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Universal scaling behaviour of surface tension of molecular chains

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We use and extend the universal relationship recently proposed by Galliero [G. Galliero, J. Chem. Phys. **133**, 074705 (2010)], based on a combination of the corresponding-states principle of Guggenheim [E. A. Guggenheim, J. Chem. Phys. **13**, 253 (1945)] and the parachor approach of Macleod [J. Macleod, Trans. Faraday Soc. **19**, 38 (1923)], to predict the vapour-liquid surface tension of fully flexible chainlike Lennard-Jones molecules. In the original study of Galliero, the reduced surface tension of short-chain molecules formed by up to five monomers is expressed as a unique function of the difference between the liquid and vapour coexistence densities. In this work, we extend the applicability of the recipe and demonstrate that it is also valid for predicting the surface tension of two different chainlike molecular models, namely, linear tangent chains that interact through the Lennard-Jones intermolecular potential and fully flexible chains formed by spherical segments interacting through the square-well potential. Computer simulation data for vapour-liquid surface tension of fully flexible and rigid linear Lennard-Jones, and fluid flexible square-well chains is taken from our previous works. Our results indicate that the universal scaling relationship is able to correlate short- and long-chain molecules with different degrees of flexibility and interacting through different intermolecular potentials. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4731660]

I. INTRODUCTION AND THEORETICAL BACKGROUND

Among the thermodynamic and structural properties associated to interfaces, surface tension is undoubtedly the most important quantity. An accurate knowledge of this property is essential to understand the phenomenology associated to practically any interface, including the formation of micelles by amphiphilic surfactant molecules, wetting transitions in systems involving solid substrates, optoelectronic devices, such as liquid crystals, industrial processes such as oil-reservoir engineering applications, etc.

During the last years, an intensive development of reliable and predictive modelling techniques are being developed by different groups.[1,2] See the recent works of Bryk and MacDowell[3] and Jackson and co-workers for a description of the most relevant and novel methodologies introduced recently.[4–6] Although a variety of sophisticated and very accurate methods are being proposed and applied to predict the interfacial properties of complex systems from a molecular perspective, other simple and old methodologies, less theoretical-based but also able to provide an accurate description of the interfacial properties with particular emphasis on the surface tension, are being used during last years.

One of the most popular family of correlations for estimating the vapour-liquid surface tension of real substances is based on the so-called parachor approach, introduced by Macleod in 1923.[7] In this empirical method, the vapour-liquid surface tension is correlated with the difference of the bulk coexistence densities,

$$\gamma = C(\rho_L - \rho_V)^p. \tag{1}$$

Here γ is the vapour-liquid surface tension, ρ_L and ρ_V are the bulk liquid and vapour coexistence densities, respectively, and $p = 4$. C is a constant for each substance and has to be found by fitting to available experimental data, usually in the temperature range from the melting-point to the critical temperature. Despite its empirical base, the former relation is found to fit the experimental data for many substances with remarkable accuracy for the whole range of temperatures. Sugden,[8] following the approach of Macleod, wrote Eq. (1) as

$$\frac{M\gamma^{1/4}}{(\rho_L - \rho_V)} = P, \tag{2}$$

where M is the molecular weight of the substance. Sugden calls P the *parachor*, and the exponent $p = 4$ in Eq. (1) is usually called the parachor exponent. In the original works of Macleod and Sugden, the parachor exponent was equal to 4, although several authors have considered different values, obtained either from theoretical approaches or simply as empirical adjustments, leading to a *fauna* of parachor relationships which are usually written in the general form,[9,10] not only valid for pure systems but also for describing fluid-fluid interfacial tension of mixtures.[11] Despite its simplicity and

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empirical basis, a great research effort has been devoted to improve the accuracy of the parachor methodology by optimising the values of the parachor exponent p and the parachor P, which strongly depends on the parachor exponent value. Although the parachor method originally proposed by Macleod is based on an empirical approach, Fowler[12] showed that Eq. (1), with $p = 4$, can be derived as an explicit function of the intermolecular potential in the case of a stepwise density profile, which is a reasonable assumption far away from the critical point.

