Critical temperatures of real fluids from the extended law of corresponding states

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ABSTRACT

The extended law of corresponding states was proposed based on the patterns observed in the second virial coefficient for potential models of variable range. In this work, we propose the use of this law, together with a generalized Lennard-Jones (or approximate nonconformal, ANC) potential, to predict the critical temperatures of real fluids. To this end, we first observe that the temperatures obtained from the scaling law are in agreement with those obtained from molecular simulations of ANC fluids. For short ranges, however, validation is performed by mapping the ANC fluid to the square well fluid because no simulation data have been reported for the former fluid for these ranges. Overall, the analysis shows the validity of the scaling law and the ANC potential for predicting critical temperatures for any range. With this in mind, the well depths of the effective binary potentials of atoms and molecules are rescaled to apply a correction for the three-body nonadditive interaction in order to determine the critical temperatures of fluids.

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I. INTRODUCTION

The second virial coefficient (SVC) has been used mainly to describe the thermodynamic properties of real gases at low densities.¹ This virial coefficient is also relevant for the modeling of intermolecular binary potentials² and the prediction of protein crystallization.³ Indeed, the latter application leads to empirical observations that for spherical particles, as the interaction range varies, the virial coefficient remains constant at the critical temperature. This constant value has been observed to be the same for several potential models and is equal to $-6v_0$, where v_0 is the volume of the particles. When this statement is taken to be valid, the SVC gives rise to the extended law of corresponding states of Noro and Frenkel (NF),⁴ also called the scaling law. This law allows the SVC to be used instead of temperature to represent the phase diagram of fluids. However, it has been applied mainly to describe protein or colloid systems, in which the component particles have a relatively small interaction range in comparison with their sizes.⁵ Because of this, it is desirable to apply the scaling law in the prediction of the critical temperatures

of atomic or molecular fluids, i.e., systems whose components do not have short-range interactions.

The approximate nonconformal (ANC) potential is a generalization of the Lennard-Jones (LJ) potential that includes a softness parameter in its formulation for tuning the interaction range. Its SVC has an exact analytical solution, which is well defined at the Baxter sticky limit,⁶ i.e., when the potential has a vanishing range and infinite depth, its SVC is finite and different from that of the hard sphere (HS) potential. In this limit, the ANC fluid has an associated stickiness parameter, τ , obtained by analogy with the Baxter SVC.⁴ The parameter τ has been interpreted as a measure of the strength of the interaction between particles.7 The same interpretation is associated with the SVC: the dominant interaction between particles is attractive, null, or repulsive when the virial coefficient has a negative, zero, or positive value, respectively. However, the mathematical form of the stickiness parameter based on the ANC potential is different from that obtained for the square well (SW) fluid.⁶ Nevertheless, for any fluid composed of spherical particles of varying range, the asymptotic behavior at very short ranges can be

represented by mapping the SW fluid properties in the sticky limit. In addition, it should be noted that the τ of the SW fluid deviates from the constant behavior dictated by the scaling law. Namely, for ranges of less than the 10% of the effective particle size, a linear dependence of the SW SVC on the potential width can be observed, as reported in Ref. 8. The same behavior is also observed for the modified hard core Yukawa (mHCY) fluid.⁹ Consequently, it can be expected that the same linear behavior will be maintained for other fluids with varying interaction ranges. According to Refs. 8, 10, and 11, it is well known that in the Baxter sticky limit, the SVC is equal to $-4.696v_0$, which is different from the value $-6v_0$ imposed in the scaling law for all ranges. Despite this deviation, the predictions of the critical temperatures produce the correct results for the SW¹² and mHCY⁹ fluids when the interaction range is considered to be less than 15% of the effective particle size. In addition, it is important to know the SVC in the sticky HS limit because, for example, as mentioned by Gazzillo and Giacometti,¹³ this was ignored for the HCY fluid, which led to it being erroneously considered to be equivalent to the Baxter adhesive HS fluid. This is not true since, in that limit, the HCY SVC diverges.¹³ This observation led these authors to propose the mHCY potential.

