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Structure and dynamics of binary liquid mixtures near their continuous demixing transitions

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The dynamic and static critical behavior of a family of binary Lennard-Jones liquid mixtures, close to their continuous demixing points (belonging to the so-called model H' dynamic universality class), are studied computationally by combining semi-grand canonical Monte Carlo simulations and large-scale molecular dynamics (MD) simulations, accelerated by graphic processing units (GPU). The symmetric binary liquid mixtures considered cover a variety of densities, a wide range of compressibilities, and various interactions between the unlike particles. The static quantities studied here encompass the bulk phase diagram (including both the binodal and the λ -line), the correlation length, and the concentration susceptibility, of the finite-sized systems above the bulk critical temperature T_c , the compressibility and the pressure at T_c . Concerning the collective transport properties, we focus on the Onsager coefficient and the shear viscosity. The critical power-law singularities of these quantities are analyzed in the mixed phase (above T_c) and non-universal critical amplitudes are extracted. Two universal amplitude ratios are calculated. The first one involves static amplitudes only and agrees well with the expectations for the three-dimensional Ising universality class. The second ratio includes also dynamic critical amplitudes and is related to the Einstein–Kawasaki relation for the interdiffusion constant. Precise estimates of this amplitude ratio are difficult to obtain from MD simulations, but within the error bars our results are compatible with theoretical predictions and experimental values for model H' . Evidence is reported for an inverse proportionality of the pressure and the isothermal compressibility at the demixing transition, upon varying either the number density or the repulsion strength between unlike particles. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4963771>]

I. INTRODUCTION

Upon approaching continuous phase transitions at T_c , the order parameter fluctuations with long wavelengths become prevalent.^{1,2} This is accompanied by the unlimited increase of the bulk correlation length $\xi(\tau \rightarrow 0^\pm) \simeq \xi_0^\pm |\tau|^{-\nu}$, where $\tau = (T - T_c)/T_c$ is the reduced temperature and ν is one of the standard bulk critical exponents. The coefficients ξ_0^\pm are *per se* non-universal amplitudes but they form a universal ratio ξ_0^+/ξ_0^- . This divergence of ξ leads to singularities in and scaling behavior of various thermodynamic and transport properties, commonly known as critical phenomena.^{1–6} Close to T_c and in line with renormalization group theory⁷ the corresponding critical exponents and scaling functions turn out to be universal, i.e., they depend only on gross features such as the spatial dimension d , the symmetry of the order parameter, the range of interactions, and hydrodynamic conservation laws, forming universality classes. Binary liquid mixtures, exhibiting second order demixing transitions, serve as experimentally particularly suitable representatives of the corresponding Ising universality class (see, e.g., Refs. 5, 8, and 9). Besides probing critical phenomena as such, recently these critical demixing transitions in confined binary liquid

mixtures have gained significant renewed attention in the context of critical Casimir forces¹⁰ and of non-equilibrium active Brownian motion of colloidal particles, driven by diffusiophoresis in binary liquid solvents.¹¹

Static critical phenomena in binary liquid mixtures are rather well understood and reported in the literature, encompassing theory,^{1–5} experiments (see, e.g., Refs. 8, 9, and 12), and computer simulations (see, e.g., Refs. 13–16). Comparatively, much less is known about their dynamic properties. In particular, simulation studies of dynamic critical phenomena are very recent and scarce. So far, most of the computational studies of critical transport properties in binary liquid mixtures have been focused on a specific and single, highly incompressible fluid. However, probing the concept of universality and its onset for these kind of systems requires simulations of various distinct binary liquid mixtures. In order to alleviate this dearth, we have performed MD simulations concerning the universal critical behavior^{3–6} of several static and dynamic quantities, for a family of five symmetric binary liquid mixtures. The fluids considered here exhibit distinct number densities ρ and compressibilities and cover a broad range of critical temperatures. Inter-alia, this allows us to investigate the density dependence of certain critical amplitudes which together with critical exponents determine the qualitative importance of the corresponding

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critical singularities. Besides the interest in them in its own right, critical amplitudes play an important role for the dynamics of critical Casimir forces,¹⁷ the understanding of which is still in an early stage. MD simulations of this phenomenon in critical binary liquid mixtures become feasible if the model permits a large bulk correlation length combined with low bulk values of the critical pressure and viscosity. Similarly, the compilation of non-universal critical amplitudes, which has been obtained from our study, will also be beneficial for future simulation studies involving the demixing of binary liquids, for which one can then select the most appropriate fluid model.

We briefly summarize the critical behavior of static and dynamic properties in the context of liquid mixtures in order to facilitate the understanding of the results presented below. The crucial feature of the static critical phenomena is the unlimited increase of the aforementioned correlation length ξ , which is a measure of the spatial extent of a typical order parameter fluctuation. In a binary liquid mixture, the order parameter for a demixing transition is the deviation of the local concentration from its critical value whereas for a liquid–vapor transition the order parameter is the deviation of the local number density from its critical value. The static critical singularities obey power laws

$$\begin{aligned} \varphi(\tau \rightarrow 0^-) &\simeq \varphi_0 |\tau|^\beta, & \xi &\simeq \xi_0^\pm |\tau|^{-\nu}, \\ \chi &\simeq \chi_0^\pm |\tau|^{-\gamma}, & C_V &\simeq A^\pm |\tau|^{-\alpha}, \end{aligned} \quad (1)$$

where φ , χ , and C_V are the order parameter, the susceptibility, and the specific heat at constant volume, respectively. For the three-dimensional (3d) Ising universality class, the static critical exponents are known to high accuracy⁵

$$\alpha \approx 0.110, \beta \approx 0.325, \gamma \approx 1.239, \text{ and } \nu \approx 0.630. \quad (2)$$

Any two of these exponents are independent; all remaining ones follow from scaling relations² such as

$$\alpha + 2\beta + \gamma = 2 \quad \text{and} \quad \nu d = 2 - \alpha, \quad (3)$$

where d is the spatial dimension. The critical amplitudes, on the other hand, are non-universal and depend on whether T_c is approached from above or from below. However, certain ratios of the critical amplitudes, such as ξ_0^+/ξ_0^- and χ_0^+/χ_0^- , are known to be universal.^{4,12}

Dynamic critical phenomena are governed by the relaxation time t_R which diverges upon approaching T_c as

$$t_R \sim \xi^z, \quad (4)$$

leading to critical slowing down.³ This entails thermal singularities in various collective transport coefficients,⁶ e.g., the mutual diffusivity D_m (also called interdiffusivity) and the shear viscosity $\bar{\eta}$,

$$D_m \sim \xi^{-x_D} \quad \text{and} \quad \bar{\eta} \sim \xi^{x_\eta}. \quad (5)$$

The dynamic critical exponents z , x_D , and x_η satisfy scaling relations as well,^{3,6}

$$x_D = d - 2 + x_\eta \quad \text{and} \quad z = d + x_\eta, \quad (6)$$

leaving scope for only one independent dynamic critical exponent. In the case of a liquid–vapor transition, the quantity

analogous to D_m is the thermal conductivity D_T , bearing the same critical exponent as $\tau \rightarrow 0$.

Transport mechanisms in near-critical fluids have to respect hydrodynamic conservation laws, specifically for mass, momentum, and internal energy. The dynamics of one-component fluids undergoing a liquid–vapor transition is described by the so-called model H ,^{6,18} which incorporates the conservation of a scalar order parameter and of the transverse part of the momentum current. The asymptotic behaviors for $\tau \rightarrow 0$ of the thermal conductivity and of the shear viscosity in model H have been well studied and the corresponding critical exponents for this universality class are known.⁶ A binary liquid mixture, on the other hand, can exhibit two kinds of transitions: liquid–vapor transitions at plait points and demixing transitions at consolute points. The reason is that there are two conserved scalar fields, viz., the concentration field and the density field. The critical dynamics in binary liquid mixtures is thus classified as model H' .⁶ The transport properties exhibit different features at the consolute and the plait points;¹⁹ for example, for $\tau \rightarrow 0$ the thermal conductivity remains finite at consolute points, but diverges at plait points.^{19,20} Moreover, the corresponding behaviors in the non-asymptotic regime are quite different as well. However, in the asymptotic regimes the leading critical exponents (including the dynamic ones) at the consolute points of a binary mixture are the same as the ones for a one-component fluid.⁶ The to date best estimate for $x_\eta \approx 0.068$ in $d = 3$ was obtained within a self-consistent mode-coupling approximation for a one-component fluid²¹ and is in agreement with previous theoretical calculations;^{4,19,22–25} it is also corroborated by experiments on xenon near its liquid–vapor critical point.²⁶ By virtue of universality and using Eq. (6), this implies for the dynamic critical exponents of model H' in $d = 3$,⁶

$$x_\eta \approx 0.068, \quad x_D \approx 1.068, \quad \text{and} \quad z \approx 3.068. \quad (7)$$

The presence of density as a secondary fluctuating field, which is coupled to the order parameter field (i.e., the concentration) through some constraint [cf. Eq. (18)], generally raises the question whether Fisher renormalization²⁷ has to be accounted for. For the present study of symmetric binary mixtures, we have no indications that this is the case, but this issue deserves further theoretical investigation.

Compared with the large body of research on static critical phenomena, there are relatively few studies on dynamic critical phenomena. Concerning theory, they are performed mainly by using *mode-coupling* theory (MCT)^{28,29} or *dynamic renormalization group* theory (RG) (see Refs. 6 and 32 for recent reviews). In parallel to that, the phenomenological *dynamic scaling* formalism³³ has also been used extensively. There are important experimental observations (see, e.g., Refs. 9, 26, 34, and 35) which have pushed the development of this field of research. Computer simulations of dynamic critical phenomena in fluids^{36–39} started only a decade ago. The first MD simulation³⁶ aiming at the critical singularities in the fluid transport quantities was performed in 2004. Although this study produced the correct values of the static critical exponents for the susceptibility and the correlation length, the reported critical

exponent for the interdiffusivity was in disagreement with theoretical predictions. There are numerical studies^{40,41} of shear and bulk viscosities close to the liquid–vapor transitions of one-component fluids too, but, without characterizing quantitatively their critical singularities. The first quantitative determinations of critical exponents and amplitudes for transport in fluids—being in accordance with MCT, dynamic RGT, and experiments—were performed by Das *et al.* by using MD simulations.^{38,42,43} Applying finite-size scaling theory,⁴⁴ the critical singularities of the shear viscosity, of the Onsager coefficient, and of the mutual diffusivity were determined. Along these lines, the critical divergence of the bulk viscosity was determined recently^{39,45} for a demixing phase transition. In this context, we are aware of only one simulation study³⁷ of the dynamic critical exponents associated with liquid–vapor transitions (model *H*). These MD simulations and also the present one have been carried out in the mixed phase, i.e., approaching T_c from above (for an upper critical demixing point). To the best of our knowledge, there are no computational investigations of the critical transport in binary liquid mixtures approaching T_c from below. The latter ones are complicated by non-standard finite-size effects changing the location of the binodals,⁴⁵ along which the transport quantities have to be calculated. Simulations below T_c could shed light on apparently contradictory theoretical predictions concerning critical amplitude ratios,^{22,32} for which there is also a lack of experimental data.

