clearly indicate that the LJ EoS is able to yield excellent results with an absolute deviation (AD) smaller than 0.3%. For the studied mixtures, as illustrated in Fig. 3, the method slightly deteriorates with the maximum absolute deviation (MAD) up to 1.4%, which is probably due to the limitation of the van der Waals one fluid approximation.

IV.2. Entropy Scaling

A. Pure Lennard-Jones Fluid

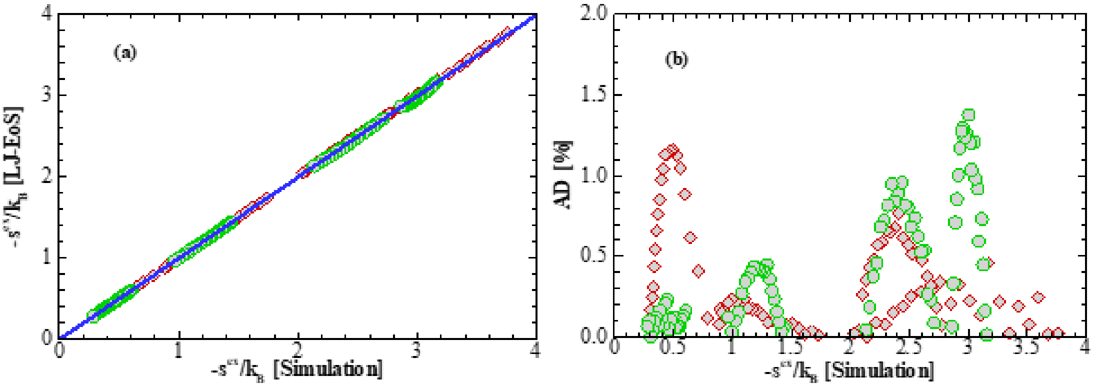

Fig. 3. Comparison between minus reduced excess entropy obtained from the molecular simulations and the LJ-EoS for the studied mixtures. (a) Simulation data versus LJ-EoS data. (b) Absolute deviation versus minus reduced excess entropy. Red diamonds correspond to mixture I. Green circles correspond to mixture II. Line corresponds to the identity function, i.e. $(-s_r^{ex})_{Simulation} = (-s_r^{ex})_{LJ-EoS}$.

First, we have investigated the three entropy scaling approaches, described in Sect. 2.1, for the pure LJ fluid over a wide range of thermodynamic conditions. To do so, we have employed a database of LJ viscosity over the range ($0.6 \leq T \leq 6$ and $0 \leq \rho \leq 1.275$) obtained from the MD simulations by Meier and Galliero *et al.* [35-36]. The zero-density viscosity η_0, used in the approaches of Novak and Galliero *et al.*, has been estimated by using Chapman-Enskog theory [37], similarly to previous works [8-9], as:

$$\eta_0 = \frac{5}{16\Omega^{(2,2)}(T)}\sqrt{\frac{T}{\pi}}, \tag{19}$$

where $\Omega^{(2,2)}$ is the collisional integral, which has been computed from the correlation given by Neufeld *et al.* [38].

Figure 4 shows the dependence of the dimensionless viscosity on the reduced excess entropy. It appears that approaches of Novak and Bell *et al.* yield reasonable convergence at the zero-density limit, whereas it is very noise for the approach of Galliero *et al.* The latter can be understood as they have defined the dimensionless viscosity for the residual viscosity, instead of using the total viscosity, which becomes very small in the dilute states and so very sensitive to the accuracy of the simulation data. In the dense fluid region, a good collapse of data is achieved with the approaches of Galliero *et al.* and Bell *et al.*, but the results are less good for the one of Novak. This is probably related to the consistency of the reduction of viscosity. More precisely, Galliero *et al.* and Bell *et al.* approaches use the macroscopic properties scalings, i.e. temperature and density, as required to apply the isomorph theory [5].