The main aim of this work is to apply the scaling law to predict the critical temperatures of atomic/molecular fluids. For this purpose, we observe that the critical temperatures obtained from molecular simulations of ANC fluids are in agreement with those predicted by the scaling law.¹⁴ Furthermore, the authors of Ref. 15 presented critical temperatures for ANC fluids; however, in that work, they used an empirical quadratic function instead of the scaling law to fit the molecular simulation data.

It is worth mentioning that the same reference presents a well parameter characterization of the ANC potential in order to reproduce the thermodynamic quantities of real gases. Given the previous evidence, we assume that the scaling law is valid for application to atoms and molecules. This extends the applicability of the scaling law since, as mentioned above, its validity has previously been assumed only when the interaction ranges are less than 15% of the effective particle size. Furthermore, considering data from real fluids allows us to gain insight into molecular complexities such as dispersion forces, polar moments, hydrogen bonds, and quantum behaviors, which are relevant for lighter particles, e.g., He, H₂, and D_2 .

This work is organized as follows. In Sec. II, the theoretical aspects concerning the scaling law are presented. Thereafter, in Sec. III, an analysis of the ANC fluid in the framework of the scaling law is presented; then, the critical temperatures of atomic and molecular fluids are predicted based on the scaling law and compared with experimental data from the literature. Finally, in Sec. IV, conclusions are drawn.

II. BASIC EQUATIONS

In this study, we use the SVC of the ANC potential in the basic equations of the scaling law. The ANC potential u(r) between particles at a distance r depends on three parameters: $u = u(r; r_m, \varepsilon, s)$, where r_m is the distance to the minimum of energy ε and s is the softness of the potential. Its mathematical expression is as follows:

$$u^{*}(z) = \left[\frac{1-a}{\xi(z)-a}\right]^{12} - 2\left[\frac{1-a}{\xi(z)-a}\right]^{6},$$
 (1)

where $u^* = u/\varepsilon$, $z = r/r_m$, a = 0.09574, and $\xi^3(z) = (z^3 - 1)/s + 1$. This potential leads to the following expression for the SVC:⁶

$$B^{*}(T^{*}) = 1 - s + sa^{3} + 3s(1 - a) \left[\frac{1}{3} (1 - a)^{2} F_{3}(T^{*}) + a(1 - a) F_{2}(T^{*}) + a^{2} F_{1}(T^{*}) \right],$$
(2)

where $B^* \equiv B/(2\pi r_m^3/3)$, $T^* \equiv k_B T/\varepsilon$ (k_B being the Boltzmann constant), and

$$F_k(T^*) = \left(\frac{2}{T^*}\right)^{k/12} \Gamma\left(\frac{6-k}{6}\right) e^{1/(2T^*)} D_{k/6} \left[-\left(\frac{2}{T^*}\right)^{1/2}\right],$$

where k = 1, 2, or 3 and the $D_y[x]$ are the parabolic cylinder functions.

We use Eq. (2) in the reduced SVC proposed by Noro and Frenkel (NF) in Ref. 4. This reduced SVC is given by

$$B_{NF}^{*}(T^{*}) \equiv \left[\sigma_{eff}^{*}(T^{*})\right]^{-3} B^{*}(T^{*}), \qquad (3)$$

where the reduced effective size, $\sigma_{eff}^* \equiv \sigma_{eff}/r_m$, is calculated from the relation

$$\sigma_{eff}^{*}(T^{*}) = \int_{0}^{\infty} \left\{ 1 - e^{-u_{rep}^{*}(z)/T^{*}} \right\} dz, \tag{4}$$

where, in turn,

$$u_{rep}^{*}(z) = \begin{cases} u^{*}(z) + 1, & \text{for } z \le 1, \\ 0, & \text{otherwise,} \end{cases}$$

In addition to the effective size, it is also possible to calculate an effective potential range,

$$\delta_{eff}^{*}(T^{*}) = \left\{1 - \frac{B_{NF}^{*}(T^{*}) - 1}{e^{1/T^{*}} - 1}\right\}^{1/3} - 1,$$
(5)



FIG. 1. The ANC potential for different values of s. The interaction range decreases as the s value decreases.

obtained by mapping Eq. (3) to the SW SVC (reduced with the HS SVC, which is expressed as $B_{HS} = 2\pi r_m^3/3$).