Simulations of dynamic critical phenomena face particular challenges such as, inter-alia, critical slowing down,²² and finite-size effects. While upon increasing the system size finite-size effects become less pronounced, the critical slowing down ($t_R \sim \xi^z \sim \tau^{-\nu z} \rightarrow \infty$) causes simulations of large systems to become expensive due to increasing equilibration times. This leads to noisy simulation data for any transport property near criticality at which large scale fluctuations are unavoidable and thus make the determination of critical singularities very difficult. This problem is even more pronounced for quantities associated with collective dynamics, such as the shear viscosity, which lack the self-averaging of tagged-particle quantities. Critical slowing down also manifests itself in long-time tails of the Green-Kubo correlators of transport quantities. In particular, for the bulk viscosity, this has been demonstrated^{39,40,45} to make the computation notoriously difficult. Moreover, there are also technical hurdles concerning the temperature control^{46,47} during long MD runs near T_c . One way of dealing with these problems is to carry out MD simulations of smaller systems and then to apply a finite-size scaling analysis, as done in Refs. 38, 39, 42, and 45. In the present study, we deal with huge system sizes such that the use of finite-size scaling is less important for determining the relevant critical singularities.

This study is organized such that in Section II the family of fluid models considered here and the simulation methodologies are described. Section III contains the simulation results for the phase diagrams. The computational observations for structural quantities and transport coefficients are reported in Sections IV and V, respectively, and compared with available theoretical and experimental predictions. Results for universal amplitude ratios are discussed in

Section VI. Finally, Section VII provides a detailed summary and perspectives.

II. MODELS AND METHODS

A. Models

As model fluids, we have considered binary mixtures of A and B particles, which interact via the Lennard-Jones (LJ) pair potential

$$u^{\text{LJ}}(r; \varepsilon, \sigma) = 4\varepsilon [(\sigma/r)^{12} - (\sigma/r)^6]. \quad (8)$$

Particles of species $\alpha, \beta \in \{A, B\}$ have different interaction strengths $\varepsilon_{\alpha\beta}$, while for reasons of simplicity all particles have the same diameter σ and mass m . The actually employed pair potentials are

$$u_{\alpha\beta}(r) = [u_{\alpha\beta}^{\text{LJ}}(r; \varepsilon_{\alpha\beta}, \sigma) - u_{\alpha\beta}^{\text{LJ}}(r_c; \varepsilon_{\alpha\beta}, \sigma)] f\left(\frac{r - r_c}{h}\right), \quad (9)$$

where the potential is smoothly truncated at a suitable cut-off distance r_c for computational benefits such that the pair force is still continuously differentiable at $r = r_c$. We used the smoothing function $f(x) = x^4\theta(-x)/(1 + x^4)$, where θ is the Heaviside step function.^{48,49} A small value of $h = 0.005\sigma$ is sufficient to ensure very good numerical stability with respect to conservation laws during long MD runs,⁵⁰ which is indispensable for the study of the critical dynamics of molecular fluids.

Throughout, we have used cubic simulation boxes of edge length L and volume $V = L^3$ with periodic boundary conditions applied along all Cartesian directions. The total number density $\varrho = N/V$ is kept constant, where $N = N_A + N_B$ is the total number of particles and N_α is the number of particles of species α . With this, the concentration is defined as $x_\alpha = N_\alpha/N$. We adopt $\varepsilon_{AA} = \varepsilon$ as the unit of energy. In turn this sets the dimensionless temperature $T^* = k_B T/\varepsilon$. For the choice $\varepsilon_{AA} = \varepsilon_{BB}$ the binary liquid mixture is symmetric. This symmetry leads to several computational advantages concerning the calculation of the phase diagram¹⁵ and improves the statistics of single-particle averages. The various fluids considered here are specified by their set of parameters $(\varepsilon_{AB}, r_c, \varrho)$ to be described next.

As to model I, we choose

$$r_{c,\alpha\beta} = 2.5\sigma, \quad \varepsilon_{AA} = \varepsilon_{BB} = \varepsilon, \quad \varepsilon_{AB} = \frac{\varepsilon}{2}, \quad (10)$$

and study various number densities ϱ . In model II, we set $r_{c,\alpha\alpha} = 2.5\sigma$ for like-particle interactions ($\alpha = \beta$) and $r_c = 2^{1/6}\sigma$ otherwise, such that the unlike particles interact via the purely repulsive Weeks–Chandler–Andersen (WCA) potential.⁵¹ For this model, we fix

$$\varrho\sigma^3 = 0.8, \quad \varepsilon_{AA} = \varepsilon_{BB} = \varepsilon, \quad (11)$$

and keep $\varepsilon_{AB}/\varepsilon$ as a tunable interaction parameter. Model II is inspired by the Widom–Rowlinson mixture,⁵² the dynamics of which has been the subject of a recent simulation study.³⁶ The Lennard-Jones potential [Eq. (8)], and certainly its truncated form [Eq. (9)], decays faster than $r^{-(d+2)}$ as $r \rightarrow \infty$ for $d = 3$, which justifies that the critical singularities of static bulk

properties belong to the universality class of 3d Ising models with short-ranged interactions.

B. Semi-grand canonical Monte Carlo simulation (SGMC)

The phase diagram and the static susceptibility χ are calculated using the semi-grand canonical Monte Carlo (SGMC) simulations.¹⁵ Within SGMC, the total particle number N is kept constant, while x_A and x_B fluctuate. The implementation of the simulation consists of two Monte Carlo (MC) moves: particle displacement and an identity switch $A \rightleftharpoons B$. Due to the identity switch also the chemical potential difference $\Delta\mu = \mu_A - \mu_B$ for the two species enters into the Boltzmann factor. However, for symmetric binary liquid mixtures the coexistence curve below T_c is given by $\Delta\mu = 0$. Accordingly, it is natural to collect the simulation data above T_c also for $\Delta\mu = 0$, which implies that the field conjugate to the demixing order parameter is zero. During the SGMC runs, the concentration x_A has been recorded at sufficiently large intervals of 10^4 MC steps, so that subsequent samples are approximately independent of each other. For $L = 27$ and $\rho\sigma^3 = 1.0$, the fluid mixture has been equilibrated over 3×10^6 MC steps. The attempted particle displacements have been chosen uniformly from the cube $[-\sigma/20, \sigma/20] \times [-\sigma/20, \sigma/20] \times [-\sigma/20, \sigma/20]$.

In the SGMC simulation the concentrations x_A and x_B fluctuate. Therefore the order parameter field $\phi := (x_A - x_B)/2$ is not conserved, but the total number density field is conserved. Accordingly, the SGMC dynamics is classified as the so-called model *C* with a scalar order parameter⁶ and is associated with a dynamic exponent $z_{\text{SGMC}} = 2 + \alpha/\nu \approx 2.175$ for $d = 3$ (see Table 3 in Ref. 6). On the other hand, if one performs MC simulations in the canonical ensemble (N_A, N_B, V , and T fixed) with rules such that the order parameter is conserved *locally*—in addition to a conserved density—the dynamics corresponds to model *D*. It has been shown that the dynamic exponent z for model *D* is the same as for model *B* ($z = 4 - \eta \approx 3.964$).^{6,53} Note that both model *B* and *D* correspond to a locally conserved order parameter field, with an additional non-critical conserved density field present in model *D*. Due to a much smaller value of z , MC simulations for model *C* are computationally faster and more advantageous than for model *D*. However, the issue of MC simulations in the canonical ensemble with an only globally (not locally) conserved order parameter field, in the presence of a conserved density field, requires further investigations.

C. Molecular dynamics simulation

Transport quantities have been calculated by using MD simulations,^{46,54} which solve Newton's equations of motion for the fluid particles within the microcanonical ensemble (N_A, N_B, V , total momentum, and total energy E fixed). Simulations of critical dynamics are intrinsically difficult due to both critical slowing down and finite-size effects.^{15,22} Even more so, the study of collective transport requires a sufficient separation of length scales ($\sigma \ll \xi \ll L$). Therefore, we have performed simulations of very large system sizes ($L \leq 50\sigma$)

containing up to $N = 87\,500$ particles with the trajectories spanning more than $10^4 t_0$ in time, with $t_0 = \sqrt{m\sigma^2/\varepsilon}$, which is at the high end of the present state of the art.

Such demanding computations have become feasible only recently based on the highly parallel architecture of so-called GPU (graphic processing units) accelerators, which are specialized on streaming numerical computations of large data sets in parallel. The success of GPU computing in the realm of MD simulations⁵⁵ has stimulated the development of GPU implementations for more advanced algorithms,⁵⁶ and today such accelerator hardware is often part of new installations in high-performance computing centers. Specifically, we have used the software *HAL's MD package* (version 1.0),^{50,57} which is a high-precision molecular dynamics package for large-scale simulations of complex dynamics in inhomogeneous liquids. The implementation achieves excellent conservation of energy and momentum at high performance by using an increased floating-point precision where necessary.^{50,58} The software minimizes disk usage by the *in situ* evaluation of thermodynamic observables and dynamic correlation functions and by writing structured, compressed, and portable H5MD output files.⁵⁹ Concerning the performance of the package, it has been shown to reliably reproduce the slow glassy dynamics of the Kob–Andersen mixture,⁵⁰ and it was used recently to shed new light on the structure of liquid–vapor interfaces.⁶⁰

For the thermalization of the initial state, we have used a Nosé–Hoover thermostat (NHT) chain^{46,61} with an integration time step of $\delta t = 0.002t_0$. We note that NHT dynamics has recently been demonstrated⁴⁷ to generate critical transport in binary liquid mixtures within the universality class of model *H'*. We have applied the following equilibration procedure: (i) Generate an initial lattice configuration with the desired particle numbers N_A, N_B , and the volume V such that the two species of the particles are randomly assigned and that the total momentum is zero. (ii) Melt this lattice at the temperature $2T$ for $100t_0$ using the NHT and further equilibrate it at T ; typical run lengths are $t = 10^4 t_0$ for $L = 42\sigma$ and $\rho\sigma^3 = 1.0$. (iii) Determine the average internal energy U at T from the previous NHT run and rescale the particle velocities such that the instantaneous total energy matches U . The resulting system state is used to compute transport quantities in a production run at fixed total energy, employing the velocity Verlet algorithm with an integration time step of $\delta t = 0.001t_0$. For model II with $\varepsilon_{AB}/\varepsilon = 1$ we have used $\delta t = 0.0005t_0$. These choices for δt result in a relative energy drift of less than 2×10^{-5} in 1.5×10^7 steps.