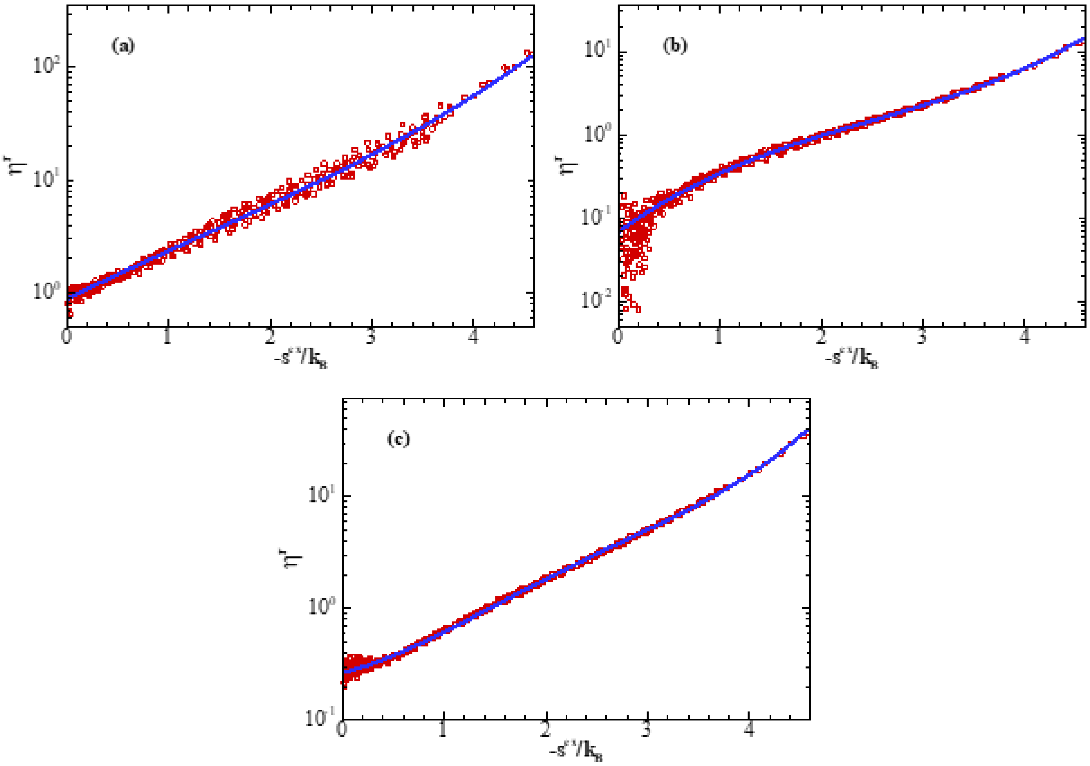

Fig. 4. Dependence of dimensionless viscosity on reduced excess entropy. (a) Novak's approach. (b) Galliero *et al.* approach. (c) Bell *et al.* approach. Lines correspond to the fitting curves.

To quantify the capability of the approaches to develop viscosity correlations, we have first regressed the dimensionless viscosity data as:

$$\eta^r = exp(\sum_{i=0}^{5} A_i(-s_r^{ex})^i), \tag{20}$$

where A_i are the fitting coefficients given in Table 3. Then, the viscosity is given by:

$$\eta_{Nov} = \eta_0 \exp(\sum_{i=0}^{5} A_{i,Nov}(-s_r^{ex})^i), \tag{21}$$

$$\eta_{Gal} = \eta_0 + (\rho)^{\frac{2}{3}}(T)^{\frac{1}{2}} \exp(\sum_{i=0}^{5} A_{i,Gal}(-s_r^{ex})^i), \tag{22}$$

$$\eta_{Bel} = (\rho)^{\frac{2}{3}}(T)^{\frac{1}{2}}(-s_r^{ex})^{-\frac{2}{3}} \exp(\sum_{i=0}^{5} A_{i,Bel}(-s_r^{ex})^i). \tag{23}$$

It has been obtained that the correlation of Novak's approach predicts the viscosity with an average absolute deviation (AAD) of 8.50%, and of 4.24% and 4.01% for the approaches of Galliero *et al.* and Bell *et al.*, respectively. For further details, the AD are illustrated in Fig. 5.

As can be seen, in the gas-like region that consists of the states with the excess entropy larger than the critical one, equal to about -0.90 [39], all the correlations yield results with similar AAD about 5.5%. In the remaining region, i.e. the liquid-like, as expected, the two correlations based on Galliero *et al.* and Bell *et al.* approaches provide even better estimation than in the gas-like region, i.e. 3.4% and 2.5% respectively, but the correlation based on Novak approach noticeably deteriorates, yielding the AAD equal 11.1%.

Table 3. Values of fitting coefficients in Eqs. (21, 22, 23).

