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“Propiedades interfaciales de fluidos no conformales”

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Presenta:

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Introducción

Uno de los principales problemas en la teoría de fluidos ha sido tratar de reproducir adecuadamente propiedades termodinámicas a partir de información microscópica. La mecánica estadística clásica utiliza funciones potenciales que representan a las interacciones entre las moléculas de algún sistema dado. La idea básica de utilizar funciones de potencial es reproducir de manera efectiva y con cierto grado de aproximación las propiedades termofísicas que sean de interés. Una de las características que presentan dichos modelos de interacción es la flexibilidad que tienen debido a sus parámetros moleculares los cuales pueden tener o no significado físico y que están relacionados en gran medida con la sustancia que se estudia. La mayoría de estos modelos de interacción permiten calcular diferentes propiedades termofísicas para un conjunto relativamente grande de sustancias sin cambiar la forma analítica del modelo mismo.

La desventaja que pueden presentar dichas interacciones es que el valor numérico asociado a los parámetros moleculares de alguna sustancia dada, no necesariamente reproducirá las diferentes propiedades termodinámicas de la misma, es decir, en general el valor asociado a dichos parámetros dependerá de la propiedad termofísica que se quiera calcular. La forma analítica del potencial también juega un papel muy importante al momento de determinar dichas propiedades. Actualmente existe una gran variedad de información acerca de dichas funciones de potencial, algunas de las cuales son construidas a partir de cálculos de mecánica cuántica. Estos modelos son complicados y dependen en general de muchos parámetros[1],[2],[3], otros son realmente simples y dependen de pocos parámetros.

Recientemente se ha propuesto en esta dirección una teoría para líquidos denominada ANC (Approximate Non Conformal Theory), que introduce una familia de potenciales tri-paramétricos U_{ANC} capaz de reproducir dentro del error experimental las propiedades de más de sesenta sustancias reales en la fase gaseosa, específicamente el segundo y tercer coeficiente virial de sustancias puras y algunas de sus mezclas [4],[5],[6],[7],[8].

También han mostrado ser adecuados cuando se usaron para predecir propiedades críticas e interfaciales de sustancias simples reales, tales como el argón, metano, propano y hexano [9]. La familia de potenciales U_{ANC} depende del diámetro molecular δ , la energía ϵ la cual representa la profundidad del pozo de potencial, además de un parámetro S , llamado suavidad, el cual toma en cuenta la forma del potencial en sus partes atractiva y repulsiva. En este anteproyecto de investigación proponemos explorar el poder predictivo de la teoría ANC cuando el parámetro de suavidad es considerado independiente para la parte repulsiva y atractiva en las interacciones moleculares. El trabajo de investigación será enfocado en el cálculo de propiedades interfaciales de moléculas reales y moléculas modelo calculados a partir de otras funciones de potencial. Mostrando de este modo que las interacciones ANC son interacciones generales capaces de reproducir propiedades termofísicas de moléculas reales y de otros modelos.

Tema de investigación

En una versión extendida de la teoría ANC el parámetro de suavidad es considerado de manera independiente en la parte repulsiva y atractiva de la interacción, de manera que en esta versión de la teoría se tienen cuatro parámetros: el tamaño molecular δ , la profundidad del pozo de potencial ϵ , la suavidad atractiva S_a y la suavidad repulsiva S_r .

En este proyecto de investigación proponemos el uso de las interacciones ANC en su versión extendida para predecir propiedades interfaciales tales como las curvas de coexistencia y puntos críticos de moléculas reales y moléculas modelo calculada a partir de otros potenciales, para ello haremos uso de simulaciones numéricas moleculares.

Objetivos

Predecir curvas de coexistencia densidad vs. temperatura y puntos críticos para moléculas reales considerando que las interacciones moleculares son gobernadas por los potenciales ANC en su versión extendida.

Mostrar que las interacciones ANC en su versión extendida son interacciones generales capaces de reproducir propiedades interfaciales calculadas a partir de otros modelos de potencial.

Marco teórico

Recientemente se ha propuesto una nueva teoría llamada ANC [5],[7], [10] (Approximate Non Conformal Theory) la cual introduce una familia de potenciales no conformales tri-paramétricos que dependen de los parámetros ϵ para la energía (profundidad del mínimo de potencial), δ para la distancia, y un parámetro adicional que toma en cuenta la forma o conformalidad del potencial denominado suavidad S , la expresión analítica de esta familia de potenciales es representada por la función:

$$U_{ANC}(z, s) = \epsilon \left\{ \left[\frac{1-a}{\xi(z, s) - a} \right]^{12} - 2 \left[\frac{1-a}{\xi(z, s) - a} \right]^6 \right\}$$

Donde $z = r/\delta$, $a = 0.09574$ y $\xi^3(z, S) = 1 - 1/S + z^3/S$. Los potenciales $U_{ANC}(z, S)$ tienen un valor mínimo $-\epsilon$ en $z = 1$; el parámetro a fue elegido de manera que cuando $S = 1$, $\zeta = z$, entonces el potencial ANC se reduce al conocido potencial de Kihara para el argón el cual es considerado como referencia en esta teoría.

La suavidad como se mencionó toma en cuenta la conformalidad o no conformalidad, según sea el caso, entre diferentes potenciales: dos potenciales de interacción U y U' son conformales si tienen la misma suavidad $S = S'$ y son no conformales cuando $S \neq S'$. En una versión más refinada la función de potencial ANC es usada con diferentes valores de S para la parte atractiva ($z > 1$) y para la parte repulsiva ($z < 1$), a esta versión de la teoría se le ha llamado aproximación-2s (ANC-2s).

El poder utilizar la versión ANC-2s de la teoría se vuelve atractivo pues nos permite variar la parte repulsiva del modelo sin modificar el alcance del mismo y viceversa. Con lo cual tenemos un grado más de libertad en el modelo. Es importante resaltar que el parámetro de suavidad, ahora para la parte repulsiva(S_r) y atractiva(S_a), sigue teniendo significado físico: dureza / suavidad de las moléculas y el alcance intermolecular respectivamente.

Una de las bondades de tener dos parámetros de forma es que podemos con mayor facilidad hacer conformal a las interacciones ANC con otros modelos de potencial que existen en la literatura, lo cual lo vuelve un modelo general.

Marco metodológico

Las fases de la materia, contienen gran variedad de propiedades interesantes lo cual es resultado de las fuerzas intermoleculares que se desarrollan entre las moléculas del sistema. Entender y predecir estas propiedades colectivas a partir de las interacciones moleculares ha sido uno de los mayores retos que enfrenta la mecánica estadística. Es a través de las simulaciones numéricas que se ha logrado un avance significativo en esta dirección[11]. Ejemplos claros de estas simulaciones lo constituyen los métodos de Dinámica Molecular y Monte Carlo.

En este trabajo de investigación utilizaremos el método de Dinámica Molecular para calcular las propiedades de interés. El método mismo se refiere al estudio de las propiedades de la materia que requieren integración directa de las ecuaciones de movimiento para un sistema de N -moléculas, para sistemas que están en equilibrio y fuera de él.