D. Data acquisition and statistics

All results presented in the following correspond to the critical composition $x_c = 1/2$ and $T^* \geq T_c^*$. Unless stated otherwise, static quantities are all averaged over 20 independent initial configurations and for dynamic quantities this number is 30. During the production runs in the NVE ensemble (i.e., N_A, N_B, V , and E constant), data are recorded over a time span of $t = 15\,000 t_0$. For example, the computing time for a system trajectory of 74 088 particles over 1.5×10^7 steps, using a single Tesla K20Xm GPU (NVIDIA Corp.),

was 7.1 h at the wall clock, including the evaluation of static and dynamic correlations.

III. PHASE DIAGRAMS

From the SGMC simulations we have obtained the demixing phase diagrams for the 5 fluids studied. For each fluid, the probability density $P(x_A)$ of the fluctuating concentration x_A of A particles has been determined at various dimensionless temperatures T^* above and below the anticipated demixing point; $P(x_A)$ is normalized: $\int_0^1 P(x_A) dx_A = 1$. In a finite system of linear size L with periodic boundary conditions along all directions, the critical transition is shifted and rounded, following the finite-size scaling relation⁴⁴ $T_c(L \rightarrow \infty) - T_c \sim L^{-1/\nu}$. In our simulations, we have used large values for L so that the finite-size effects are sufficiently small. The inset of Fig. 1 shows results for $P(x_A)$ for model I with $\rho\sigma^3 = 0.7$ and for two representative temperatures: $P(x_A)$ shows a single peak above T_c^L and assumes a double-peak structure below T_c^L . These peaks of $P(x_A)$ correspond to equilibrium states because, up to an x_A -independent constant, the free energy is given by $-k_B T \log(P(x_A))$. Accordingly, the two peaks of equal height indicate the coexistence of an A- and a B-rich phase below T_c^L . Due to the symmetry of the binary liquid mixtures, one has $P(x_A) = P(1 - x_A)$, which we have imposed on the data for $P(x_A)$. By construction, the critical composition is $x_{A,c} = x_{B,c} = x_c = 1/2$ for all the models considered by us here.

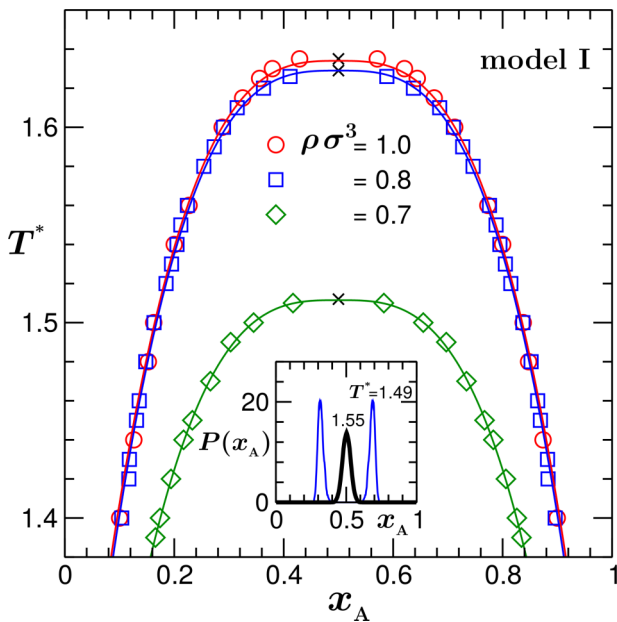


FIG. 1. Demixing phase diagrams in the x_A - T^* plane for binary liquid mixtures within model I for 3 number densities ρ [$x_A = N_A/(N_A + N_B)$ and $T^* = k_B T/\varepsilon$ with $\varepsilon = \varepsilon_{AA}$]. Open symbols indicate co-existing equilibrium states obtained from SGMC simulations. Solid lines are fits to these data yielding estimates for $T_c(\rho)$ (see the main text), and crosses mark the critical points ($x_c = 1/2, T_c$). The chosen system sizes are $L = 27\sigma, 29\sigma$, and 30σ for $\rho\sigma^3 = 1.0, 0.8$, and 0.7 , respectively. In all cases, the statistical errors do not exceed the symbol sizes. The inset shows the probability density $P(x_A)$ for model I at $\rho\sigma^3 = 0.7, L = 30\sigma$, and two values of T^* .

Accordingly, the fluctuating order parameter is given by $\phi = x_A - 1/2$, from which we have calculated the mean order parameter φ as

$$\varphi = \langle |\phi| \rangle = \int_0^1 |x_A - 1/2| P(x_A) dx_A. \quad (12)$$

Below T_c , where $\varphi > 0$, the binodal is given by the coexisting concentrations $x_A^{(1,2)}(T) = 1/2 \pm \varphi(T)$. The results are shown in Fig. 1, and one expects that they follow the asymptotic power law

$$\varphi(T \nearrow T_c) \approx \varphi_0 |T/T_c - 1|^\beta, \quad (13)$$

which defines also the amplitude φ_0 . However, deviations are expected to occur for T very close to T_c due to the finite-size effects mentioned before.^{39,62} For each of the 5 fluids studied, T_c and φ_0 have been estimated via fits of Eq. (13) to the data, with $\beta = 0.325$ fixed [Eq. (2)]. Ideally, all three parameters (φ_0, β, T_c) can be obtained from a single fit procedure as described above. However, trying to extract an unknown exponent close to T_c from data for finite-sized systems is a delicate task which usually leads to large uncertainties. Already for the extraction of φ_0 and T_c alone one has to choose the fit range judiciously: data points very close to T_c suffer from finite-size effects, while the asymptotic law is not expected to hold at temperatures far away from T_c . Exemplarily for $\rho\sigma^3 = 0.7$, we have chosen $x_A \in (0.2, 0.4)$. Note that the power law in Eq. (13) provides a good description of the binodal even at the lowest temperatures investigated.

We have refined the estimates for T_c with Binder's cumulant intersection method.^{13,14} It is based on the dimensionless cumulant

$$U_L(T) = 1 - \frac{\langle \phi^4 \rangle}{3\langle \phi^2 \rangle^2}, \quad (14)$$

which interpolates between the limiting values $U_L(T \rightarrow 0) = 2/3$ and $U_L(T \rightarrow \infty) = 0$ and, at T_c , it attains a universal value $U_L(T_c)$ for sufficiently large L . Plotting $U_L(T)$ vs. T for various system sizes L , the set of curves exhibits a common point of intersection, from which one infers an accurate estimate for T_c . This is demonstrated in Fig. 2, showing a family of intersecting curves $U_L(T)$ for model I with $\rho\sigma^3 = 0.7$ and for three values of L . The figure corroborates the critical value¹⁴ $U_L(T_c) \approx 0.4655$ for the Ising universality class, from which we read off $T_c^* = 1.5115 \pm 0.0008$.

The main results for all 5 fluids studied here have been compiled in Table I. For model II, we have found much higher values for T_c than for model I. This can be understood as follows. The AA and BB interaction potentials are identical both within and between the two models, which differ only with respect to the AB interaction potential. Upon construction [see Eq. (9)], the AB interaction is more repulsive in model II than in model I (u_{AB}^{II} is purely repulsive whereas u_{AB}^{I} exhibits also an attractive part). A repulsive AB interaction favors the formation of domains rich in A and of domains rich in B and thus promotes demixing, which leads to a higher value of T_c . Within model II, increasing ε_{AB} makes u_{AB}^{II} more repulsive and thus renders the same trend. In particular, increasing within model II the attraction strength ε_{AB} by a factor of 4 yields

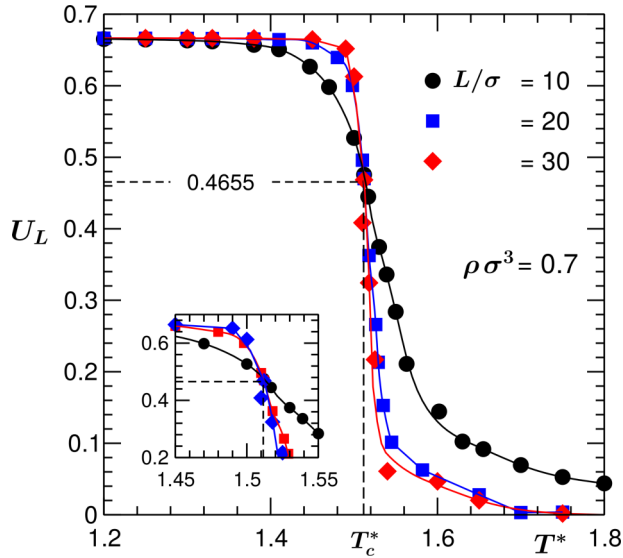


FIG. 2. Binder cumulant $U_L(T)$ [Eq. (14)] for model I with $\rho\sigma^3 = 0.7$ and for 3 values of L . The solid lines are interpolating weighted splines and the dashed lines mark the common intersection point. The inset provides an enlarged view of the neighbourhood of the intersection point at T_c^* .

a 1.7-fold increase of T_c . The binodal for model II with $\varepsilon_{AB}/\varepsilon = 1$ (but $u_{\alpha\alpha}$ truncated at $r_c/\sigma = 4.2$) was determined in Ref. 63, and the rough estimate of T_c there agrees with our result. Model I was studied by Das *et al.*⁶² for $\rho\sigma^3 = 1.0$, but using sharply truncated interaction potentials [$f(x) \equiv \theta(-x)$ in Eq. (9)]. They found $T_c^* = 1.638 \pm 0.005$, which is very close to our result $T_c^* = 1.635 \pm 0.003$, however different from $T_c^* \approx 1.423$ as obtained for the force-shifted potentials

used in Ref. 42. The respective similarities and differences in the critical temperatures appear because the smoothing function $f(x)$ alters $u_{\alpha\beta}(r)$ only marginally in the vicinity of r_c , unlike the force shift which amounts to modify the interaction potentials globally. Within model I, the amplitude φ_0 of the order parameter is, within the accuracy of our data, insensitive to the density ρ (see Table I). Within model II, φ_0 changes only slightly upon increasing the strength ε_{AB} of the repulsion.