Other popular approaches are based on the corresponding-states principle of Guggenheim,[13] probably one of the most useful results of the van der Waals equation of state. The corresponding-states principle of Guggenheim, applicable to different kind of substances, states that many properties including the critical state, the density coexistent phases, and the vapour pressure of the liquid among many others, can be described using universal functions when are expressed in terms of reduced magnitudes with respect to their critical values. In particular, the corresponding-states principle was extended by Guggenheim to deal with surfaces assuming that the excess free energy due to the presence of an interface of surface area $\mathcal{A}$ containing N_s molecules is given by a universal function that only depends on the reduced temperature $T^* = k_B T/\epsilon_0$ and surface area per molecule $\mathcal{A}^* = A/N_s R_0^2$, with ϵ_0 the minimum intermolecular potential energy and R_0 a measure of the intermolecular potential range.[13] Using this extension of the corresponding-states principle, Guggenheim proposed a simple form for an empirical relationship between the surface tension γ and the temperature T. The approach of Guggenheim is able to correlate the vapour-liquid surface tension of a number of substances in excellent agreement with experimental data,[13]

$$\gamma = \gamma_0 \, (1 - T/T_c)^{11/9}\,, \tag{3}$$

where γ_0 represents the "zero-temperature" surface tension. As we will see below, this expression is not in exact agreement with the relation of Macleod.[7] In particular, Guggenheim estimated the parachor exponent as $p = 11/3$, a value lower than 4 obtained by Macleod (and corroborated from a theoretical point of view by Fowler assuming restricted approximations), and that provides a better description of the surface tension dependence on density than this latter approach.

Although both the Macleod and the corresponding-states principle of Guggenheim are clearly empirical approaches, their functional expressions have a theoretical basis founded in the more fundamental and modern renormalization group theory (RGT). According to that, a fluid close to the critical region exhibits large density fluctuations that could be quantified by the correlation length of density fluctuations (correlation length of the distribution function),[14] $\xi \sim |1 - t|^{-\nu}$, where t is the reduced temperature to the critical temperature, $t = T/T_c$, and ν is the well-know correlation length critical exponent. The most accurate experimental values for this critical exponent gives $\nu \approx 0.629\,(3)$ according to recent works.[14,15] RGT indicates that the vapour-liquid surface tension should vanish as $T \to T_c^-$ following the well-known scaling relationship,[14]

$$\gamma \sim |1 - t|^{\mu}, \tag{4}$$

where μ is the critical exponent associated to the vapour-liquid surface tension. μ is related with other critical exponents associated to the correlation length of density fluctuations through the hyperscaling relation proposed by Widom in 1960s,[16] $\mu = (d - 1)\nu$. Here d is the dimensionality of the system, and since we are dealing with three-dimensional systems, $d = 3$ and $\mu = 1.258\,(6)$ when the value of the correlation length critical exponent, $\nu = 0.629\,(3)$, is used. Note that this value is very close to that found by Guggenheim in 1945,[13] $\mu \approx 1.22$, using the empirical corresponding-states correlation previously presented in Eq. (3).

It is possible to write the scaling law given by Eq. (4) in terms of the difference between the vapour and liquid densities. This allows to understand, from a more fundamental point of view, the parachor relation proposed by Macleod in 1923.[7] Probably, the best-known scaling law near the vapour-liquid critical point is given by the difference in densities as a function of the temperature,[14] i.e.,

$$\rho_L - \rho_L \sim |1 - t|^{\beta}, \tag{5}$$

where β is the vapour-liquid critical exponent given by $\beta \approx 0.326(2)$ according to the current experimental estimates.[15] The vapour-liquid surface tension can be expressed in terms of the difference of vapour and liquid densities combining Eqs. (4) and (5), i.e.,

$$\gamma \sim |1 - t|^{\mu} \sim (\rho_L - \rho_V)^{\mu/\beta} \sim (\rho_L - \rho_V)^{(d-1)\nu/\beta}. \tag{6}$$

The comparison between the previous expression and Eq. (1) gives the parachor exponent in terms of the critical exponents obtained from RGT, $p = (d - 1)\nu/\beta = 3.86\,(3)$, which is similar to that proposed by Macleod in 1923 (Ref. 7) ($p = 4$) and with that found by Guggenheim[13] in its seminal work on the corresponding-states principle, $p = 11/3 \approx 3.67$.