	Novak's approach	Galliero *et al.* approach	Bell *et al.* approach
A_0	-0.1249	-2.6870	-1.3260
A_1	1.0410	2.0540	0.4854
A_2	-0.07374	-0.4905	0.5091
A_3	0.01827	0.0650	-0.1760
A_4	N/A	N/A	0.02057

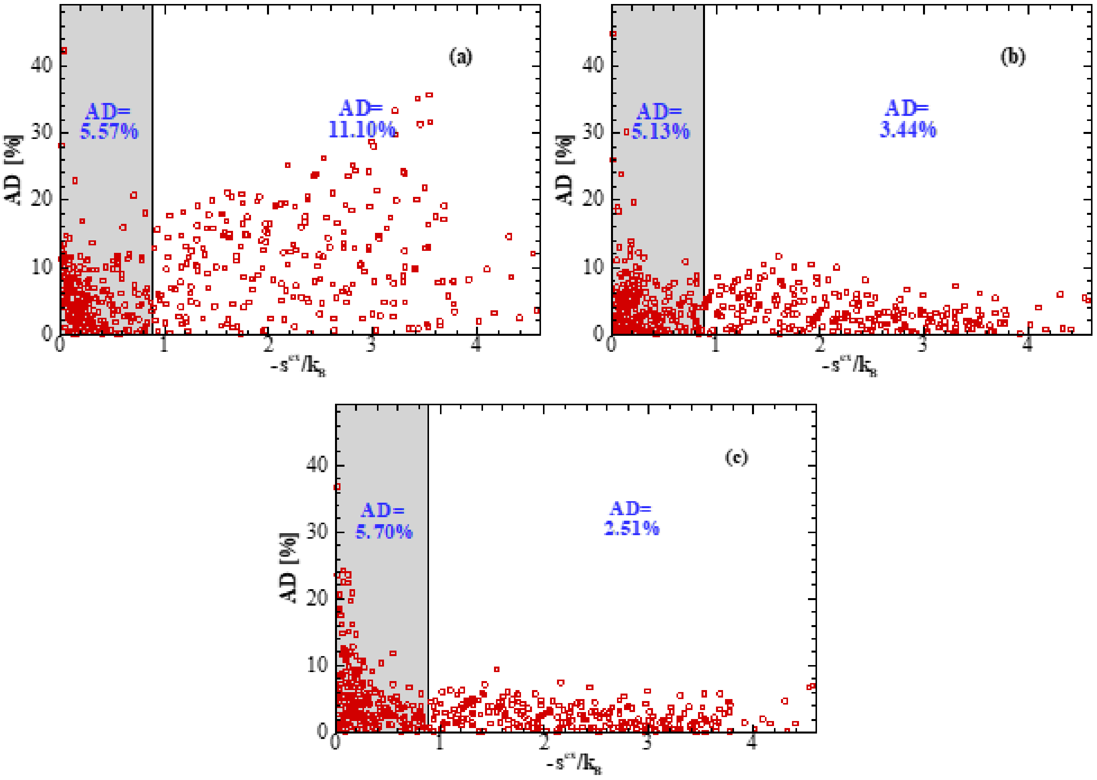

Fig. 5. Variation in absolute deviation of viscosity between predicted and simulations ones with reduced excess entropy. (a) Novak's approach. (b) Galliero *et al.* approach. (c) Bell *et al.* approach. Shadowed regions correspond to the gas-like behavior.

B. Binary Mixtures of Lennard-Jones Fluids

In this section, we evaluate the capability of the viscosity correlations based on the entropy scaling approaches when applied to binary mixtures of LJ fluids. To do so, we have performed MD simulations to provide a viscosity database on LJ mixtures. Similarly, to previous work [15], the zero-density viscosity of mixture is computed by using the approximation of Wilke [40] given by:

$$\eta_{0,m} = \sum_i \frac{x_i \eta_{0,i}}{\sum_j x_i \varphi_{ij}} \tag{24}$$

with

$$\varphi_{ij} = \frac{[1 + (\frac{\eta_{0,i}}{\eta_{0,j}})^{\frac{1}{2}} (\frac{M_j}{M_i})^{\frac{1}{4}}]^2}{[8(1 + \frac{M_i}{M_j})]^{\frac{1}{2}}} \tag{25}$$