In Ref. 4, it is empirically shown that the critical temperatures T_c^* obtained for varying potential ranges are such that the following relation holds:

$$B_{NF}^{*}(T_{c}^{*}) \approx -1.5.$$
 (6)

This observation is valid for several potential models of variable range.⁴ From Eq. (1), we have $u^* = u^*(z; s)$, where *s* is the parameter of nonconformality, i.e., the interaction range of the reduced potential depends on *s* (see Fig. 1). In a similar way, $B_{NF}^* = B_{NF}^*(T^*;s)$, $\sigma_{eff}^* = \sigma_{eff}^*(T^*;s)$, and $\delta_{eff}^* = \delta_{eff}^*(T^*;s)$ also depend on the softness parameter. Finally, to investigate the validity of $B_{NF}^*(T^*) = -1.5$ in the critical state, the following temperaturelike parameter has also been used:⁴

$$\tau(T^*) \equiv \frac{1}{4} \left\{ 1 - B_{NF}^*(T^*) \right\}^{-1}.$$
 (7)

III. PREDICTIONS OF CRITICAL TEMPERATURES

In this section, we present an analysis of the scaling law for any softness of the ANC potential; special emphasis is placed on short ranges (s < 0.2), where no critical temperatures have been reported for the ANC fluid. Subsequently, we present a simple prediction of the critical temperatures of atomic/molecular fluids.

A. The ANC fluid and the scaling law

We show that the critical temperatures of the ANC fluid can be obtained using the scaling law for any range. In Fig. 2, the results of the scaling law are compared with previously reported data from molecular simulations. Figure 2(a) shows the critical temperatures of the ANC,^{14,15,17} LJ,¹⁶ sticky hard sphere (SHS),⁸ and SW⁸ fluids. We can observe that for the ANC fluid, the predictions and molecular simulation data are in agreement. We notice that the qualitative trend of the $T_c^*(s)$ curve is similar to those exhibited by other fluids: SW,^{8,9,18,19} HCY,^{18,19} and mHCY.⁹ On the other hand, Fig. 2(b)



FIG. 2. (a) Critical temperature as a function of the softness parameter and (b) values of τ_c evaluated at $T_c^*(s)$. In both panels, the solid lines correspond to the case in which the NF SVC is equal to -1.5, while the other results are reported values from molecular simulations. The symbols are as follows: blue dots for the ANC fluid,¹⁴ an orange diamond for the LJ fluid,¹⁶ a red star for the SHS fluid,⁸ and empty squares for the SW fluid.⁸ The discrete data in (b) were computed using Eq. (3) and were evaluated at the $T_c^*(s)$ values indicated in panel (a).

presents the results obtained by evaluating τ at $T_c^*(s)$, i.e., τ_c . As we can see, there is a deviation between the values assumed based on the scaling law, $\tau_c = 0.1$, and the τ_c values obtained from ANC computer simulations. Larger differences are systematically found at smaller values of s. An analysis of Fig. 2 leads us to infer that the SW data show convergence behavior similar to that of the ANC fluid as the softness value decreases. The figure shows an equivalence between the range of the SW fluid and the softness of the ANC fluid, which deserves a brief explanation: We find the s and T_c^* values such that $\delta_{eff}^*(T_c^*;s)$, Eq. (5), reproduces a given δ_{SW}^* value (where δ_{SW}^* is the dimensionless SW range, reduced with the HS diameter). Therefore, under the assumption that the equality $\delta_{eff}^*(T_c^*;s) = \delta_{SW}^*$ holds, this equivalence is obtained. However, it is worth noting that the critical temperatures of the equivalent ANC and SW fluids are different, as seen in Table I. This table gives the critical temperatures for various ranges δ_{SW}^{*} as well as their equivalent *s* and $T_c^{*}(s)$ values. This information is used to graph the SW data in Fig. 2, for which τ is computed using the following expression:

$$\tau^{-1}(T_c^*) = 4 \left[(1 + \delta_{SW}^*)^3 - 1 \right] \left[e^{1/T_c^*} - 1 \right].$$
(8)