Algo importante que hay que resaltar es que las fuerzas de este sistema cambian continuamente a medida que las moléculas se mueven, es entonces que se vuelve necesario integrar las ecuaciones de movimiento de forma aproximada mediante un algoritmo numérico. De manera general un algoritmo de integración hace lo siguiente: dadas las posiciones y velocidades moleculares y alguna otra información dinámica en el tiempo t , obtiene las posiciones y velocidades a tiempo $t+dt$ con un grado suficiente de aproximación. La elección del paso de integración depende del algoritmo en particular, pero siempre será mucho menor que el tiempo típico que le toma a la molécula viajar su propia longitud.

Para poder emplear la metodología de Dinámica Molecular, es necesario que conozcamos las posiciones y velocidades (o momentos) de todas las moléculas de nuestro sistema. Para ello es necesario calcular las fuerzas existentes sobre cada molécula de nuestro sistema, a partir de la función de potencial U . Por lo tanto también es necesario conocer a la función de potencial U antes de comenzar con este método de simulación.

El procedimiento durante la simulación consiste en colocar varias réplicas de la caja cúbica en las tres direcciones cartesianas de tal forma que se tiene una red periódica infinita, durante la simulación cuando una molécula se mueve en la caja original también lo hacen sus imágenes en cada una de las cajas vecinas. Cuando una molécula sale de la caja central, una de sus imágenes entrará por la cara opuesta a donde sale la molécula. De este modo se eliminan el efecto de las paredes de la caja cúbica y no habrá moléculas en la superficie y por tanto la densidad de moléculas en la caja central se mantiene constante.

Es importante también, al momento de resolver las ecuaciones de movimiento del sistema, conocer las fuerzas que actúan sobre las moléculas y las condiciones iniciales a partir de las cuales comienza el algoritmo. Después de fijar adecuadamente nuestras condiciones iniciales, es necesario que corramos la simulación lo suficiente como para asegurarnos que el sistema se encuentra en un estado de equilibrio. Debemos tomar en cuenta que el tiempo para que un sistema relaje al equilibrio es muy particular y depende de las características del sistema.

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Separating the effects of repulsive and attractive forces on the phase diagram, interfacial and critical properties of simple fluids

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Abstract

Molecular simulations in the canonical and isothermal–isobaric ensembles were performed to study the effect of varying the shape of the intermolecular potential on the phase diagram, critical and interfacial properties of model fluids. The molecular interactions were modeled by the Approximate Non-Conformal Theory (ANC) potentials. Unlike the Lennard-Jones or Morse potentials, the ANC interactions incorporate parameters (called softnesses) that modulate the steepness of the potential in their repulsive and attractive parts independently. This feature allowed us to separate unambiguously the role of each region of the potential on setting the thermophysical properties.

In particular, we found positive linear correlation between all critical coordinates and the attractive and repulsive softness, except for the critical density and the attractive softness which are negatively correlated. Moreover, we found that the physical properties related to phase coexistence (such as span of the liquid phase between the critical and triple points, variations in the P - T vaporization curve, interface width and surface tension) are more sensitive to changes in the attractive softness than to the repulsive one. Understanding the different roles of attractive and repulsive forces on phase coexistence may contribute to developing more accurate models of liquids and their mixtures.

Keywords: Molecular Dynamics, interfacial properties, effective potentials, liquid-vapour interface, surface tension, molecular thermodynamics.

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1. INTRODUCTION

One of the main problems in the theory of liquids has been trying to understand, reproduce and predict adequately thermodynamic properties from microscopic information. Classical statistical mechanics often uses empirical potential functions, which represent interactions among molecules in particular systems, in order to reproduce with some degree of approximation the thermophysical properties that are of interest. These models are quite versatile but their effective parameters may or may not have physical interpretation.

There are numerous such models, among the best known we can mention the square well, the Lennard-Jones n -6 potentials with spherical symmetry, [1, 2] as well as the Gay-Berne potential which depends on the molecular orientations [3]. Some other potentials are specifically built to a particular system: for instance, the Slaman-Aziz potential was built for simple molecules such as argon and krypton [4]; this model is among the best molecular interaction to reproduce thermodynamic properties of these substances. Another kind of models are developed from quantum mechanical calculations, which can be very accurate but analytically complicated; when written in functional form, they usually depend on many molecular parameters, some of them lack a manifest molecular interpretation [4-6].

In this way, it is desirable to have interaction models that are analytically simple and that depend on just a few physically-sensible molecular parameters, while still allow one to calculate different thermophysical properties of simple and complex systems. Other important features to consider for these models are a wide thermodynamic range of validity and its generality. Sometimes this last quality allows one to reproduce results which are obtainable also from other models.

A key idea, separating the repulsive and attractive effects in the molecular interaction and studying their roles perturbatively, can be traced back to van der Waals' Ph.D. thesis formulated in 1873 [14]: large, short-range repulsive forces reduce the volume available to molecules, determining the structure of the liquid and its configurational entropy. Weak long-range attractive forces give rise to an energetic effect that reduces the pressure and internal energy compared to those of a hard-sphere fluid at the same temperature and density [15].

In this context, it is of great interest to quantify the separate role of these effects on different thermophysical properties of liquids such as the liquid-vapour coexistence curve, the

vaporization curve, the transition to solid, the superficial tension and the behaviour of critical properties. Researchers have gauged the role of repulsion and attraction by varying the “repulsion” exponent 12 in the well known Lennard–Jones 12-6 interactions and observing the effects on the liquid–vapour equilibrium [16–19], as well as in critical [17] and transport properties [20, 21]. Similarly, Sadus studied systematically the repulsive and attractive effects on the liquid-solid transition of Lennard–Jones fluids of the $n - 6$ type [22] and also estimated the triple points of such systems. However, in these works the effects of the repulsive and attractive forces are not considered independently, since modifying the exponent n in the Lennard–Jones potentials changes both types of forces simultaneously.

Similarly, for Morse potentials, Valencia *et al.* found that the surface tension curve for large repulsive forces is lowered with respect to that of less repulsive ones [23], while Ibarra-Tandi *et al.* quantified the repulsive-force intensity effect on physical adsorption phenomena for a binary mixture of simple fluids [24]. While using the Morse potential in simulations have the benefit of a very short cut-off distance, the minima of the attractive well for Morse interaction does not remain fixed as the repulsive intensity is varied and, instead, the curves cross each other. In other words, attraction and repulsion are not fully decoupled in such studies.

In this direction, the Approximate Non Conformal (ANC) Theory for fluids introduced a family of intermolecular potentials that depend on molecular size and molecular energy, plus new parameters called softnesses, which modulate the shape of the potential in their repulsive and attractive regions independently [7, 8]. In particular, ANC potentials have a fixed minimum and do not cross between them for all values of the repulsive and softness parameters, s_R and s_A . With the two-softness version of ANC potentials used in this research, we have analyzed independently the effects of the repulsive and attractive parts of the interaction by means of computer simulation.

In this work, we have found that there is a positive linear correlation between the critical temperature, pressure and density with both the attractive and repulsive softness, with the exception of the critical density and the attractive softness which are negatively correlated. We also found that the span of the liquid phase between the critical and triple points, variations in the P - T vaporization curve, interface width and surface tension are more sensitive to changes in the attractive softness than to the repulsive one. These findings allow us to discriminate better among the effects of attractive and repulsive forces on phase

coexistence and, therefore, contribute to improving molecular models of liquids.