Although it is important to understand and justify the functional form and exponent values of the parachor of Macleod from a fundamental point of view, another interest question arises from the ensuing discussion. Is it possible to use the above description to find a universal relationship to describe the behaviour of the vapour-liquid surface tension of several substances? Different studies carried out in the past have showed that the relations previously introduced here are essential, although an additional ingredient must be included. In the seminal work of the corresponding-states principle,[13] Guggenheim argues that not the vapour-liquid surface tension but the surface tension reduced with respect to two critical properties should be a universal function of t, the reduced temperature to the critical temperature ($t = T/T_c$). The particular choice of Guggenheim, widely used in the literature, is given by[13,17]

$$\gamma_r = \gamma\, (k_B T_c)^{-1}\, (\rho_c/M)^{-3/2} = \frac{\gamma}{k_B T_c\, (\rho_c/M)^{3/2}}, \tag{7}$$

where ρ_c and T_c are the critical density and temperature of a substance, and M is the molecular mass of the substance. A slightly different but equivalent reduced surface tension could be obtained by reducing it with respect to critical temperature

T_c and pressure P_c, as suggested recently by Galliero.[17] This author, as well as Garrabos *et al.*,[10] have shown that this universal scaling approach is also able to deal with real fluids, except for systems with specific interactions, such as hydrogen bonding.

Galliero[17] has also proposed a different but useful way of reducing the surface tension using the critical temperature, T_c, and pressure, P_c, as

$$\gamma_r = \gamma^* \, (k_B T_c)^{-1/3} \, P_c^{-3/2} = \frac{\gamma^*}{(k_B T_c)^{1/3} \, P_c^{3/2}}. \qquad (8)$$

Although both recipes provide similar results, as pointed by Galliero,[17] we have only used the approach given by Eq. (7) since we have not calculated the critical pressure of the systems under consideration.

The reduced surface tension recipe given by Eq. (7) is a universal function of t for spherical fluids with different potential parameters, as pointed by several authors.[13,18–20] Unfortunately, it is not able to predict a universal behaviour of the surface tension of Lennard-Jones (LJ) chainlike molecules of different length when the surface tension is represented as a function of t. However, as pointed recently by Galliero,[17] a combination of the scaling proposed originally by Guggenheim and the Macleod's parachor approach, i.e., plotting the surface tension reduced according to Eq. (7) as a function of $(\rho_L - \rho_V)/\rho_c$, accounts for a universal behaviour of short-chain LJ molecules with different length. Here we show that this approach can be also exploited to fit into the same universal master curve the properties of different types of chainlike molecules.

In a previous work, we have determined the interfacial properties of fully flexible (FF) LJ chains with different chainlengths.[21,22] We have studied the effect of the cutoff distance of the intermolecular potential on interfacial properties, with particular emphasis on surface tension. Additionally, we have extended and improved the inhomogeneous long-range corrections proposed by Janeček[23] to deal with molecular systems. In all cases, the test-area (TA) approach of Gloor *et al.*[24] and the wandering interface method (WIM) of MacDowell and Bryk[25] have been used to determined the vapour-liquid surface tension of these systems.

More recently, we have also determined the interfacial properties of a similar but slightly different molecular chain model, namely, the rigid linear (RL) LJ chainlike model.[26] The flexible model has neither bending nor torsional potentials between the monomers in a chain. Contrary, in rigid linear chains the bond length, bond angles, and internal degrees of freedom are fixed. In other words, whereas in the first model the molecules can adopt any bond angle or torsional state, as corresponds to flexible molecules, these degrees of freedom are frozen in the rigid linear chain. In this latter case, we have used the TA methodology[24] and the inhomogeneous long-range corrections following the MacDowell and Blas recipe[22] (based on the Janeček's method[23]) to determine the vapour-liquid surface tension of RL chains formed by 3, 4, and 5 monomers that interact through the LJ intermolecular potential.

We have also determined the interfacial properties of FF square-well (SW) chains with a potential range $\lambda = 1.5\sigma$ and chain lengths equal to 4, 8, 12, and 16 monomers[28] using the TA methodology and the WIM approach. Recently, Chapela and Alejandre[29] have also determined the surface tension of SW chains formed by several chain lengths and intramolecular bond lengths.

The goal of this work is to extend the approach proposed by Galliero[17] to deal with longer FFLJ chains (up to molecules formed by sixteen segments), short RLLJ molecules, and SW chains. The surface tension data corresponding to Lennard-Jones and SW chains are taken from our previous works.[21,22]

II. RESULTS

Following the previous work of Galliero,[17] we have first reduced the vapour-liquid surface tension of FFLJ chains obtained by MacDowell and Blas[22] using the TA and WIM approaches for molecules formed by different chainlengths using the original recipe of Guggenheim given by Eq. (7). In addition to that, we have also reduced the surface tension of RLLJ chainlike molecules of different chain lengths as obtained by Moreno-Ventas Bravo *et al.*[26] We have then represented the reduced surface tension of LJ chainlike molecules (both FF and RL) as a function of the different between liquid and vapour coexistence densities (reduced with respect to the critical density). The critical temperature T_c and density ρ_c have been obtained using the standard technique, i.e., the simulation results for the vapour and liquid coexistence data and the scaling relation for the width of the coexistence curve given by Eq. (5) and the law of rectilinear diameters,

$$\frac{\rho_L + \rho_V}{2} = B + CT, \qquad (9)$$

where B and C are constants. A universal value of $\beta = 0.326$ is assumed here.[14] See the works of Blas, MacDowell, and collaborators[21,22] for further details.