The dependence of the demixing transition on the total number density ρ gives rise to a line $T_c(\rho)$ of critical points, known as the λ -line (Fig. 3). For model I, we have found that $T_c(\rho)$ is an increasing function for $\rho\sigma^3 \lesssim 0.9$; for higher densities, it decreases. Such a non-monotonic dependence implies a re-entrance phenomenon: increasing the density isothermally, the binary liquid mixture undergoes a phase transition from a mixed state at low density to a phase-separated one and mixes again at high densities. One may speculate that such a behavior can be rationalized by the non-monotonicity of the internal energy as a function of density, which arises from the non-monotonic form of the pair potential. However, this proposition calls for further computational studies using various kinds of like and unlike particle interactions.

The initial increase of $T_c(\rho)$ is in qualitative agreement with a previous grand-canonical MC study⁶⁴ using a variant of our model I ($\varepsilon_{AB} = 0.7\varepsilon_{AA}$). For this choice of the interaction potentials, it was found that the λ -line ends at a critical end point near $\rho\sigma^3 \approx 0.59$, where the λ -line hits the first-order liquid–vapor transition of the fluid. It was suggested⁶⁴ that upon decreasing ε_{AB} further the critical end point moves

TABLE I. Simulation results for the five binary fluids investigated here along with results from Ref. 42: values of the critical temperature T_c and of the pressure P_c , the internal energy U_c [Eq. (16)], and the isothermal compressibility κ_c at the critical point; further, the critical amplitudes of the correlation length ξ_0 [Eq. (21)], of the order parameter φ_0 , and of the static susceptibility χ_0 [Eq. (21)], as well as of the shear viscosity η_0 [Eqs. (33) and (34)] and the Onsager coefficient \mathcal{L}_0 [Eqs. (26)–(28)]. The amplitudes $D_{m,0}$ of the interdiffusion constant have been computed from Eq. (32). Finally, the values of two universal ratios of static and dynamic amplitudes, $R_\xi^+ R_c^{-1/d}$ and R_D [see Eqs. (38) and (39), respectively], are reported. Numbers in parentheses indicate the uncertainty in the last digit(s).

	Model I			Model II		Reference 42
	0.7	0.8	1.0	0.8	0.8	1.0
$\rho\sigma^3$	0.7	0.8	1.0	0.8	0.8	1.0
$\varepsilon_{AB}/\varepsilon$	1/2	1/2	1/2	1/4	1	1/2
$r_{c,AB}/\sigma$	2.5	2.5	2.5	$2^{1/6}$	$2^{1/6}$	2.5+force shift
T_c^*	1.5115(8)	1.629(1)	1.635(3)	2.608(2)	4.476(2)	1.4230(5)
P_c^*	2.58(5)	4.81(3)	12.70(4)	8.29(5)	16.31(6)	
U_c/ε	-0.617(3)	-0.584(3)	-0.572(4)	2.643(4)	6.557(6)	
κ_c^*	0.11(4)	0.05(3)	0.02(3)	0.04(4)	0.02(4)	
φ_0	0.76(2)	0.77(2)	0.745(16)	0.77(3)	0.70(2)	0.765(25)
χ_0^*	0.157(9)	0.112(7)	0.068(4)	0.056(4)	0.06(2)	0.076(6)
ξ_0/σ	0.53(3)	0.47(2)	0.42(2)	0.45(3)	0.53(2)	0.395(25)
$R_\xi^+ R_c^{-1/d}$	0.71(7)	0.70(6)	0.72(6)	0.72(8)	0.65(9)	0.69(8)
η_0^*		1.46(10)	3.63(10)	1.35(5)	1.80(7)	3.87(30)
\mathcal{L}_0^*	0.0143(5)	0.0082(4)	0.0024(3)	0.0049(4)	0.0032(4)	0.0028(4)
$\mathcal{L}_{b,0}^*$	0.0082(7)	0.0040(6)	0.0028(4)	0.0025(5)	0.0013(7)	0.0033(8)
$D_{m,0}^*$	0.091(8)	0.073(6)	0.035(5)	0.088(7)	0.053(6)	0.037(8)
R_D		0.95(17)	0.993(21)	1.00(21)	0.96(25)	1.06(40)

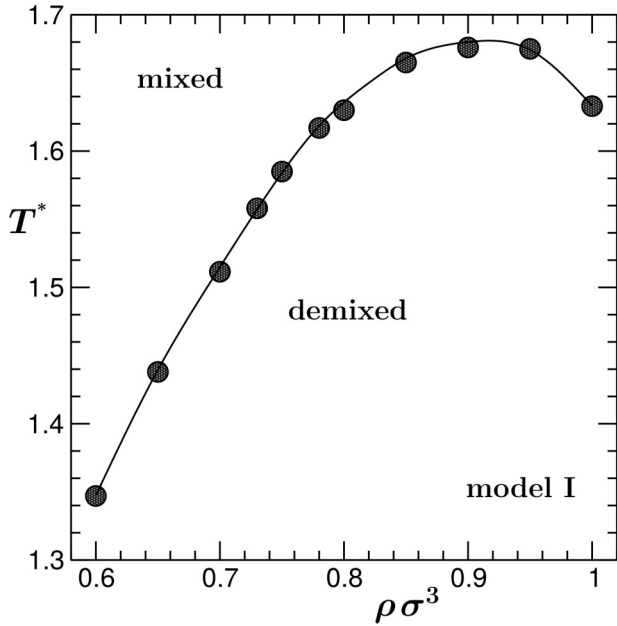


FIG. 3. Loci of the critical points $T_c(\varrho)$ for the demixing transition in the ϱ - T^* plane with $T^* = k_B T / \varepsilon$, obtained from SGM simulations for model I. The solid line is an interpolating weighted spline. For details of the interaction potentials, see the main text and Table I. Error bars are smaller than the symbol sizes.

towards the line of liquid–vapor critical points until both lines of critical points meet for $\varepsilon_{AB} \approx 0.6\varepsilon_{AA}$ and form a tri-critical point, as observed in a two-dimensional spin model.¹⁶ The determination of the full phase diagrams of binary liquid mixtures, encompassing the complete λ -line, the line of liquid–vapor critical points, and the solid phases, is a non-trivial and computationally demanding task (for density functional approaches in this direction see Refs. 65–67). It remains as an open question whether there is a tri-critical point in model I ($\varepsilon_{AB} = 0.5\varepsilon_{AA}$) or not (see below for further discussions).

For completeness, Table I also lists the critical values for the dimensionless pressure $P_c^* = P_c \sigma^3 / \varepsilon$ at the respective demixing points, which have been obtained, following the standard procedures for a homogeneous and isotropic fluid, from the trace of the time-averaged stress tensor, $P = \text{tr}(\Pi(t)) / 3V$, with the instantaneous stress tensor given by⁶⁸

$$\Pi(t) = \sum_{i=1}^N \left\{ m \mathbf{v}_i(t) \otimes \mathbf{v}_i(t) + \sum_{j>i}^N \mathbf{r}_{ij}(t) \otimes \mathbf{F}_{ij}(t) \right\}, \quad (15)$$

where $\mathbf{v}_i(t)$ is the velocity of particle i , $\mathbf{r}_{ij}(t) = \mathbf{r}_i(t) - \mathbf{r}_j(t)$, $\mathbf{F}_{ij}(t)$ is the force acting on particle j due to particle i , and \otimes denotes a tensor product. We also specify the internal energy per particle,

$$U = \frac{1}{N} \sum_{i=1}^N \left\{ \frac{m}{2} \mathbf{v}_i(t)^2 + \sum_{j>i}^N u_{\alpha_i \alpha_j}(|\mathbf{r}_{ij}(t)|) \right\}, \quad (16)$$

at the critical points, which characterizes the microcanonical ensemble probed by MD simulations; $\alpha_i \in \{A, B\}$ denotes the species of particle i .

IV. SPATIAL CORRELATIONS

A. Static structure factors

The structural properties of binary liquid mixtures arise from the two fluctuating fields, given by the microscopic partial number densities $\varrho_\alpha(\mathbf{r})$ of each species α . Their fluctuating parts are⁶⁸

$$\delta \varrho_\alpha(\mathbf{r}) = -\frac{N_\alpha}{V} + \sum_{j=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_j^{(\alpha)}), \quad (17)$$

where the set $\{\mathbf{r}_j^{(\alpha)}\}$ denotes the positions of the N_α particles of species α . It is favorable to (approximately⁶²) decouple the spatial fluctuations into the overall density contribution $\delta \varrho(\mathbf{r})$ and into the composition contribution $\delta c(\mathbf{r})$ and, accordingly, to consider the linear combinations⁶⁹

$$\delta \varrho(\mathbf{r}) = \delta \varrho_A(\mathbf{r}) + \delta \varrho_B(\mathbf{r}) \quad (18a)$$

and

$$\delta c(\mathbf{r}) = x_B \delta \varrho_A(\mathbf{r}) - x_A \delta \varrho_B(\mathbf{r}), \quad (18b)$$

$\delta \varrho(\mathbf{r})$ fluctuates around the total density $\varrho = (N_A + N_B) / V$. In Fourier space, the corresponding spatial correlation functions are defined as

$$S_{\varrho\varrho}(|\mathbf{k}|) = \frac{1}{N} \langle \delta \varrho_{\mathbf{k}}^* \delta \varrho_{\mathbf{k}} \rangle, \quad (19a)$$

$$S_{cc}(|\mathbf{k}|) = N \langle \delta c_{\mathbf{k}}^* \delta c_{\mathbf{k}} \rangle, \quad (19b)$$

and

$$S_{\varrho c}(|\mathbf{k}|) = \text{Re} \langle \delta \varrho_{\mathbf{k}}^* \delta c_{\mathbf{k}} \rangle, \quad (19c)$$

where, e.g., $\delta \varrho_{\mathbf{k}} = \int_V e^{i\mathbf{k}\cdot\mathbf{r}} \delta \varrho(\mathbf{r}) d^3r$ and, see below, $\delta \varrho_{\mathbf{k}}^{(\alpha)} = \int_V e^{i\mathbf{k}\cdot\mathbf{r}} \delta \varrho_\alpha(\mathbf{r}) d^3r$.