2. APPROXIMATE NON-CONFORMAL POTENTIALS

The ANC potentials used in this work depend on four parameters, the position of the minimum of the potential, δ , the minimum's depth, ε , and two non-dimensional quantities, called the repulsive and attractive softness (s_R and s_A), that control the shape of the potential in the respective repulsive and attractive regions:

$$u_{ANC}(r; \delta, \varepsilon, s_R, s_A) = \begin{cases} \varepsilon u_{ANC}^*(r/\delta, s_R) & r \leq \delta, \\ \varepsilon u_{ANC}^*(r/\delta, s_A) & r > \delta, \end{cases} \quad (1)$$

where u_{ANC}^* is a modified Kihara potential,

$$u_{ANC}^*(z, s) = \left\{ \left[\frac{1-a}{(1+(z^3-1)/s)^{1/3}-a} \right]^{12} - 2 \left[\frac{1-a}{(1+(z^3-1)/s)^{1/3}-a} \right]^6 \right\} \quad (2)$$

with $a = 0.09574$ chosen to ensure that when $s = 1$ the ANC potential is conformal with that of argon.

Figure 1 shows how the repulsive and attractive regions of the ANC potentials change independently as a function of the corresponding softness parameters. On the one hand, when one keeps the attractive softness fixed, the repulsive barrier becomes steeper as the repulsive softness s_R is decreased. Alternatively, defining the molecular diameter σ as the root of the potential, one can see that σ increases as s_R is decreased. In the limit $s_R \rightarrow 0$, the repulsive part of the interaction would become a hard-sphere potential. On the other hand, as one keeps the repulsive softness constant, the range of attractive forces increases as the attractive softness s_A is increased.

It is precisely because of this independent control of the repulsive and attractive forces that the two-softness version of the ANC potentials becomes relevant to allow a systematic study of the repulsive and attractive effects of the intermolecular interaction. (For a brief introduction to the ANC theory that supports the use of ANC potentials, see the Appendix.)

3. SIMULATION METHODOLOGY

Molecular dynamics (MD) in the canonical ensemble was used to obtain the liquid-vapour coexistence curve from the slab method of Chapela et al. [25]. For the transition to the

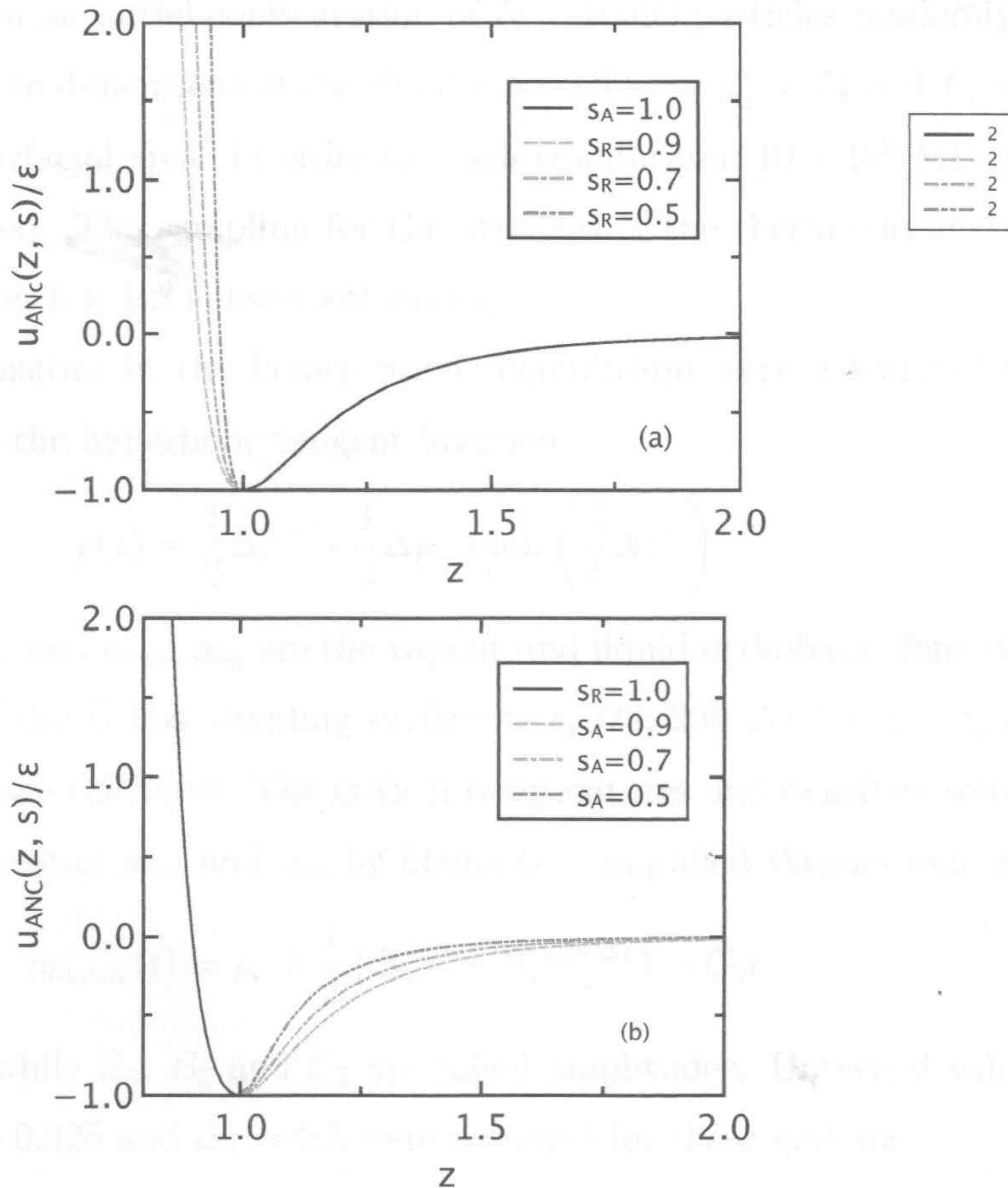


FIG. 1. Approximate Non-Conformal (ANC) potentials with varying softness (a) s_R in the repulsive part and (b) s_A in the attractive part of the potential. Small values of the softness parameters correspond to steeper potentials: small s_R yields harder repulsive cores, while smaller s_R result in narrower attractive wells.

solid, MD in the isobaric-isothermal ensemble was used. In what follows, all starred variables denote reduced physical quantities measured in a system where δ is the unit length and ϵ is the unit of energy.

Equations of translational motion were integrated using the velocity-Verlet algorithm and periodic boundary conditions [26], [27]. The Nose-Hoover thermostat [26] was used with a time step $\Delta t^* = 0.0015$. To speed up the code, the neighbor-list method was implemented in a parallel MD program based in the MPI (Message Passing Interface) protocol.

The average density used in the slab simulations was $\rho^* = 0.30$. All results presented

here were obtained from an initial configuration of $N = 10000$ particles randomly placed in a parallelepiped cell. The dimensions of the simulation cell were $L_z^* = 74$ and $L_x^* = L_y^* = 15$, and $L_x^* \times L_y^*$ is the interfacial area. In order to reach equilibrium, 10×10^6 MD cycles were performed and discarded. The sampling for the averages of the thermophysical properties of interest was done over 8×10^6 subsequent cycles.