As can be seen in Fig. 1, the reduced surface tension of FFLJ and RLLJ long-chain molecules exhibits a universal behaviour as a function of $(\rho_L - \rho_V)/\rho_c$. We have not included the data corresponding to short-chain molecules presented by Galliero for clarity. Since our data also includes the case of chains formed by four segments, a system that is also studied by Galliero,[17] the surface tension of long-chain molecules exhibits the same universal behaviour previously shown in Ref. 17.

It is interesting to remark that the universal behaviour for the vapour-liquid surface tension is applicable to different molecular models, FFLJ and RLLJ chains, that are indeed radically different. Although both models interact through the same intermolecular potential, their Hamiltonians are radically different, producing differences in their vapour-liquid coexistence curves. Galindo *et al.*[27] have demonstrated several years ago that the vapour-liquid phase diagram of RLLJ chains are slightly thicker than that of FFLJ chains with the same chainlength. As a consequence of this, the vapour-liquid surface tension of RL molecules is higher than the corresponding to the FF model with the same chain length.

Although the results shown in Fig. 1 are very satisfactory since indicate a universal scaling relationship between the

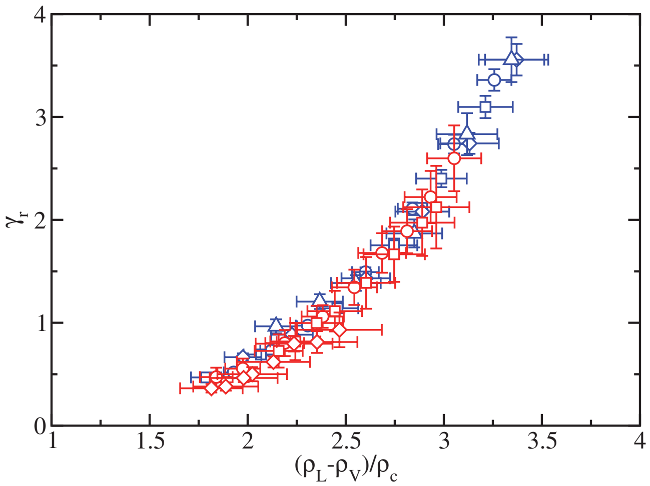

FIG. 1. Reduced vapour-liquid surface tension of LJ chains with different chain lengths as a function of the difference between the vapour and liquid coexistence densities with respect to the critical density. The reduced surface tension is calculated according to Eq. (7). Blue symbols represent the surface tension values of FFLJ chains with 4 (circles), 8 (squares), 12 (diamonds), and 16 (triangles) monomers, and the red symbols are the surface tension values of RLLJ chains with 3 (circles), 4 (squares), and 5 (diamonds) segments.

surface tension of short- and long-chain RLLJ and FFLJ molecules, there is still a remaining question. Is it possible to describe the surface tension, as a universal function of $(\rho_L - \rho_V)/\rho_c$ for a third (different) molecular model? We have used the vapour-liquid surface tension data corresponding to FFSW chains obtained recently by us[28] and represent the reduced surface tension of Guggenheim given by Eq. (7) as a function of the difference between the liquid and vapour densities. As can be seen in Fig. 2, the same scaling relationship is able to predict a universal scaling relation between the surface tension and $(\rho_L - \rho_V)/\rho_c$. Comparison between the results corresponding to LJ and SW systems indicate that the dispersion in the case of SW chains is larger than for LJ chainlike molecules, especially for the longest molecules. This is expected since the interfacial properties of systems interacting through discontinuous intermolecular potentials, particularly the SW, are difficult to obtain with the same accuracy than for systems interacting with continuous potentials (LJ). This is especially true in the case of the surface tension, a property very sensitive to the interface stability, size of the system, and length of the simulation run (number of microstates sampled along the simulation).