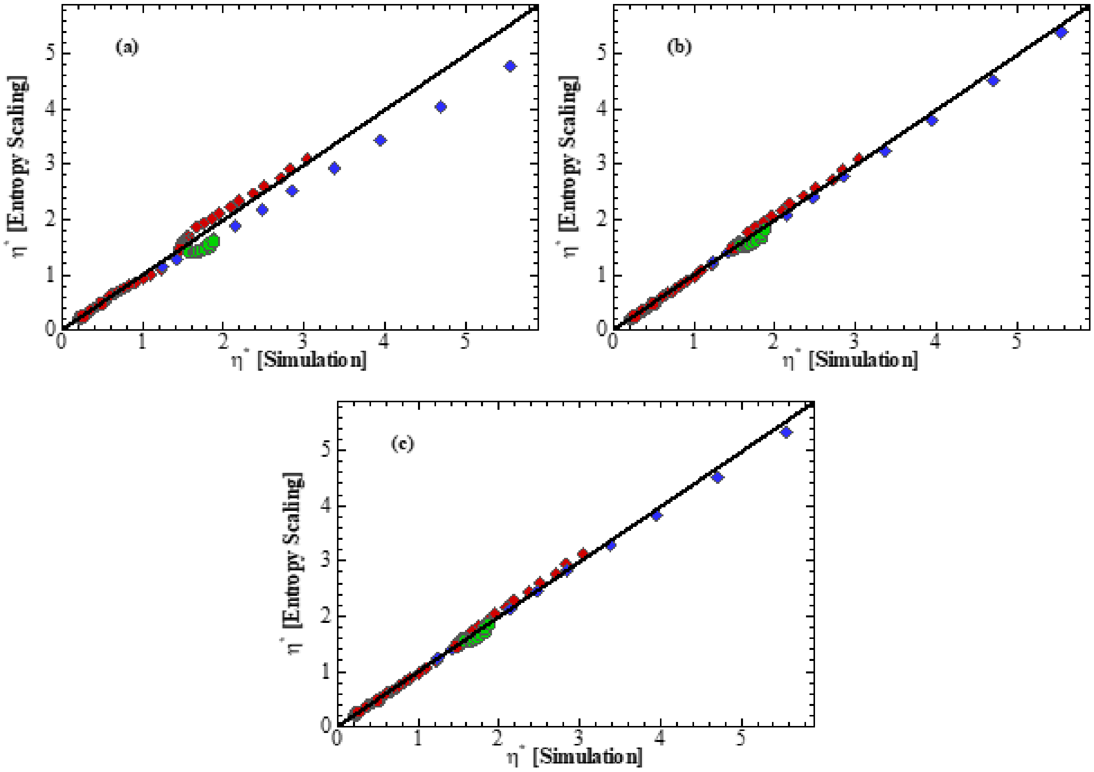

Fig. 6. Viscosity computed from the entropy scaling approaches versus the viscosity provided from the MD simulations. (a) Novak's approach. (b) Galliero *et al.* approach. (c) Bell *et al.* approach. Diamonds correspond to mixture I. Circles correspond to mixture II. Red color corresponds to gas-gas mixtures. Green color corresponds to liquid-liquid mixtures. Blue color corresponds to gas-liquid mixtures. Line corresponds to the identity function, i.e. $\eta_{Sim} = \eta_{Ent}$.

Viscosity obtained from the entropy scaling correlations is displayed against the simulation data in Fig. 6. Interestingly, results indicate that the correlations based on Galliero *et al.* and Bell *et al.* approaches are able to provide a good estimation of viscosity of the LJ mixtures considered, whatever phase behavior: gas-gas, liquid-liquid and liquid-gas, even when the partial molar properties of the components are very different from each other. However, the results are less good for the correlation based on Novak's approach, in particular for densest states, i.e. largest values of $\frac{-s_r^{ex}}{k_B}$, see Fig. 7. This is consistent with the results obtained on pure LJ fluids.