Figure 2 also includes the results for the LJ and SHS fluids, which are analyzed below. The LJ potential is recovered from the ANC potential when s = 1.13 because in the ANC theory, a fixed value of a = 0.09574 is considered in Eq. (1). For this parameter value, the scaling law predicts $T_c^* = 1.3238$, which is close to the accepted value of 1.3126.¹⁶ This result is included in Fig. 2, as indicated by the orange diamond symbol. The prediction obtained from the scaling law provides a closer approximation than those obtained through more sophisticated theoretical computations based on virial expansion of the equation of states²⁰ ($T_c^* = 1.300$) and the Binder parameter²¹ ($T_c^* = 1.100$). Moreover, Fig. 2 also includes the result for the SHS fluid. For the ANC SVC, the Baxter sticky limit can be expressed as⁶

TABLE I. Mapping of the ANC fluid to the SW fluid. Note that the *s* and T_c^* values of the ANC fluid are such that $\delta_{\text{eff}}^*(T_c^*; s) = \delta_{SW}^*$.

SW ^a		Al	NC
δ^*_{SW}	T_c^*	S	T_c^*
0.005	0.2007	0.0320	0.1954
0.01	0.2328	0.0566	0.2260
0.02	0.2769	0.0984	0.2678
0.03	0.3106	0.1350	0.3002
0.04	0.3398	0.1685	0.3283
0.05	0.3658	0.1998	0.3540
0.10	0.4780	0.3389	0.4659
0.20	0.667	0.5782	0.6714
0.30	0.847	0.7937	0.8868
0.40	1.029	0.9916	1.1245
0.50	1.220	1.1715	1.3906
0.60	1.430	1.3314	1.6894
0.70	1.665	1.4703	2.0242
0.80	1.940	1.5877	2.3982

^aThese data are taken from Ref. 8.

$$\lim_{\substack{T^* \to 0\\ s \neq 0}} B^*(T^*) \approx 1 - \frac{1}{4\tau_{sANC}},\tag{9}$$

where

$$\tau_{sANC}^{-1} \equiv \sqrt{\pi} A \left[\left(1 - \frac{1}{2} \delta(s) \right)^3 - 1 \right] T^{*1/2} e^{1/T^*}$$
(10)

$$A = 2(1-a)/([2^{-1/6}(1-a)+a]^3 - 1),$$

$$\delta(s) = 2[1-\sigma(s)],$$

$$\sigma(s)^3 = s\{[2^{-1/6}(1-a)+a]^3 - 1\} + 1,$$

(11)

where $\sigma(s)$ is the distance at which $u^*(\sigma) = 0$. Equation (10) defines the stickiness parameter τ_{sANC} of the adhesive HS fluid obtained from the ANC fluid. The form of Eq. (9) allows the ANC SVC to remain finite in such a way that the Baxter sticky limit is reached, i.e., τ_{sANC} is a measure of the strength of adhesion between particles.⁷ According to the work of Largo *et al.*,⁸ the accepted value of τ_c is 0.115, while according to the scaling law, τ_c is equal to 0.1. Other theoretical results for the critical stickiness parameter are 0.0976 and 0.1185, as obtained via the Percus-Yevick compressibility⁷ and energy²² routes, respectively, using the Baxter potential; other values include 0.1200, 0.1150, and 0.1070, as obtained from self consistent Ornstein-Zernike approximation using the mHCY,⁹ SW,²³ and HCY²³ potentials, respectively. However, we should recall at this point that the HCY SVC diverges in the limit of the SHS fluid, and therefore, these latter fluids cannot be equivalent.