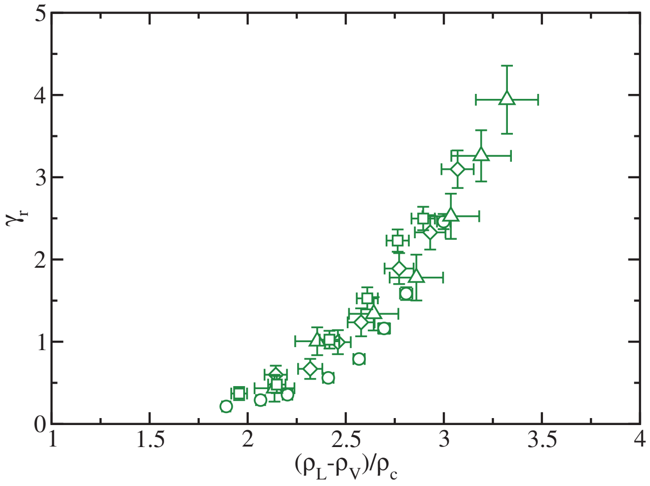

FIG. 2. Reduced vapour-liquid surface tension of FFSW chains of different chain lengths as a function of the difference between the vapour and liquid coexistence densities with respect to the critical density. The reduced surface tension is calculated according to Eq. (7). Green symbols represent the surface tension values of chains with 4 (circles), 8 (squares), 12 (diamonds), and 16 (triangles) monomers.

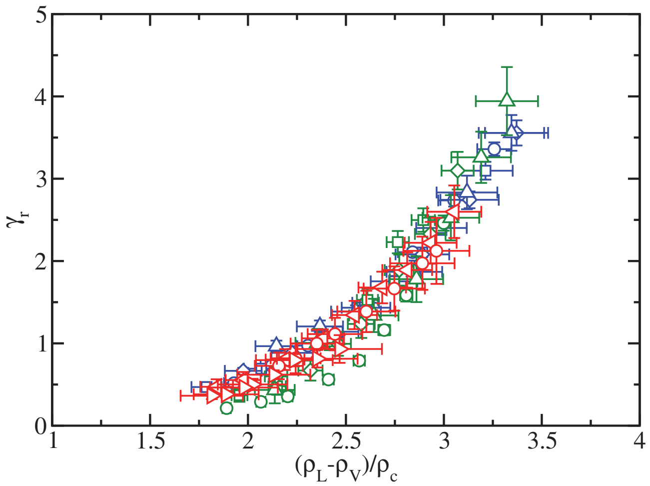

FIG. 3. Reduced vapour-liquid surface tension of FFLJ, RLLJ, and FFSW chains with different chain lengths as a function of the difference between the vapour and liquid coexistence densities with respect to the critical density. The reduced surface tension is calculated according to Eq. (7). Blue symbols represent the surface tension values of FFLJ chains with 4 (circles), 8 (squares), 12 (diamonds), and 16 (triangles) monomers, red symbols are the surface tension values of linear tangent (rigid) Lennard-Jones chains with 3 (circles), 4 (squares), and 5 (diamonds) segments, and the green symbols correspond to the surface tension values of FFSW chains with 4 (circles), 8 (squares), 12 (diamonds), and 16 (triangles) monomers.

We have represented the surface tension data for the three molecular models considered in this work in the same figure to assess the adequacy of the proposed relationship in predicting the same universal surface tension as a function of the difference in liquid and vapour densities. As can be seen in Fig. 3, the surface tension of the three molecular models seems to correlate in a unique and universal curve, although results corresponding to the FFSW systems deviate slightly from the universal behaviour at the region of low density differences. Our results suggest that both models obey approximately the same equation, indicating that the reduced surface tension as a function of the difference in liquid and vapour coexistence densities results from a more fundamental universal scaling behaviour in which intermolecular details are irrelevant at this level, including intermolecular potential (LJ and SW) and molecular architecture (FF and RL).

III. CONCLUSIONS

We have extended the approach proposed recently by Galliero, in which an appropriate reduced vapour-liquid surface tension, originally proposed by Guggenheim, can be represented as a universal function of the difference between the vapour and liquid coexistence densities for several chainlike molecular models. In particular, we have considered long-chain FFLJ chains, RLLJ molecules, and FFSW chains with several chain lengths. Our results indicate that the universal scaling relationship used by Galliero is able to describe, as a unique function, the vapour-liquid surface tension of longer FFLJ chains. In addition to that, we have also applied the same universal scaling relationship to account for the surface tension of linear tangent Lennard-Jones chains and FFSW chains of different chain lengths. All the interfacial tension data seems to correlate in the same universal curve, confirming that the universal relationship is able to describe three different molecular models.

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