From on-the-fly calculations of the MD simulations, we have determined the partial structure factors⁶⁸ $S_{\alpha\beta}(|\mathbf{k}|) = (f_{\alpha\beta} / N) \langle \delta \varrho_{-\mathbf{k}}^{(\alpha)} \delta \varrho_{\mathbf{k}}^{(\beta)} \rangle$, where $f_{\alpha\beta} = 1$ for $\alpha = \beta$ and $f_{\alpha\beta} = 1/2$ for $\alpha \neq \beta$, which allow us to determine

$$S_{\varrho\varrho}(k) = S_{AA}(k) + S_{BB}(k) + 2S_{AB}(k), \quad (20a)$$

$$S_{cc}(k) = x_B^2 S_{AA}(k) + x_A^2 S_{BB}(k) - 2x_A x_B S_{AB}(k), \quad (20b)$$

and

$$S_{\varrho c}(k) = x_B S_{AA}(k) - x_A S_{BB}(k) + (x_B - x_A) S_{AB}(k). \quad (20c)$$

Here, we are primarily interested in the critical fluctuations of the composition, which are borne out by $S_{cc}(k)$ for small k . The latter is of the (extended) Ornstein–Zernike form^{2,68}

$$S_{cc}(k) \simeq \frac{\varrho k_B T \chi}{[1 + k^2 \xi^2]^{1-\eta/2}}, \quad k\sigma \ll 1, \quad (21)$$

which defines both the static order parameter susceptibility $\chi \sim \tau^{-\gamma}$ and the correlation length $\xi \sim \tau^{-\nu}$ which in real space governs the exponential decay of the correlation functions. The anomalous dimension $\eta \approx 0.036$ follows from the exponent relation⁵ $\gamma = \nu(2 - \eta)$ and the values in Eq. (2). Exemplary results for $S_{cc}(k)$ and $S_{\varrho\varrho}(k)$ are shown in Fig. 4, for model I with $\varrho\sigma^3 = 0.7$, on double-logarithmic scales. For the studied range of temperatures, $T_c^* \leq T^* \leq 2.3$, all curves for $S_{cc}(k)$ display a minimum near $k\sigma \approx 3$ and are not sensitive to

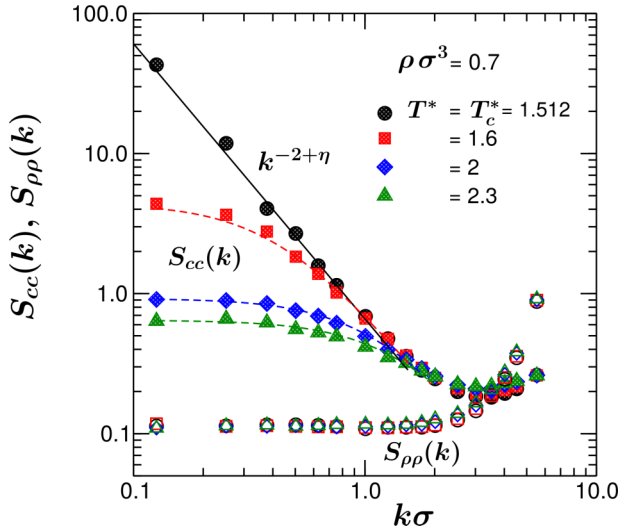


FIG. 4. Static structure factors $S_{cc}(k)$ (filled upper symbols) and $S_{\rho\rho}(k)$ (open lower symbols) for model I ($\rho\sigma^3 = 0.7$, $L = 50\sigma$) at four dimensionless temperatures $T^* \geq T_c^* = 1.512$ [see Eq. (19)]. The dashed lines show fits to the extended Ornstein-Zernike form [Eq. (21)] for $T > T_c$. The solid line indicates the critical law $S_{cc}(k, T = T_c) \sim k^{-2+\eta}$, $\eta = 0.036$, which appears as a straight line on the double-logarithmic scales. Error bars are of the size of the symbols.

temperature for k larger than this. $S_{cc}(k)$ increases as $k \rightarrow 0$, which, due to the divergence of $\chi \sim \tau^{-\gamma}$ at T_c , becomes stronger as $T \rightarrow T_c$. This reflects the enhancement of the critical composition fluctuations with a concomitant increase of the correlation length ξ . The data for $S_{cc}(k)$ for $T > T_c$ exhibit a nice consistency with the theoretical extended Ornstein-Zernike form, depicted by the dashed lines in Fig. 4, over approximately one decade in wavenumber k . Right at T_c , the data for $S_{cc}(k)$ follow for one decade in k the expected critical power law²

$$S_{cc}(k \rightarrow 0, T = T_c) \sim k^{-2+\eta}, \quad (22)$$

emerging from Eq. (21) for $k\xi \gg 1$.

To the contrary, the density fluctuations, described by $S_{\rho\rho}(k)$, do not change appreciably within the temperature range considered (Fig. 4). There is no critical enhancement for small wave numbers and the spatial range of the density-density correlations is short near the demixing transition with $\rho\sigma^3 = 0.7$. The value of $S_{\rho\rho}(k \rightarrow 0) = \rho k_B T \kappa_T$ yields the isothermal compressibility $\kappa_T = \kappa_T^* \sigma^3 / \varepsilon$ of the fluid, which diverges at a liquid-vapor critical point. Along the λ -line $T_c(\rho)$, it increases from $\kappa_c^* := \kappa_T^*(T = T_c) \approx 0.02$ for the highly incompressible fluid at $\rho\sigma^3 = 1$ to $\kappa_c^* \approx 0.11$ at $\rho\sigma^3 = 0.7$ (Table I). In all cases one has $S_{\rho\rho}(k \rightarrow 0) \ll S_{cc}(k \rightarrow 0)$. From this we conclude that, for the densities considered here, the liquid-vapor and the demixing critical points are sufficiently well separated.

In order to probe the location of the line of the liquid-vapor critical points, we have lowered the density along the isotherm $T^* = 1.51 \approx T_c^*(\rho\sigma^3 = 0.7)$. Indeed, for $\rho\sigma^3 \lesssim 0.6$ the corresponding structure factors $S_{\rho\rho}(k)$, shown in Fig. 5, display the emergence of critical density fluctuations via a monotonic increase of the compressibility by a factor of 19. Further, the value of $\kappa_T^*(\rho\sigma^3 = 0.3, T^* = 1.51)$ is

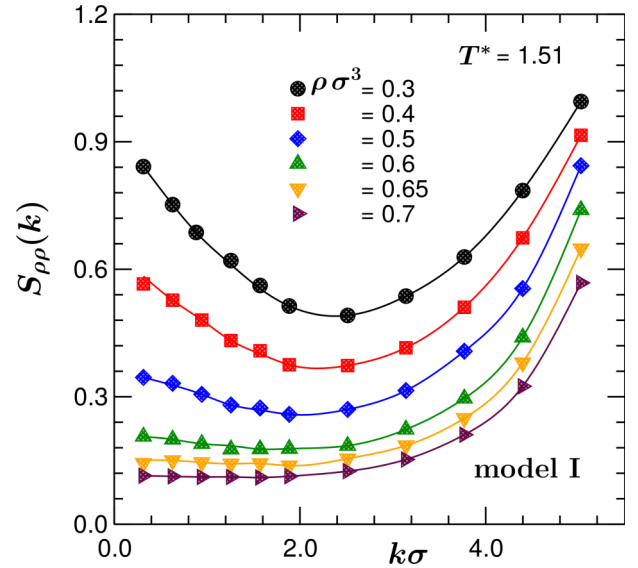


FIG. 5. Static structure factor $S_{\rho\rho}(k)$ for model I ($L = 20\sigma$) for six number densities ρ and fixed dimensionless temperature $T^* = 1.51$. Lines are drawn by using suitable splines.

ca. 7.4 times larger than $\kappa_c^* \approx 0.25$ at $T_c(\rho\sigma^3 = 0.6)$, following the λ -line (Fig. 3). This suggests that κ_T^* does not diverge along the λ -line, which implies that the λ -line and the line of liquid-vapor critical points do not meet, thus rendering the occurrence of a tri-critical point in model I as to be unlikely.

B. Correlation length and static order parameter susceptibility

For a broad range of temperatures $T_c \leq T \leq 2T_c$, we have run extensive MD simulations for three binary liquid mixtures in model I and two binary liquid mixtures in model II. Fitting Eq. (21) to the data for $S_{cc}(k)$ we have obtained the static order parameter susceptibilities $\chi(T)$ and the correlation lengths $\xi(T)$. The data nicely follow the asymptotic power laws

$$\chi(T \rightarrow T_c) \approx \chi_0 \tau^{-\gamma}, \quad \xi(T \rightarrow T_c) \approx \xi_0 \tau^{-\nu} \quad (23)$$

near the respective critical temperatures T_c with the 3d Ising critical exponents γ and ν (see Figs. 6 and 7 for the binary liquid mixtures in model I). Finite-size effects become apparent for $\tau \leq 0.02$, for which the data for both quantities fall short of the asymptotic law. Interestingly, this occurs already for correlation lengths $\xi \approx 4\sigma \approx L/10$. The fit has also identified a temperature range, where corrections to the asymptotic power laws are not yet important. The necessity for such corrections is reflected by the data for $\chi(\tau)$ at $\rho\sigma^3 = 0.7$, which bend upwards for $\tau \geq 0.2$ (Fig. 6). The amplitudes χ_0 and ξ_0 are non-universal quantities and are listed in Table I for each fluid. The trend of a decreasing χ_0 upon increasing ρ (model I) may be explained by the fact that the re-arrangement of particle positions becomes more costly (in terms of potential energy) at denser packing, reducing the response of the system. Even smaller values of χ_0 have been found for model II, with no pronounced dependence on the strength ε_{AB} of the repulsion. Across all five binary mixtures