For the ANC fluid, we must indirectly estimate T_c^* when 0 < s < 0.2 (or $0 < \delta_{eff}^* < 0.05$) because for these short ranges, no corresponding data have been reported in the literature. To this end, we take advantage of the SW data in Table I for $\delta_{SW}^* < 0.05$. Thus, we must prove that the well forms of the ANC and SW potentials are very similar, i.e., their ranges are close to each other. First, the δ parameter defined in Eq. (10) allows us to estimate the well width when the range approaches that of sticky spheres.⁶ Consequently, for short ranges, this width is expected to be equivalent to



FIG. 3. The solid line is the graph of δ_{eff}^* obtained using Eq. (5). The dashed line is the δ well width defined in Eq. (10). The inset shows a close-up view of the plot for s < 0.1.

that of the SW potential,⁸ which has no ambiguities in its definition. Graphs of δ and $\delta_{eff}^*(T_c^*;s)$ are shown in Fig. 3, providing evidence that they have similar values when $s \leq 0.1$ or $\delta_{eff}^* \leq 0.02$ (see the inset figure). Beyond this range, we can observe that the difference between δ and δ_{eff}^* increases as the softness value increases. We note also from Table I that the percentage error between the T_c^* values obtained from the SW molecular simulations and the ANC predictions is less than 1% for $s \leq 0.2$, while it is approximately 5% for s = 0.3. Therefore, the scaling law works well when $s \leq 0.1$. Based on this information, we can say that for short ranges, the ANC and SW fluids are equivalent, having critical temperatures that are very similar to each other.

In summary, the scaling law predictions of critical temperatures obtained using the ANC potential are in agreement with the molecular simulation results for ANC fluids. This is true even though the constraint in Eq. (6) is not exactly fulfilled because τ shows deviations of up to 15% relative to computer simulation results as the interaction range tends toward zero. Consequently, τ is highly prone to deviate from the scaling law as *s* varies, while $T_c^*(s)$ does not.

B. Application to real fluids

In this section, the critical temperatures of real fluids are predicted using the scaling law. For this purpose, we use the effective ANC potentials of atoms and molecules, considering that their parameters include only the effects of the two-body interaction.¹⁵ The characteristic values of the parameters *s* and ε are given in columns 2 and 3, respectively, of Table II.¹⁵

The predictions for the fluids in Table II are obtained by finding the value of T_c^* for the associated softness value. From $\varepsilon T_c^*/k_B$, we obtain predictions of the critical temperatures that overestimate the experimental values.^{24,25} We attribute these inconsistencies to the fact that the ε values, given in the third column, did not consider the three-body or higher order N-body contributions. Moreover, there is sufficient evidence to indicate that the three-body forces are necessary to calculate the critical temperatures of real fluids; for instance, molecular simulations of fluids in dense phases have been done to estimate their critical point. In-depth studies in this regard have been done for argon, which take into account exact binary potentials and effective three-body interactions.^{26–28} These studies showed that the best predictions of the critical temperature are achieved when the three-body interactions are included. In fact, molecular simulations of real liquid are regularly done with binary potentials, on the understanding that they include the contribution of three-body or higher order N-body contributions in an effective way.²

It is important to mention that the effect of including the threebody interaction in a binary potential, either explicitly or effectively, is to decrease the force between molecules, i.e., the three body interaction has an attractive character.^{30,31} This latter point has been proven, even when nonrealistic potentials are used in modeling, e.g., the square well potential of argon is more deep for low density properties³² than for the critical point.³³ In addition, the virial expansion of the equation of state has the ability to predict critical temperature with good accuracy as long as binary and three-body energy contributions are considered.^{34,35}

Considering the aforementioned phenomena, we make a simple correction based on the observation that the three-body interaction effectively decreases the well depth ε by approximately 10%