The coexistence densities in the liquid-vapour equilibrium were calculated fitting the density profiles $\rho(z)$ to the hyperbolic tangent function

$$\rho(z) = \frac{1}{2}\Delta\rho^+ - \frac{1}{2}\Delta\rho^- \tanh\left(\frac{2}{\delta}\Delta z^-\right) \quad (3)$$

where $\Delta\rho^\pm = \rho_{liq} \pm \rho_{vap}$ and ρ_{vap} , ρ_{liq} are the vapour and liquid orthobaric densities, respectively. The position of the Gibbs' dividing surface is z_0 [28, 29], $\Delta z^- = z - z_0$ and $\delta/2$ is a measure of the interface thickness. The critical temperatures and densities were obtained from the orthobaric densities ρ_{vap} and ρ_{liq} by fitting the simplified Wegner expansion [30]

$$\rho_{liq,vap}(t) = \rho_c \pm \frac{1}{2} (B_0 t^\beta + B_1 t^{\beta+\Delta_1}) + C_2 t \quad (4)$$

where $t = 1 - T^*/T_c^*$ while B_0 , B_1 and C_2 are called amplitudes. Universal values for the critical exponents, $\beta = 0.325$ and $\Delta_1 = 0.5$ were assumed for these systems.

The surface tension was estimated from the diagonal components of the pressure tensor $P_{\alpha\alpha}$ through the mechanical definition

$$\gamma = \frac{L_z^*}{2} \left[\langle P_{zz} \rangle - \frac{1}{2} \langle P_{xx} + P_{yy} \rangle \right] \quad (5)$$

where L_z^* is the box-size perpendicular to the interfacial area $A = L_x^* \times L_y^*$. The factor $1/2$ takes into account the presence of two interfaces in the slab. The pressure-tensor components were calculated from

$$P_{\alpha\beta}V = \sum_{i=1}^N m_i v_{i\alpha} v_{i\beta} + \sum_{i=1}^{N-1} \sum_{j>1}^N (\mathbf{r}_{ij})_\alpha (\mathbf{F}_{ij})_\beta \quad (6)$$

where m_i and \mathbf{r}_i are the mass and position of the i -th particle.

[26], [27].

Finally, the critical pressure P_c was obtained by extrapolating the Clausius-Clapeyron relation,

$$\log P = \frac{C_1}{T} + C_2,$$

to the critical temperature T_c , where C_1 and C_2 were found by fitting the coexistence pressure and temperature data from the simulations.

4. RESULTS

4.1 Liquid-vapour and liquid-solid coexistence

Figure 2a shows the effect of varying the repulsive softness on the liquid-vapor (LV) orthobaric, $0.3 < s_R < 0.9$, keeping the attractive softness fixed ($s_A = 1.0$). As the repulsive softness is increased, the critical point is displaced towards higher temperatures and larger densities. Also, for a fixed temperature, the saturated vapor and liquid densities decrease and increase, respectively, as s_R is incremented, but the change in the liquid branch is larger than for the vapor branch. This is consistent with the positive slope of the locus of critical points observed in Fig. 2a.

Fig. 2b shows the results of NPT simulations used to locate the liquid-solid (LS) transition. The inset in that Figure shows extrapolations of both the LV and LS liquid branches of the coexistence curves, for $s_R = 0.3$ and 0.9 ; this allows us to estimate the location of the triple point. In order to exhibit non-conformality, these curves are rescaled with the corresponding critical density and temperature, allowing us to remark that among the two branches of the LV coexistence it is the one for the liquid that changes more noticeably.

For the critical temperature it is well known that, as the repulsive effects increase, or the attractive ones decrease, the liquid-vapour coexistence tends to disappear: in the limit when s_R and s_A tend to zero the ANC interactions are conformal with the hard sphere potential, which is known to lack a liquid-vapour coexistence. Here, as s_R is reduced, the molecular diameter σ increases and therefore the width of the attractive well of the potential becomes smaller; this results in smaller critical temperatures.

Now, for the effects of varying the attractive softness, Fig. 3a shows the phase diagrams in the $T^*-\rho^*$ plane corresponding to fixed repulsive softness ($s_R = 1.0$) and varying attractive

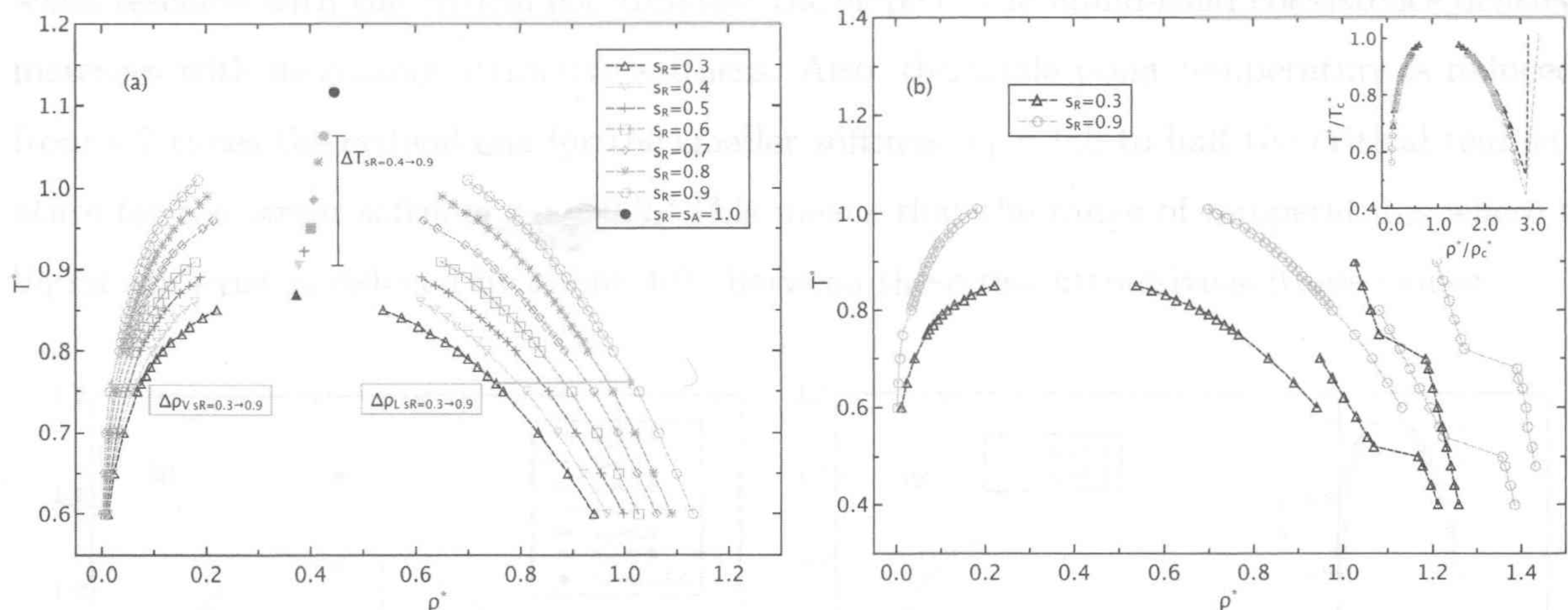


FIG. 2. Phase diagram of ANC fluids with constant attractive softness ($s_A = 1$) and variable repulsive softness $s_R = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 : (a) Orthobaric curves and critical-point estimates of this work deviate linearly with s_R from the results of the single-softness system simulated by del Río et al. [13]. Increasing s_R yields a larger change for the liquid than for the vapour branch. (b) The liquid-solid coexistence for $s_R=0.3$ and 0.9 was estimated from NPT simulations. The inset shows the phase-coexistence curves rescaled by the critical temperature and density: the main effect of increasing the repulsive softness is depressing the rescaled temperature of the triple point.

softness: $0.4 < s_A < 0.9$. As s_A is increased, the critical temperature is increased but, opposite to the previous case, the critical density decreases.