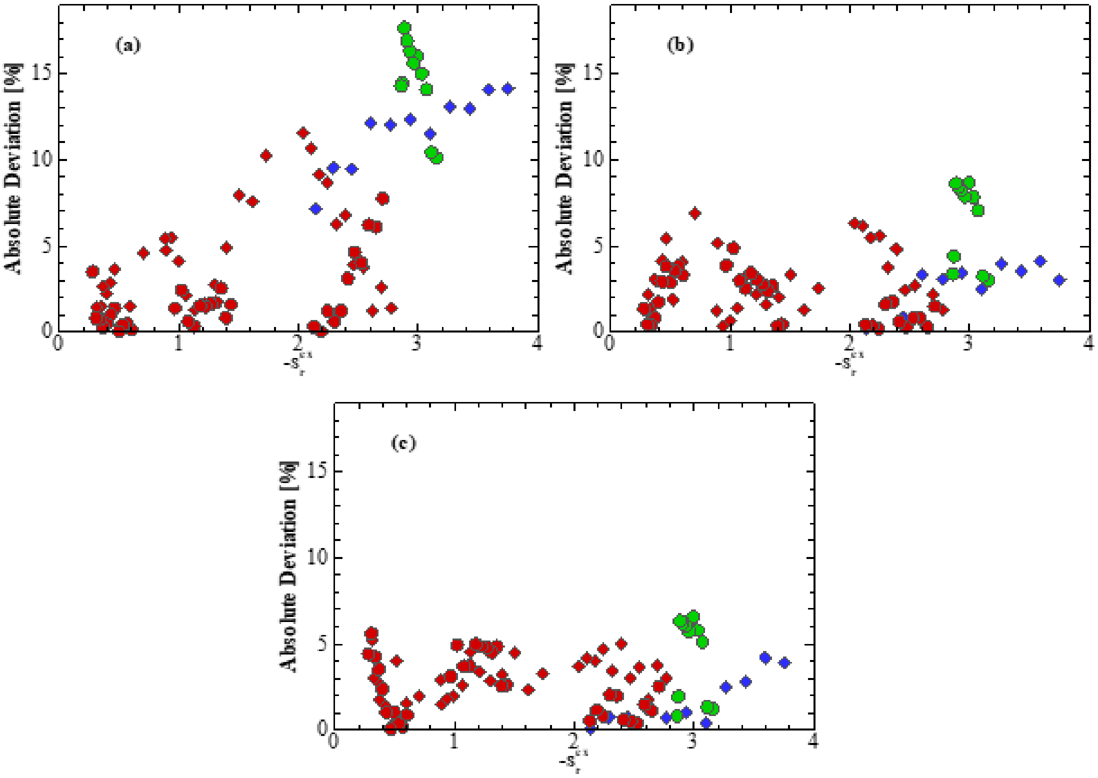

Fig. 7. Dependence of absolute deviation between viscosities computed by the entropy scaling approaches and the MD simulations on the minus reduced excess entropy. (a) Novak's approach. (b) Galliero *et al.*' approach. (c) Bell *et al.* approach. Legend of this figure is the same as that given in Fig. 5.

V. CONCLUSIONS

In this work, we have investigated three excess entropy approaches, that are proposed to circumvent the inconsistency of Rosenfeld approach at the zero-density limit, for the pure Lennard-Jones fluids and their mixtures. One approach, proposed by Novak, uses zero-density viscosity to define dimensionless viscosity, whereas the other two, proposed by Galliero *et al* and Bell *et al*, are based on density and temperature to perform the scaling. An equation of state has been used to compute the excess entropy both pure and mixture fluids. Viscosity data of pure fluid covering a wide range of thermodynamic conditions provided in the literature has been employed. For the mixtures that are composed of species differing in terms of either the molecular energy or the molecular diameter at various thermodynamic conditions containing different component-phase behaviors: gas-gas, liquid-liquid and liquid-gas, we have performed the molecular dynamics simulations to compute their viscosities.

First, we have verified the accuracy of the equation of state to provide the excess entropy by comparing the results with the molecular simulations. It has been shown that the EoS is able to yield excellent results for pure LJ fluids, but slightly deteriorates for the studied mixtures, probably because of the limitation of the van der Waals one fluid approximation.

Then, the three excess entropy approaches have been investigated for the pure LJ fluid. Results have shown that the Novak and Bell *et al.* approaches yield a good convergence at the zero-density limit, whereas it is less the case for the Galliero *et al.* one. However, in the dense states, only the approaches of Galliero *et al.* and Bell *et al.* lead to a good collapse of data.

In addition, we have developed viscosity correlations of pure LJ fluids based on these three approaches. It has been obtained the correlations based on Novak and Galliero *et al.*, Bell *et al.* approaches yield results with the average absolute deviation (AAD) of 8.50%, 4.24% and 4.01% respectively. For more details, we have computed the AAD in the gas-like and the liquid-like regions. The correlations result in a similar AAD about 5.5% in the gas-like region, but different values in the liquid-like, i.e. about 11.10%, 3.44% and 2.51% respectively.

Finally, we have applied these viscosity correlations to the LJ mixtures. It has been found that the two correlations based on Galliero *et al.* and Bell *et al.* approaches provide good results for the mixtures considered, whereas the other one deteriorates for dense mixtures, particularly mixtures containing a liquid component. This finding is consistent with the pure fluid results.

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