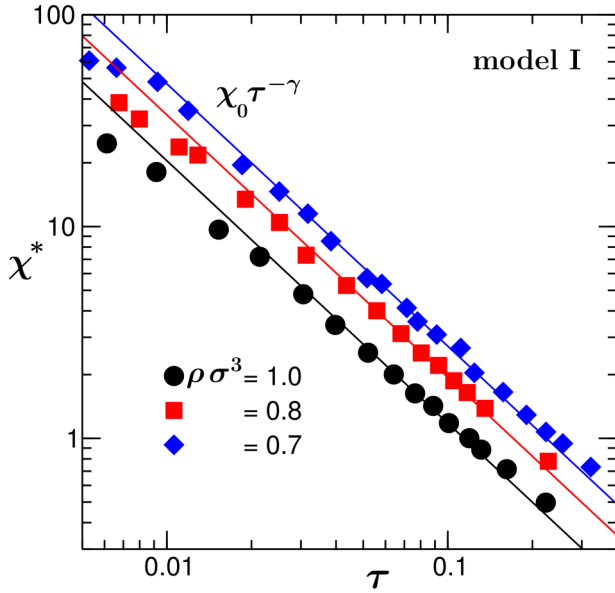


FIG. 6. Reduced static order parameter susceptibility $\chi^* = \chi \varepsilon \sigma^{-3}$ [Eqs. (21) and (23)] as function of $\tau = (T - T_c)/T_c$ within model I for three number densities. The system sizes are $L/\sigma = 42, 47$, and 50 for $\rho\sigma^3 = 1.0, 0.8$, and 0.7 , respectively. Straight lines indicate the asymptotic power law $\chi(T \rightarrow T_c) \approx \chi_0 \tau^{-\gamma}$ with $\gamma = 1.239$. Error bars are smaller than the symbol sizes.

the amplitude ξ_0 of the correlation length varies only mildly between 0.42σ and 0.53σ .

For comparison, we have also determined the order parameter susceptibility χ via the SGMC simulations above T_c from the variance of the fluctuating composition.^{2,68} For the symmetric binary liquid mixtures as considered here, one has $\rho k_B T \chi = N(\langle x_A^2 \rangle - \langle x_A \rangle^2)$ with $\langle x_A \rangle = 1/2$ at $T = T_c$ due to the model symmetry and above T_c for the mixed phase. We have found that the results obtained from these two approaches agree.

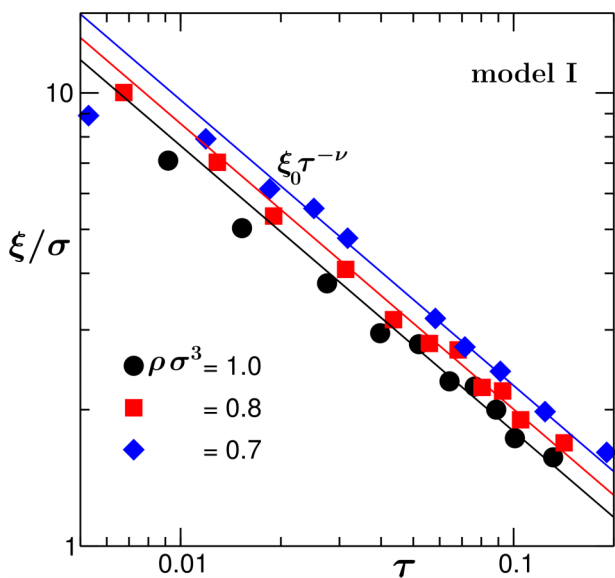


FIG. 7. Correlation length ξ of the concentration fluctuations [Eqs. (21) and (23)] as a function of τ on double-logarithmic scales. Straight lines refer to the asymptotic power law $\xi(T \rightarrow T_c) \approx \xi_0 \tau^{-\nu}$ with $\nu = 0.630$. All simulation parameters are the same as in Fig. 6. Relative error bars are within 1%–9%.

V. TRANSPORT COEFFICIENTS

A. Interdiffusion constant

A critical point leaves its marks both in space and time: upon approaching criticality the correlation length diverges and the relaxation of a fluctuation or of a perturbation slows down. The latter manifests itself in terms of universal power-law behaviors of transport coefficients upon approaching T_c . For example, a gradient in the composition field $\delta c(\mathbf{r}, t)$ [Eq. (18b)] generates a collective current^{42,70,71}

$$\mathbf{J}_{AB}(t) = x_B \sum_{i=1}^{N_A} \mathbf{v}_i^{(A)}(t) - x_A \sum_{i=1}^{N_B} \mathbf{v}_i^{(B)}(t), \quad (24)$$

the magnitude of which is captured by the interdiffusion constant D_m . This coefficient controls the collective diffusion of the composition field and obeys a Green–Kubo relation,^{42,70,71}

$$D_m = \frac{1}{d N S_{cc}(k=0)} \int_0^\infty \langle \mathbf{J}_{AB}(t) \cdot \mathbf{J}_{AB}(0) \rangle dt, \quad (25)$$

where d is the spatial dimension and $S_{cc}(k=0) = \rho k_B T \chi$. The interdiffusion constant is a combination of a static property, i.e., the concentration susceptibility χ , and a pure dynamic quantity, the concentration conductivity or Onsager coefficient^{42,70,71}

$$\mathcal{L} = \chi D_m. \quad (26)$$

\mathcal{L} connects gradients in the chemical potentials with the current \mathbf{J}_{AB} ; as its dimensionless form we use $\mathcal{L}^* := \mathcal{L} \varepsilon_0 \sigma^{-5}$.

The numerical evaluation of the time integral in Eq. (25) is difficult due to statistical noise and hydrodynamic long-time tails of the current correlators.⁶⁸ An alternative route to compute \mathcal{L} is based on the generalized Einstein relation^{45,71,72}

$$\mathcal{L} = \lim_{t \rightarrow \infty} \frac{N_\alpha^2}{2 \rho N k_B T} \frac{d}{dt} \delta \mathcal{R}_\alpha^2(t) \quad (27)$$

for $\alpha \in \{A, B\}$ with the collective mean-square displacement

$$\delta \mathcal{R}_\alpha^2(t) = \left\langle \left| \int_0^t \mathbf{V}_\alpha(t) dt \right|^2 \right\rangle, \quad \mathbf{V}_\alpha(t) = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \mathbf{v}_i^{(\alpha)}(t), \quad (28)$$

defined in terms of the centres-of-mass velocity $\mathbf{V}_\alpha(t)$ by considering particles of species α only. Note that $\mathbf{V}_A(t) = -\mathbf{V}_B(t)$ for a symmetric mixture ($m_A = m_B$, $N_A = N_B$) due to conservation of the total momentum, $\sum_\alpha m_\alpha N_\alpha \mathbf{V}_\alpha = 0$. Our simulation data tell that the results for \mathcal{L} as obtained from both methods [Eqs. (25) and (27)] coincide within the error bars. The latter route, however, exhibits superior averaging properties, in line with previous findings for a different system concerning the motion of a tagged particle.⁷³ The success of the method hinges on evaluating $\delta \mathcal{R}_\alpha^2(t)$ by using a certain “blocking scheme,”^{46,50} which resembles a non-averaging multiple- τ correlator and naturally generates a semi-logarithmic time grid, particularly suitable for the description of slow processes. With this, the time derivative in Eq. (27) can simply be computed from central difference quotients. The results for \mathcal{L} presented here have been obtained by applying this method.

The interdiffusion constant [Eq. (25)] can be decomposed as $D_m = \Delta D_m + D_b$ into a singular contribution ΔD_m stemming from critical fluctuations in the fluid at large length scales and an omnipresent analytic background term D_b arising due to short-length-scale fluctuations.⁷⁴ As predicted by MCT and dynamic RGT, asymptotically close to the critical temperature ΔD_m follows the Einstein–Kawasaki relation^{22,75}

$$\Delta D_m(T \rightarrow T_c) \simeq \frac{R_D k_B T}{6\pi\bar{\eta}\xi} \simeq D_{m,0} \tau^{\nu x_D}, \quad (29)$$

where R_D is a universal dimensionless number which will be discussed in Sec. IV [see Eq. (39) below]; the asymptotic equality on the right defines the critical amplitude $D_{m,0}$ with its dimensionless form $D_{m,0}^* := D_{m,0} t_0 \sigma^{-2}$. Note that the critical divergences of $\bar{\eta}$ [Eqs. (5) and (6)] and ξ imply the power-law singularity of ΔD_m [Eq. (29)] and the scaling relation $x_D = 1 + x_\eta$ [see Eqs. (1), (6), and (7)]. It was demonstrated before^{38,39,42} that the background contribution must be taken into account for a proper description of the simulation data. Anticipating that also the background term is proportional to temperature,⁴³ $D_b(T) = \mathcal{L}_b(T)/\chi(T) \simeq \mathcal{L}_{b,0} k_B T / \chi(T)$, suggests that the ratio $\mathcal{L}(T)/k_B T$ is described by the asymptotic law

$$\frac{\mathcal{L}(T)}{k_B T} \simeq \mathcal{L}_0 \tau^{-\nu x_\lambda} + \mathcal{L}_{b,0}, \quad T \rightarrow T_c, \quad (30)$$

with the exponent combination

$$\nu x_\lambda = \nu(1 - \eta - x_\eta) \approx 0.567, \quad (31)$$

where we have used Eqs. (1) and (26). The connection to the amplitude of the interdiffusion constant is provided by

$$D_{m,0} = \mathcal{L}_0 k_B T_c / \chi_0. \quad (32)$$

We have computed \mathcal{L} for five binary liquid mixtures for a wide range of temperatures, $1.01T_c \leq T \lesssim 2T_c$ (see Fig. 8; the

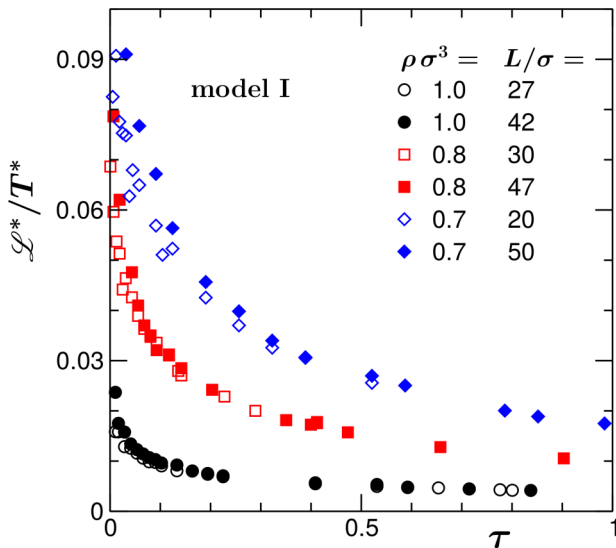


FIG. 8. Plot of \mathcal{L}^*/T^* with $\mathcal{L}^* = \mathcal{L} \varepsilon t_0 \sigma^{-5}$ [Eqs. (25)–(28)] for model I as a function of the reduced temperature τ , for three number densities ρ . For each ρ , data for two different system sizes L are presented. Relative error bars are within 3%–9%.