Decreasing s_A implies reducing the attractive well width and hence a decrease in the critical temperatures, but we point out that the critical temperature varies more strongly as a function of the attractive softness than with the repulsive one: the absolute change in the critical temperature ΔT_c for a change between 0.4 and 1.0 in s_A is about twice that observed for the same variation in s_R .

Again, to exhibit the non-conformality effects in the coexistence curves, we show them rescaled with their critical properties in the inset of Fig. 3b for the cases $s_A = 0.5$ and 0.9 : the changes of shape between them are noticeable, away from the critical point, in both the liquid and vapour branches.

More noticeable are the drastic effects on the liquid-solid coexistence and the triple point,

when rescaled with the critical coordinates: the slope of the liquid-solid coexistence density increases with increasing attractive softness. Also, the triple point temperature is reduced from 0.7 times the critical one for the smaller softness $s_A = 0.5$ to half the critical temperature for the larger softness $s_A = 0.9$. This means that the range of temperatures where a liquid can exist is reduced by about 40% between these two attractive-softness values.

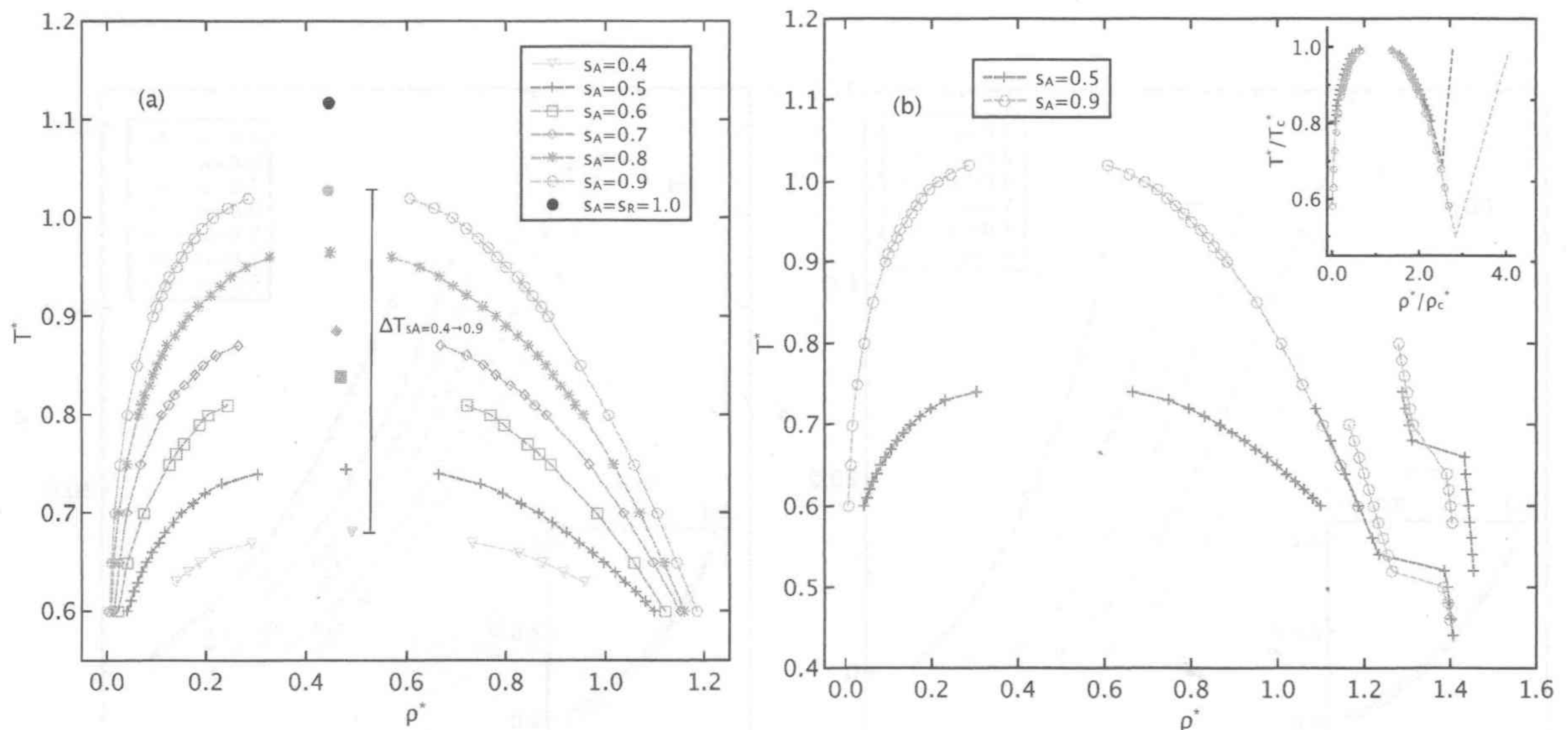


FIG. 3. Phase diagram of ANC fluids with constant repulsive softness ($s_R = 1$) and variable attractive softness $s_A = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0 . Again, (a) orthobaric curves and critical-point estimates of this work deviate linearly with s_A from the results of the single-softness system simulated by del R o et al. [13], but now the critical density decreases with increasing s_A . (b) The liquid-solid coexistence for $s_R=0.5$ and 0.9 was estimated from NPT simulations, and the inset shows the phase-coexistence curves rescaled by the critical temperature and density: the rescaled temperature of the triple point is more sensitive to the attractive softness than to the repulsive one.

4.2 Vaporization curve

Figure 4 shows the effects of varying the two softness s_R and s_A on the vaporization curve in the plane P^* vs T^* . As either of the two softnesses is increased, the temperature required

to reach a fixed pressure is increased, i.e. the curves are shifted towards higher temperatures. Nevertheless, when the vaporization curves are rescaled with the critical coordinates, the variation with softness is much smaller: for the case of varying s_R the curves are practically collapsed in a master curve, while for the case of varying s_A there remains some observable variation. This means, once more, that the non-conformality effects are more noticeable when the attractive softness is changed than when the repulsive one is modified.