Fluid ^a	s ^b	(ε/k_B) (K)	<i>T_c</i> (K)	$T_{c,Exp}$ (K)	PE
Ne	1.05830.43586	40.447	44.781	44.4918	0.649
Ar	0.99930.40406	145.906	150.687	150.687	0.000
Kr	0.99930.40406	202.846	209.493	209.48	0.006
Xe	0.99930.40406	280.643	289.839	289.733	0.036
Rn	0.99930.40406	365.000	376.960	377	0.011
N ₂	0.91720.36135	132.744	124.385	126.192	1.432
O ₂	0.94320.37469	160.280	154.903	154.581	0.208
F ₂	0.91080.35809	150.426	139.882	144.41	3.136
Cl ₂	0.78970.29806	507.965	407.974	417	2.165
CH_4	0.90730.35631	210.468	194.899	190.564	2.275
CF ₄	0.65580.23502	325.410	220.611	227.54	3.045
C_2H_6	0.80880.30733	361.088	296.888	305.36	2.774
C_3H_8	$0.7008_{0.25584}$	515.021	370.047	369.9	0.040
$n-C_4H_{10}$	0.61480.21637	671.420	431.173	425.2	1.405
$n-C_5H_{12}$	$0.5503_{0.18767}$	805.645	473.703	469.7	0.852
$n-C_6H_{14}$	0.51190.17097	929.867	517.741	507.5	2.018
<i>n</i> -C ₇ H ₁₆	$0.4693_{0.15281}$	1059.178	553.978	540.1	2.570
$n - C_8 H_{18}$	$0.4388_{0.14006}$	1174.158	586.304	568.7	3.095
C_2F_6	$0.5742_{0.19821}$	487.175	296.098	292.9	1.092
C_3F_8	$0.4943_{0.16342}$	653.650	354.762	345.03	2.821
$n - C_4 F_{10}$	0.43820.13981	808.025	403.106	386.3	4.350
$n - C_5 F_{12}$	0.39460.12199	957.750	445.973	421.8	5.731
$n - C_6 F_{14}$	$0.3584_{0.10758}$	1094.775	480.089	451	6.450
<i>n</i> -C ₇ F ₁₆	0.32940.09634	1230.646	513.246	477	7.600
NH ₃	0.45100.14513	820.728	417.561	405.56	2.959
HCl	$0.5434_{0.18465}$	561.283	326.846	324.7	0.661
e-NO	0.54450.18513	317.318	185.066	180	2.815
CO	0.88760.34635	145.246	131.370	132.86	1.121
CO_2	$0.5994_{0.20945}$	486.120	305.779	304.13	0.542
C_2H_4	0.80880.30733	341.791	281.022	282.35	0.470
SF ₆	0.60680.21277	479.891	304.887	318.723	4.341
H_2O	0.36920.11184	1591.186	710.590	647.14	9.805
D_2O	0.32010.09279	1700.261	697.457	643.847	8.327
H ₂	$1.3192_{0.59187}$	22.183	33.593	32.938	1.988
D ₂	$1.3192_{0.59187}$	23.984	36.320	38.2	4.921
He	$1.1152_{0.46755}$	7.264	8.601	5.1953	65.547

TABLE II. Critical temperatures of real fluids obtained with the	scaling law.
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^aThe values of the ANC parameters and the experimental critical temperatures are taken from Refs. 15 and 24 respectively (note that $T_{c,Exp}$ for D₂ is taken from Ref. 25).

^bThe subscripts are the corresponding δ_{eff} values calculated with Eq. (5).

for the LJ fluid.³⁶ This correction is a well approximation for the ANC fluid modeling the argon (Ar), for which the critical temperature is exactly obtained when the well depth is rescaled by $\Delta \varepsilon / \varepsilon = 0.0898$. Column 4 of Table II presents the predictions obtained using $\varepsilon_c = \varepsilon - \Delta \varepsilon$ for the potential energy in the critical state. Rescaling ε in this way yields excellent predictions for most of the fluids. The deviations of the theoretical results from the experimental data are given in column 6. These deviations are calculated as the absolute percentage errors,

$$PE = 100 \times \left| \frac{T_{c,Exp} - T_c}{T_{c,Exp}} \right|,$$
(12)

where $T_{c,Exp}$ is the experimental critical temperature and $T_c = \varepsilon_c T_c^* / k_B$ is the prediction obtained from the scaling law. From the PE values, it is clear that the greatest errors are observed for (1) atoms and molecules with quantum effects (He, H₂, and D₂), (2) light and heavy water (H₂O and D₂O), and (3) molecules containing fluorine (F₂, SF₆ and perfluoroalkanes). Regarding the molecules with quantum effects, the incorrect predictions can be attributed to the inversion of the potentials. The parameters in columns 2 and 3 are obtained by fitting a classical theory to experimental data for gases with a significant quantum contribution. Consequently, although it is possible to obtain a curve that can well represent the SVC experimental data, the resulting parameters are meaningless.