data for model II are not shown). For the three binary liquid mixtures belonging to model I and within the investigated range of temperatures, $\mathcal{L}/(k_B T)$ increases by factors between 4.3 and 7.5 upon approaching T_c . This indicates the onset of the expected divergence [Eq. (30)]. The remaining task is to determine the values of the critical amplitude \mathcal{L}_0 and the background contribution $\mathcal{L}_{b,0}$ for each mixture such that Eq. (30) describes the data. Here, automated fitting relying on non-linear regression algorithms is not suitable due to the asymptotic nature of power laws. Instead, the value for $\mathcal{L}_{b,0}$ has been adjusted first, such that plotting $\Delta \mathcal{L}(T)/(k_B T) := \mathcal{L}(T)/(k_B T) - \mathcal{L}_{b,0}$ as a function of τ on double-logarithmic scales renders the data to follow straight lines of slope $-\nu x_\lambda$ for intermediate temperatures $0.1 \lesssim \tau \lesssim 0.5$ (Fig. 9). Indeed, subsequently for all investigated mixtures, the critical singularity $\Delta \mathcal{L}(T)/k_B T \sim \tau^{-\nu x_\lambda}$ [Eq. (30)] can be identified in the data, which allows us to infer the critical amplitudes \mathcal{L}_0 (Table I).

However, for small $\tau \lesssim 0.1$, the data for $\Delta \mathcal{L}^*/T^*$ systematically deviate from the asymptotic power law. This is expected due to the emergence of finite-size corrections close to T_c ,^{38,39,42} which are significant despite the large simulation boxes used ($L/\xi \gtrsim 7$). We find that \mathcal{L}_0 increases by a factor of ≈ 6 upon decreasing the number density ρ of the fluid. On the other hand, the background contribution $\mathcal{L}_{b,0}$ turns out to be almost insensitive to changes in the density so that the background term in Eq. (30) becomes less relevant for smaller ρ .

B. Shear viscosity

Another transport quantity of central interest is the shear viscosity $\bar{\eta}$ (not to be confused with the critical exponent η of the structure factor). Due to critical slowing down, $\bar{\eta}(T)$ is expected to diverge at T_c . We have computed this quantity using both the Green–Kubo and the Einstein–Helfand

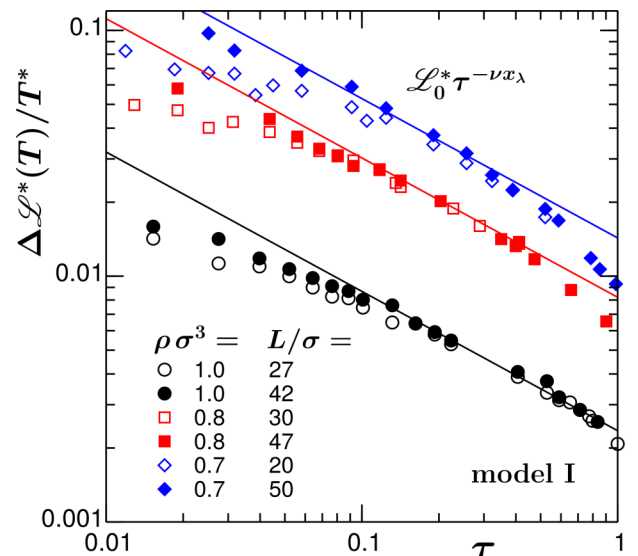


FIG. 9. The same data as in Fig. 8 in terms of $\Delta \mathcal{L}^*/T^* = \mathcal{L}^*/T^* - \mathcal{L}_{b,0}^*$ after adjusting the background contribution $\mathcal{L}_{b,0}^*$. Solid lines refer to the power law $\Delta \mathcal{L}/(k_B T) \simeq \mathcal{L}_0 \tau^{-\nu x_\lambda}$ with $\nu x_\lambda = 0.567$ [Eq. (31)].

formulae, involving the stress tensor as the generalized current. The Green–Kubo formula reads^{68,76}

$$\bar{\eta} = \frac{\rho}{3k_B T} \int_0^\infty [C_{xy}(t) + C_{yz}(t) + C_{xz}(t)] dt, \quad (33)$$

and is based on the autocorrelators $C_{ij}(t)$ of the off-diagonal elements of the stress tensor Π_{ij} [Eq. (15)],

$$C_{ij}(t) = \frac{1}{N} \langle \Pi_{ij}(t) \Pi_{ij}(0) \rangle. \quad (34)$$

The autocorrelators $C_{ij}(t)$ are normalized by N in order to render a finite value of $C_{ij}(t)$ in the thermodynamic limit.

Starting with the Helfand moments^{76,77}

$$\delta G_{ij}^2(t) = \frac{1}{N} \left\langle \left(\int_0^t \Pi_{ij}(t') dt' \right)^2 \right\rangle, \quad (35)$$

we have computed $\bar{\eta}$ alternatively by means of the Einstein–Helfand formula^{76,77}

$$\bar{\eta} = \lim_{t \rightarrow \infty} \frac{\rho}{6k_B T} \frac{d}{dt} [\delta G_{xy}^2(t) + \delta G_{yz}^2(t) + \delta G_{xz}^2(t)]. \quad (36)$$

The expressions in Eqs. (34) and (36) explicitly include averages over the different Cartesian directions due to isotropy of the mixed phase. We have checked that both routes yield the same values of $\bar{\eta}$, with the Einstein–Helfand formula generating smaller error bars.

The thermal singularity of $\bar{\eta}$ in model H' is the same as in model H and reads^{6,23}

$$\bar{\eta} \approx \eta_0 \tau^{-\nu x_\eta}, \quad \nu x_\eta \approx 0.043, \quad (37)$$

which can be expressed as $\bar{\eta} \approx \eta_0 \xi_0^{-x_\eta} \xi^{x_\eta}$ with $\xi \approx \xi_0 \tau^{-\nu}$ [compare Eq. (5)]. Figure 10 shows the shear viscosity $\bar{\eta}(\tau)$

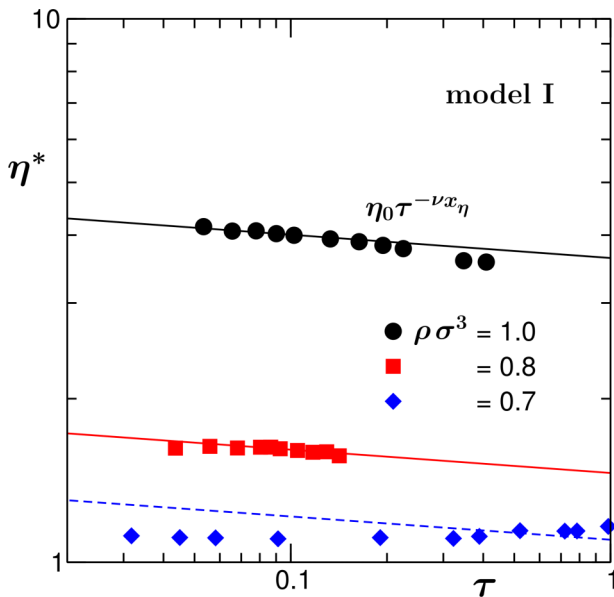


FIG. 10. Dimensionless shear viscosity $\bar{\eta}^* = \bar{\eta}\sigma^3/\varepsilon t_0$ as a function of τ , for model I and three number densities. The chosen system sizes are $L = 47\sigma$, 42σ , and 50σ for $\rho\sigma^3 = 1.0$, 0.8 , and 0.7 , respectively. The straight lines indicate the asymptotic critical exponent $\nu x_\eta \approx 0.043$; solid lines are fits to the data. For $\rho\sigma^3 = 0.7$, the large error bars have precluded a fit to the amplitude η_0 ; instead, η_0 has been estimated from Eq. (39) using $R_D = 1.0$ (dashed line). Relative errors in $\bar{\eta}$ vary between 2% and 8%. The resulting values of η_0 are reported in Table I.

for three number densities ρ on double-logarithmic scales. The observed increase of $\bar{\eta}$ by a factor of ≈ 3.3 as $\rho\sigma^3$ is varied from 0.7 to 1.0 supports the intuitive picture that transport is slower in denser fluids. In order to facilitate the direct determination of η_0 , instead of performing a finite-size scaling analysis,⁴⁷ we have considered particularly large system sizes (see the caption of Fig. 10). By fixing the critical exponent to $\nu x_\eta = 0.043$, we have obtained the amplitude η_0 by fits of Eq. (37) to the data in the temperature range that is unaffected by finite-size effects; the results are listed in Table I. The data for $\bar{\eta}$ at $\rho\sigma^3 = 1.0$ and 0.8 are compatible with the critical power law (see solid lines in Fig. 10); the divergence, however, is hardly inferred from the figure due to the tiny value of the exponent νx_η , albeit the present error bars for $\bar{\eta}$ are much smaller compared to those reported in the literature. For $\rho\sigma^3 = 1.0$, due to corrections the data for $\bar{\eta}$ fall short of the asymptotic line for $\tau > 0.2$. For $\rho\sigma^3 = 0.7$, we refrain from providing a value for η_0 because for this low density the determination of η_0 requires enormous statistical averaging, which we have not yet achieved. Yet, from the value $R_D = 1.0$ of the universal amplitude ratio [Eq. (39) below] one finds $\eta_0 \approx 1.1$. The dashed line in Fig. 10 corresponds to this predicted value.

Actually, as in the case of the Onsager coefficient \mathcal{L} , Eq. (37) has also to be augmented by an analytic background contribution η_b . For the shear viscosity, this background term has been argued to be of multiplicative character,⁷⁸ i.e., the universal amplitude η_0 is proportional to the background viscosity and takes the form $\eta_0 = \eta_b(q_0\xi_0)^{x_\eta}$ with a certain (necessarily system-specific) wavenumber q_0 .^{33,43} Thus, in contrast to the case of the Onsager coefficient, the analysis of the critical divergence of the shear viscosity is not hampered by the presence of an analytic background.