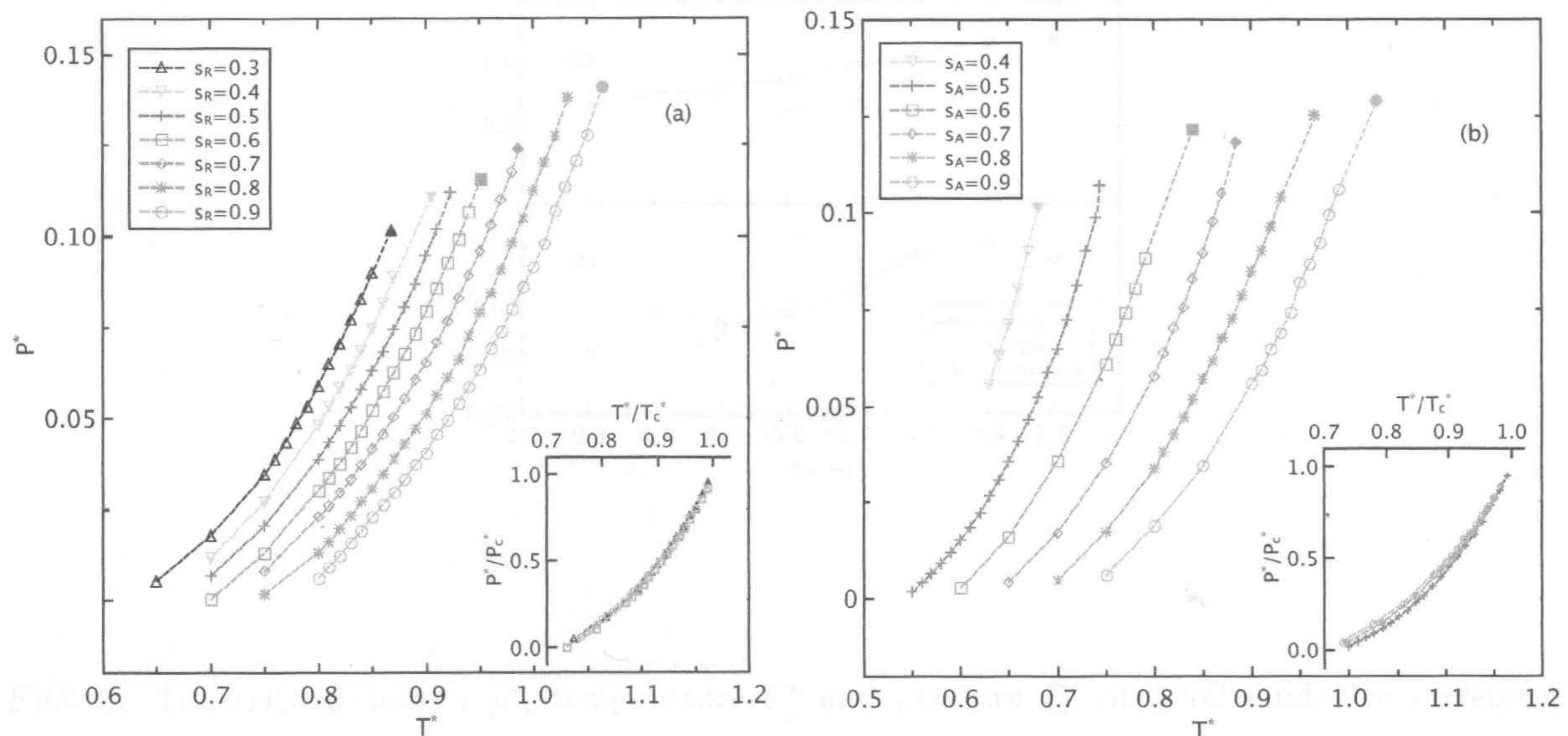


FIG. 4. Vaporization pressures as functions of temperature of ANC fluids for (a) varying repulsive softness s_R (at constant $s_A = 1$) and (b) varying attractive softness s_A (at constant $s_R = 1$). The insets in (a) and (b) display these vaporization curves rescaled with the critical pressure and temperature: differences due to non-conformality, i.e. different shapes of the potential, are apparent only when the attractive softness is changed.

4.3 Critical properties

Ramos and co-workers correlated the critical temperature, density and pressure for ANC systems with $s_R = s_A$ as linear or quadratic polynomials in the softness and then applied the ANC theory to a set of real fluids [10, 31]. Analogously, in this work we have found that the three critical coordinates display linear behaviour with s_R or s_A , as corresponds to

each case (see Fig. 5). Tables I and II contain the values of T_c^* , ρ_c^* and P_c^* for the systems simulated here.

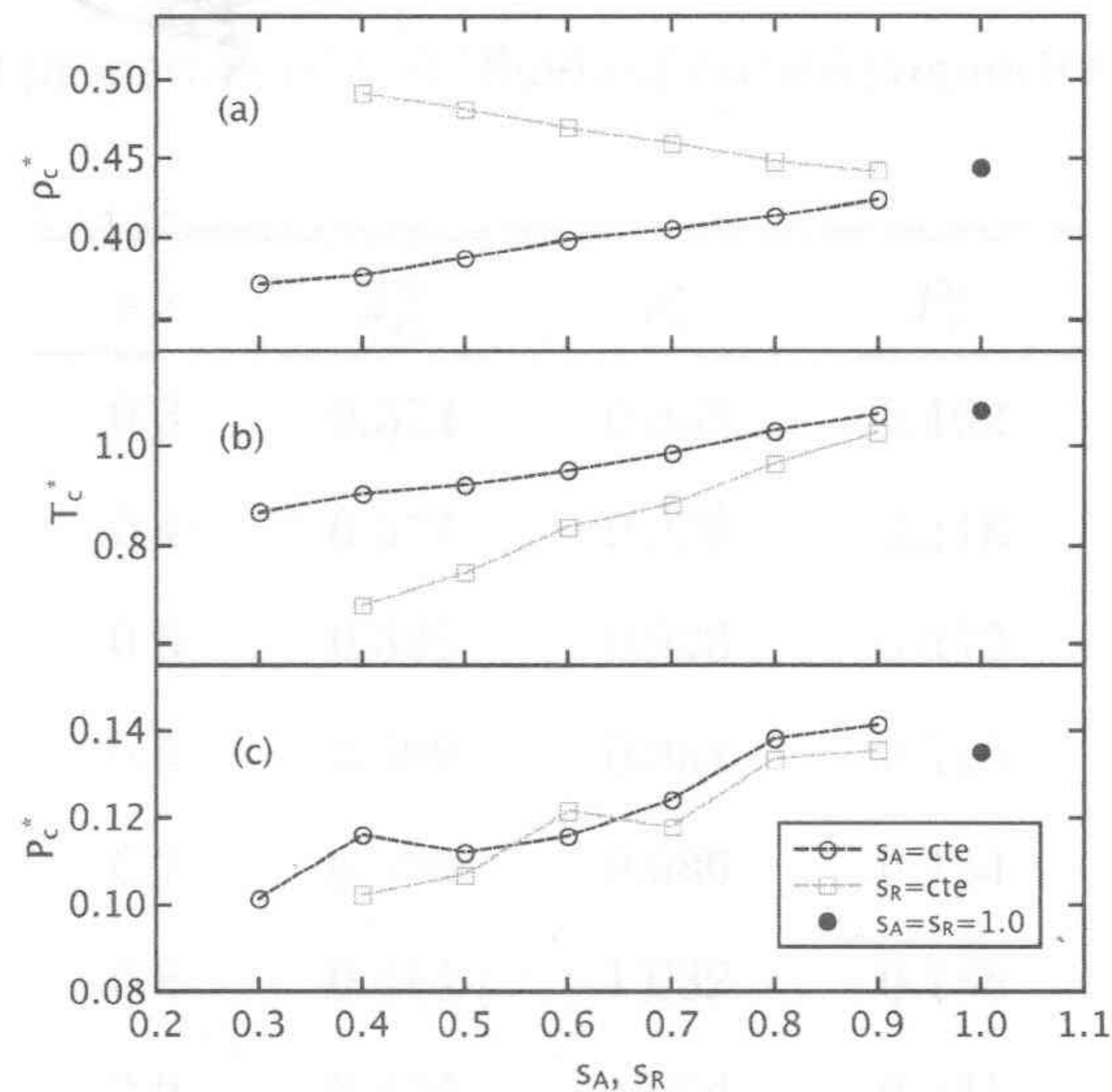


FIG. 5. The critical density ρ_c^* , temperature T_c^* and pressure P_c^* of ANC fluids are correlated linearly with the repulsive and attractive softness, the only negative linear correlation observed is that for the critical density of systems with variable attractive softness. The critical properties of the system with $s_R = s_A = 1.0$ are taken from del Río et al. [13].