For light and heavy water, it is interesting to note that good predictions can be obtained by simply multiplying by 0.82893, which is equivalent to decreasing the well depth ε for water by approximately 18%. This reduction is consistent with the estimate obtained in Ref. 37 for the contribution of the many-body terms in liquid water; in that study, it was found that two-body interactions contribute 75%-80% of the total interaction energy, while three-body nonadditive interactions contribute 15%-20%. Notably, the threebody contribution is greater than 10% because water molecules have a high polarization.³⁸ Taking this argument to be valid, an analogous observation can be made for other molecules with a high degree of polarization, for example, molecules containing fluorine. On the other hand, for *n*-alkanes, an increase in the error is observed when the number of carbons in the molecules increases. Therefore, we can attribute the increase in PE for perfluoroalkanes to the longer chain length as well as to the saturation of fluorines around an atom; for example, the discrepancies in the predictions are (1) greater for CF₄ than for C₂F₆ and (2) greater for SF₆ than for CF₄. Regarding the PE value, roughly, we consider a prediction to be good when this quantity is close to or less than 3%. Given this criterion, we can say that good estimates of T_c , using the scaling law, are achieved for the following fluids containing fluorine: F2, CF4, C2F6, and C3F8. Similarly, we can also include the *n*-alkanes in the classification of fluids for which good predictions are obtained. In summary, 26 of the predictions are in agreement with the experimental critical temperatures, while the remaining 10 predictions have PE values greater than 3%. However, we attribute the deviations of these latter fluids to the presence of quantum effects or the fact that the effective threebody nonadditive interaction shows a significant deviation from the assumed contribution of 10%. Namely, such a deviation may indicate the effective magnitude of the three-body energy, which could be determined by the $\Delta \varepsilon / \varepsilon$ value that leads to a correct predict of T_c using the scaling law.

IV. CONCLUSIONS

This work aims to encourage the use of the scaling law as an alternative means of predicting the critical temperatures of atomic or molecular fluids. For this purpose, a generalized LJ potential is used in the NF SVC; see Eq. (3). We validate the predictions against the results obtained from molecular simulations of ANC fluids. Similarly, the results for the SW fluid are used to validate the scaling law for short-range interactions with respect to the equivalent ANC fluid. It is worth mentioning that the relation $B_{NF}^{*}(T_c^*) \approx -1.5$ does not hold in general; for example, for the adhesive HS fluid, we have $B_{NF}^{*}(T_c^*) \approx -1.207$. Despite these deviations, which are mainly observed in a range of less than 10%, very good predictions of critical temperature can be obtained via the scaling law.

With a 10% rescaling of the well depth of the binary interaction, the scaling law can be used to predict the critical temperatures of real fluids. We have analyzed 36 fluids; for 26 of them, the predictions are in agreement with the experimental critical temperatures, meaning that the percentage error is less than 3%. The remaining 10 fluids show deviations greater than 3% because of either (1) the application of a classical theory to fluids with significant quantum effects or (2) the molecular polarity, which is highly sensitive to the presence of a third body. Even so, for these latter fluids, the corrections needed to predict their critical temperatures may indicate the effective contribution of the three-body interaction to the potential energy. If this is so, the extended law of corresponding states could be used as an indirect method of calculating such three-body contributions.

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REFERENCES

¹J. H. Dymond, K. N. Marsh, R. C. Wilhoit, and K. C. Wong, *Virial Coefficients of Pure Gases*, edited by M. Frenkel and K. N. Marsh (Springer, Berlin, Germany, 2003), Vols. 21A and 21B.

²M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 1989).

³G. A. Vliegenthart and H. N. W. Lekkerkerker, J. Chem. Phys. 112, 5364 (2000).

- ⁴M. G. Noro and D. Frenkel, J. Chem. Phys. 113, 2941 (2000).
- ⁵R. P. Sear, J. Chem. Phys. **111**, 4800 (1999).

⁶A. González-Calderón and A. Rocha-Ichante, J. Chem. Phys. 142, 034305 (2015).

⁷R. J. Baxter, J. Chem. Phys. **49**, 2770 (1968).