We fitted the critical constants and found

$$\rho_c^* = 0.0886s_R + 0.3442, \quad (7)$$

$$T_c^* = 0.3239s_R + 0.7671, \quad (8)$$

$$P_c^* = 0.0626s_R + 0.0837, \quad (9)$$

for the case of varying the repulsive softness and

$$\rho_c^* = -0.1011s_A + 0.5310, \quad (10)$$

$$T_c^* = 0.7005s_A + 0.4019, \quad (11)$$

$$P_c^* = 0.0690s_A + 0.0747, \quad (12)$$

when the attractive softness is changed.

Is important to note that the dispersion observed in the critical properties is related to the difficulty of estimating them from simulation, as slight changes in the orthobaric densities near the critical region give rise to noticeable changes in the estimates of the critical points.

TABLE I. Reduced critical properties of ANC fluids of variable repulsive softness (at fixed attractive softness $s_A = 1$).

s_R	T_c^*	ρ_c^*	P_c^*
0.3	0.372	0.868	0.102
0.4	0.377	0.905	0.116
0.5	0.388	0.923	0.112
0.6	0.399	0.951	0.116
0.7	0.406	0.986	0.124
0.8	0.414	1.032	0.138
0.9	0.424	1.064	0.141

TABLE II. Reduced critical properties of ANC fluids of variable attractive softness (at fixed repulsive softness $s_R = 1$).

s_A	T_c^*	ρ_c^*	P_c^*
0.4	0.491	0.680	0.102
0.5	0.481	0.744	0.103
0.6	0.469	0.840	0.137
0.7	0.460	0.885	0.118
0.8	0.448	0.965	0.133
0.9	0.442	1.029	0.135

4.4 Liquid-vapour interface and surface tension

We quantified the effects of the repulsive and attractive regions of the potential on the liquid-vapor interface width. Figure 6 shows the change in the interface width with s_R and s_A , at the fixed temperatures of $T^* = 0.8$ and $T^* = 0.65$, respectively. These temperatures

were chosen so that the liquid-vapour coexistence was present for all the softness explored in each case. The interface width decreases as either the repulsive or attractive softness is increased. As the attractive softness is increased, the molecules tend increasingly to get together in the interface so that its width decreases: the interface for $s_A = 0.4$ is almost three times wider than that for $s_A = 0.9$. On the other hand, a small repulsive softness implies more repulsion between molecules and a wider interface; nevertheless, the width for $s_R = 0.4$ is just twice that for $s_R = 0.9$. The inset in Fig. 6 shows the changes in the size of the liquid drop (coexisting with the vapor) as we varied s_R and s_A . In both cases the drop size decreases linearly: when the attractive effects are increased, cohesion in the liquid phase is favored and the drop is small. On the other hand, if the repulsive effects are increased, the drop is enlarged.

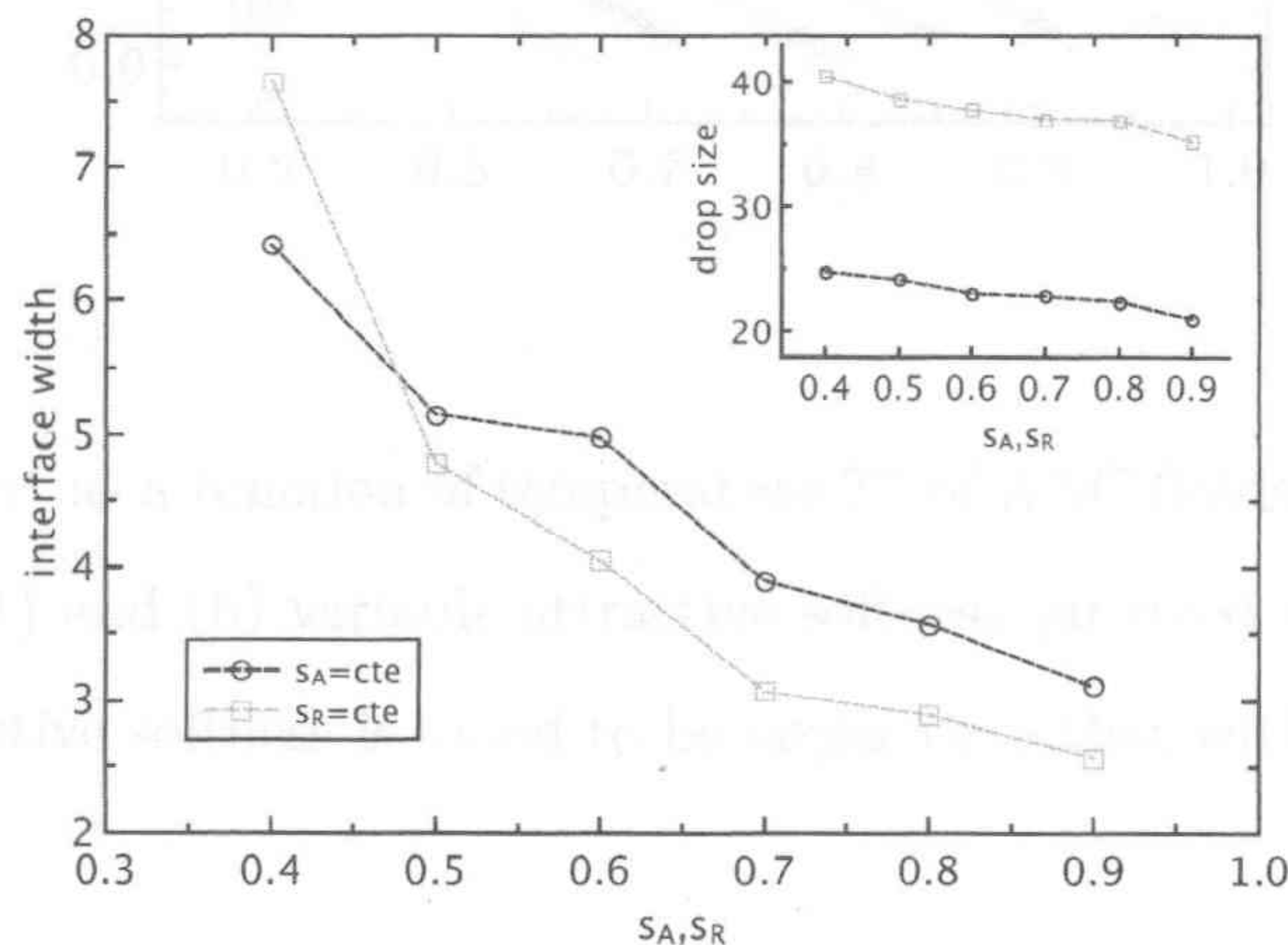


FIG. 6. The interface width (main panel) and drop size (inset) of ANC fluids as functions of attractive and repulsive softness: the decrease of the interface width is more sensitive to the attractive softness than to the repulsive one.

Figure 7 shows the the surface tension as function of the temperature for the set of repulsive and attractive softness considered. As s_R increases, the molecules become softer and can be packed more closely. When s_A increases, the width of the attractive well (and the importance of cohesion) also increases. Either way, as one or the other softness is increased the surface tension also increases, due to a larger number of interacting molecules per unit area or to enhanced cohesion between them at the interface.

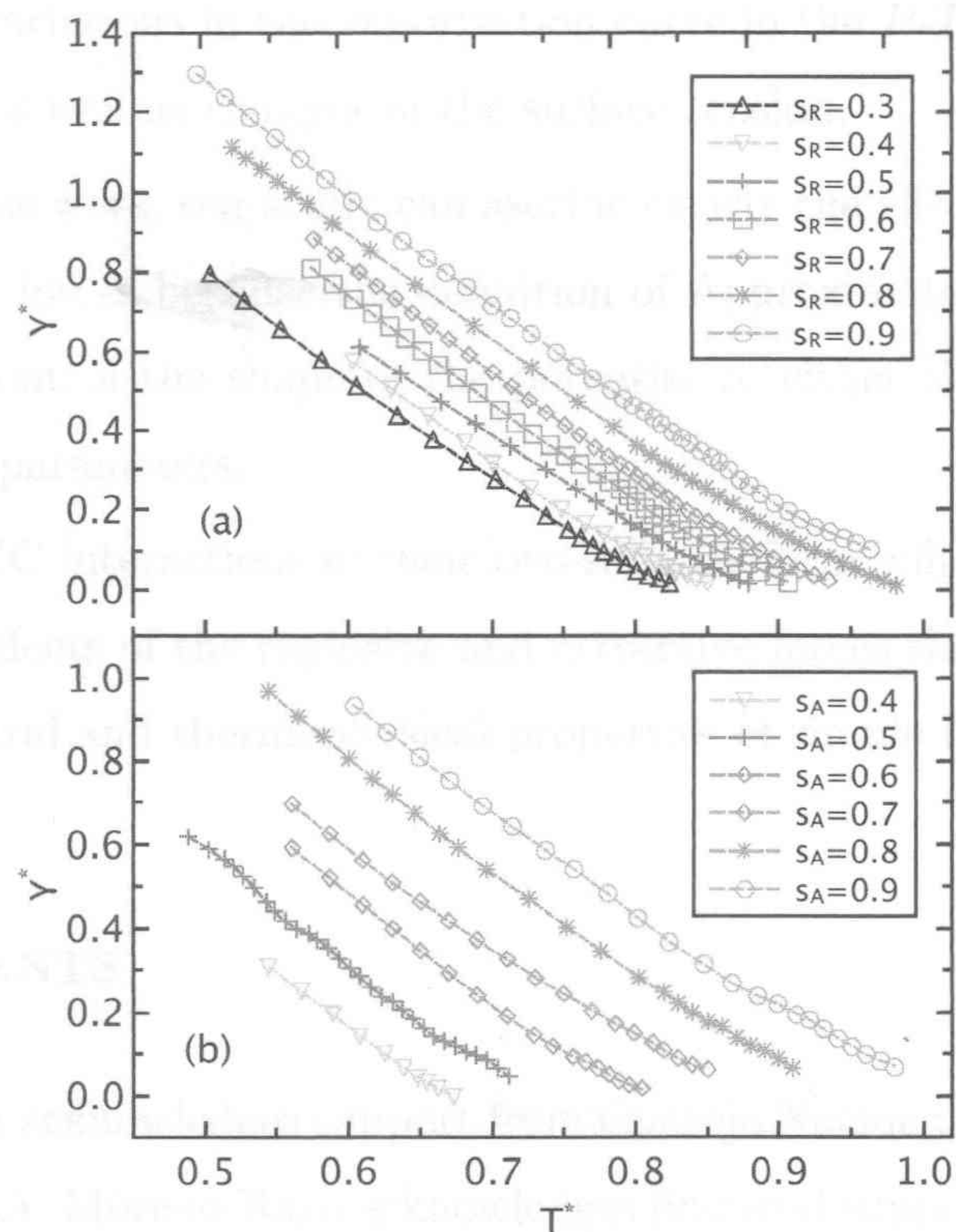


FIG. 7. Surface tension γ^* as a function of temperature T^* of ANC fluids for (a) variable repulsive softness (at fixed $s_A = 1$) and (b) variable attractive softness (at fixed $s_R = 1$). Once more, the variation with the attractive softness is found to be larger than that with the repulsive one.

5. CONCLUSIONS

We have performed a systematic study of the independent effects of the attractive and repulsive regions of the intermolecular potential on the phase diagram, critical and interfacial properties of simple liquid.

The three critical coordinates (temperature, pressure and density) were found to vary linearly with either softness. All of them increase with increasing softness, with the sole exception of a decreasing critical density with increasing attractive softness, which amounts to a widening of the attractive well of the potential.

Although the repulsive interactions are key determinants of the liquid-phase structure, we observed larger effects on the properties related to phase coexistence when we altered the attractive softness than when we varied the repulsive one: the span between the critical

and the triple point, variations in the vaporization curve in the P - T plane, the LV interface width and drop size, as well as changes in the surface tension.

Contrary to previous work, our study can ascribe clearly the effects due to changes in the repulsive or attractive forces because the definition of Approximate Non-Conformal (ANC) potentials allows to control the shape of the potential to either side of its minimum with two different softness parameters.

We expect that ANC interactions in their two-softness form will enable future work that address the detailed effects of the repulsive and attractive forces that are required to model accurately the structural and thermophysical properties of simple fluids.

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APPENDIX

Approximate Non-Conformal interactions, with a single softness parameter for the repulsive and attractive forces, have been used to reproduce within experimental error the thermodynamic properties for more than 90 substances and some of their mixtures (second and third virial coefficients, shear viscosity and thermal conductivity of diluted pure gases [7–12]), as well as critical and interfacial properties of simple liquids such as argon, methane, propane and hexane [13].

The ANC potentials $u_{ANC}(z)$, defined in Eq. 1, have a minimum value $-\varepsilon$ at $z = 1$; they are defined so that when the softness parameter $s = 1$ they have approximately the same shape as the potential for noble gases [9]. A precise definition of softness for any spherical potential is obtained by inverting the relation $\phi = u_{ANC}^*(z) + 1$ to calculate the derivative $(\partial z^3 / \partial \phi)$; the local softness of $u_{ANC}^*(z)$ with respect to a reference potential $u_1^*(z_1, s = 1)$ is

defined as a ratio of slopes,

$$s(\phi) = \frac{(\partial z^3 / \partial \phi)}{(\partial z_1^3 / \partial \phi)}. \quad (13)$$

From the equation above, one can see that decreasing the value of the softness leads to a steeper potential. In the limit $s \rightarrow 0$, $u_{ANC}(z)$ tends to the hard-sphere potential. Simple real fluids were found to have values of softness between 0.4 and 1, although some models have softnesses greater than unity, such as the Lennard-Jones 12-6 potential with $s = 1.13$ [7, 8]. For two-softness ANC potentials, the definition in Eq. 2 ensures that the local softness is constant and equal to the parameters s_R and s_A in the repulsive and attractive regions of the potential, respectively.

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