⁸J. Largo, M. A. Miller, and F. Sciortino, J. Chem. Phys. 128, 134513 (2008).

⁹S.-P. Elisabeth, N. E. Valadez-Pérez, A. L. Benavides, and R. Castañeda-Priego, J. Chem. Phys. **139**, 184902 (2013).

¹⁰M. A. Miller and D. Frenkel, Phys. Rev. Lett. **90**, 135702 (2003).

¹¹M. A. Miller and D. Frenkel, J. Chem. Phys. **121**, 535 (2004).

¹²D. Frenkel, <u>Science</u> **314**, 768 (2006).

¹³D. Gazzillo and A. Giacometti, Mol. Phys. **101**, 2171 (2003).

¹⁴P. Orea, A. Romero-Martínez, E. Basurto, C. A. Vargas, and G. Odriozola, J. Chem. Phys. **143**, 024504 (2015).

- ¹⁵F. Del Río, I. A. Mclure, J. Chávez, J. E. Ramos, and E. Ávalos, Mol. Phys. 104, 3757 (2006).
- ¹⁶J. Peréz-Pellitero, P. Ungerer, G. Orkoulas, and A. D. Mackie, J. Chem. Phys. 125, 054515 (2006).
- ¹⁷F. del Río, O. Guzmán, J. E. Ramos, and B. Ibarra-Tandi, Fluid Phase Equilib. 259, 9 (2007).
- ¹⁸L. Acedo and A. Santos, J. Chem. Phys. 115, 2805 (2001).
- ¹⁹P. Orea, C. Tapia-Medina, D. Pini, and A. Reiner, J. Chem. Phys. **132**, 114108 (2010).
- ²⁰L. G. MacDowell, C. Menduiña, C. Vega, and E. de Miguel, J. Chem. Phys. **119**, 11367 (2003).
- ²¹ H. Watanabe, N. Ito, and C.-K. Hu, J. Chem. Phys. 136, 204102 (2012).
- ²²R. O. Watts, D. Henderson, and R. J. Baxter, Adv. Chem. Phys. 21, 421 (1971).
- ²³D. Pini, A. Parola, J. Colombo, and L. Reatto, Mol. Phys. 109, 1343 (2011).
- ²⁴W. M. Haynes, CRC Handbook of Chemistry and Physics, 95th ed. (CRC Press; Taylor & Francis Group, Boca Raton, Florida, 2014).
- ²⁵H. J. Hoge and J. W. Lassiter, J. Res. Natl. Bur. Stand. 47, 75 (1951).
- ²⁶R. J. Sadus, Fluid Phase Equilib. 144, 351 (1998).
- ²⁷J. A. Anta, E. Lomba, and M. Lombardero, Phys. Rev. E 55, 2707 (1997).
- ²⁸P. S. Vogt, R. Liapine, B. Kirchner, A. J. Dyson, H. Huber, G. Marcelli, and R. J. Sadus, Phys. Chem. Chem. Phys. 3, 1297 (2001).
- ²⁹ J. Vrabec, J. Stoll, and H. Hasse, J. Phys. Chem. B 105, 12126 (2001).
- ³⁰G. Marcelli and R. J. Sadus, J. Chem. Phys. **112**, 6382 (2000).
- ³¹E. K. Goharshadi and M. Abbaspour, J. Chem. Theory Comput. 2, 920 (2006).

³² A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. 41, 429 (1964).
³³ J. A. White and S. Zhang, Int. J. Thermophys. 19, 1019 (1998).
³⁴ L. G. MacDowell, C. Menduiña, C. Vega, and E. de Miguel, Phys. Chem. Chem. Phys. 5, 2851 (2003).

- ³⁵O. Guzmán, F. del Río, and J. Eloy Ramos, Mol. Phys. 109, 955 (2011).
 ³⁶G. Marcelli and R. J. Sadus, J. Chem. Phys. 111, 1533 (1999).
 ³⁷J. Cui, H. Liu, and K. D. Jordan, J. Phys. Chem. B 110, 18872 (2006).
 ³⁸J. Li, Z. Zhou, and R. J. Sadus, J. Chem. Phys. 127, 154509 (2007).