VI. UNIVERSAL AMPLITUDE RATIOS

Generically, critical amplitudes are non-universal and depend on microscopic details of the systems. However, certain ratios of critical amplitudes are known to be universal. One such ratio for static quantities is^{4,5,79}

$$R_\xi^+ R_c^{-1/d} = \xi_0^+ \left(\frac{\varphi_0^2}{k_B T_c \chi_0^+} \right)^{1/d}, \quad (38)$$

as predicted by the hypothesis of two-scale factor universality. Here, the superscript “+” emphasizes that (apart from φ_0) the amplitudes correspond to $T > T_c$. For binary liquid mixtures belonging to the 3d Ising universality class, the value of $R_\xi^+ R_c^{-1/d}$, as estimated theoretically and experimentally, lies within the ranges $[0.68, 0.70]$ and $[0.67, 0.72]$, respectively.⁵

The so-called Kawasaki amplitude $R_D = 6\pi\bar{\eta}\xi/(k_B T \Delta D_m)$ [Eq. (29)] is a universal amplitude ratio involving transport coefficients, i.e., the critical enhancement ΔD_m of the mutual diffusivity [Eq. (29)]. Inserting the asymptotic singular behaviors of ξ , χ , and $\bar{\eta}$ [Eqs. (23) and (37)] as well as $\Delta D_m \approx \mathcal{L}_0 \tau^{-\nu x_\lambda} / \chi_0$ [see Eqs. (26) and (30)], the temperature dependence drops out and one finds

$$R_D = \frac{6\pi\eta_0\xi_0\mathcal{L}_0}{\chi_0}. \quad (39)$$

This combination of non-universal static and dynamic critical amplitudes has been shown to be a universal number.⁷⁴ Theoretical calculations based on dynamic RGT predict²⁴ $R_D \approx 1.07$, while MCT provides³³ $R_D \approx 1.03$; experimental data yield^{33,74} $R_D = 1.01 \pm 0.04$.

A calculation of the amplitude ratio $R_\xi^+ R_c^{-1/d}$ in Eq. (38) combines the uncertainties in the separately determined amplitudes φ_0 , ξ_0 , and χ_0 . Table I lists these values. Equivalently, the universal ratio is given directly as the limit $\tau \searrow 0$ of the combination $Z(\tau) := \xi(\tau)[\phi(\tau)^2/(k_B T_c \chi(\tau))]^{1/3}$. However, the omnipresent finite-size corrections prohibit us from taking the limit rigorously. Yet, one can expect to find a temperature range close to T_c in which all quantities ϕ , ξ , and χ follow their asymptotic critical laws. This implies that in this temperature range $Z(\tau)$ displays a plateau at the value of $R_\xi^+ R_c^{-1/d}$. Figure 11 provides a test of this approach for the three mixtures within model I. Indeed, a plateau may be inferred for each data set after averaging out the scatter of the data points. The estimates of $R_\xi^+ R_c^{-1/d}$ obtained this way (0.738 ± 0.016 , 0.70 ± 0.03 , 0.722 ± 0.023 for $\rho\sigma^3 = 1.0, 0.8, 0.7$, respectively, within model I) match well with those obtained from Eq. (38) by inserting the critical amplitudes, but exhibit slightly smaller errors. The results for the 5 binary mixtures studied here as well as the results of Ref. 42 corroborate that $R_\xi^+ R_c^{-1/d}$ is a universal number with a value of 0.70 ± 0.01 (Fig. 12). Our estimate for $R_\xi^+ R_c^{-1/d}$ is in good agreement with previous values for this universal ratio obtained from theory and experiments [see text below Eq. (38)].

Concerning the dynamic amplitude ratio R_D , we report results for model I only for $\rho\sigma^3 = 1.0$ and 0.8 because it is difficult to resolve the critical behavior of the viscosity at low densities. A similar analysis as above in terms of

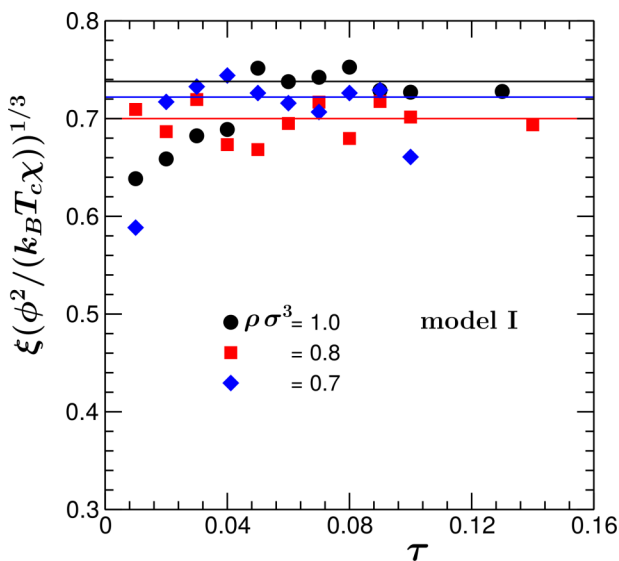


FIG. 11. Temperature dependence of the dimensionless and supposedly universal quantity $\xi(\phi^2/(k_B T_c \chi))^{1/3}$ within model I for three number densities. Symbols correspond to simulation data and solid lines represent averages of the data points.

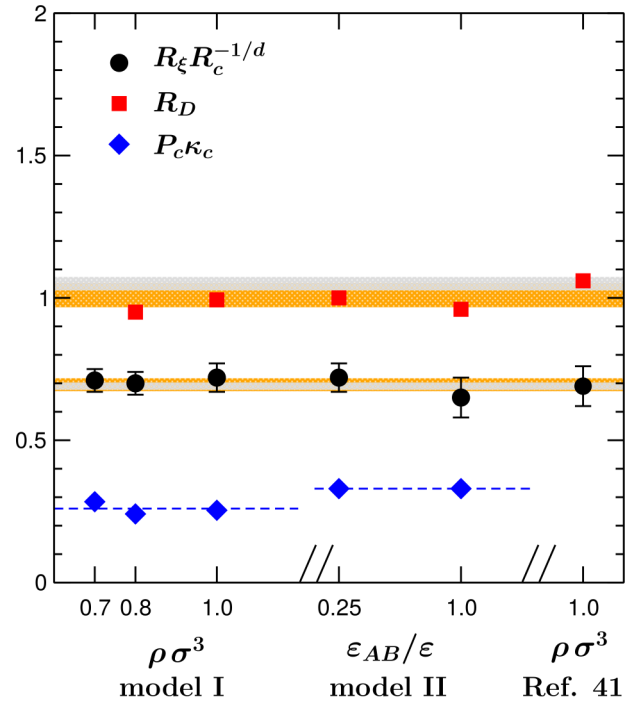


FIG. 12. The universal static amplitude ratio $R_\xi^+ R_c^{-1/d}$, the dynamic universal amplitude ratio R_D , and the dimensionless quantity $P_c \kappa_c$ at criticality for various binary liquid mixtures within models I and II. The grey and orange regions represent the ranges of the theoretical and experimental predictions, respectively. The dashed lines correspond to the averages for $P_c \kappa_c$ within models I and II, respectively. The relative error bars of R_D are about 20%.

$Y(\tau) = 6\pi\eta\xi\Delta\mathcal{L}/k_B T \chi$ has turned out to be inconclusive, in that no plateau in $Y(\tau)$ has emerged. We attribute this to the fact that the critical range of temperatures (free from both asymptotic and finite-size corrections) for the Onsager coefficient is located at higher temperatures than for the other quantities entering Eq. (39) (see also Figs. 6, 7, 9, and 10). Therefore, Table I lists the values for R_D as obtained from Eq. (39). Despite significant error bars of about 20%, the estimates coincide surprisingly well with the expectation $R_D \approx 1.0$ (Fig. 12).

Finally, we note that the dimensionless product $P_c \kappa_c$ of pressure and compressibility at the demixing transition appears to stay almost constant at 0.26 ± 0.02 within model I (insensitive to the density ρ) and at ca. 0.33 for model II (insensitive to the strength ϵ_{AB} of repulsion). This is remarkable because P_c and κ_c separately vary across these ranges by almost an order of magnitude. However, here we point out that the product $P_c \kappa_c$ is not related to the order parameter field, which is the concentration, but to the number density field, which in model H' serves as a secondary conserved field.⁶ Thus, there is no theoretical basis to consider $P_c \kappa_c$ as a universal number; indeed the values of $P_c \kappa_c$ are different for models I and II.

VII. SUMMARY AND CONCLUSIONS

We have computationally investigated the static and dynamic properties of five symmetric binary liquid mixtures close to their continuous demixing transitions. To this end, we

have employed a combination of Monte Carlo simulations in the semi-grand canonical ensemble and molecular dynamics (MD) simulations. While the former is suited best to determine the phase diagram, only the latter obeys the conservation laws of actual liquid mixtures and thus properly captures the critical dynamics associated with model H' . Previous computational studies of the critical behavior of such mixtures have been based on small system sizes in conjunction with suitable finite-size scaling analyses. A massively parallel implementation of the MD simulations using GPUs made it possible to explore much larger system sizes than before, which has allowed us to determine the critical amplitudes directly.

The chosen mixtures represent a wide range of critical temperatures T_c , number densities ρ , and isothermal compressibilities κ_T . For the family of mixtures considered, the particles interact via truncated Lennard-Jones potentials. The interaction potential $u_{AB}(r)$ for pairs of unlike particles has been chosen to either include the usual attractive part or to be purely repulsive, which we refer to as models I and II, respectively. For the fluids in model I, the density ρ has been varied, while within model II the strength ε_{AB} of the repulsion between unlike species has been varied. All results of the data analysis have been compiled in Table I. The main findings of our work are the following:

(i) For each fluid, we have calculated the phase diagram in the temperature–composition plane, from which the corresponding critical temperatures T_c have been extracted by using the critical scaling of the order parameter (Fig. 1) and Binder's cumulant intersection method (Fig. 2). We have found that the values of T_c within model II are a factor of ca. 2 higher than for otherwise comparable fluids in model I. Within model II, reinforcing the repulsion ε_{AB} leads to a drastic increase of T_c . Further, at the demixing transition, we have computed the pressure P_c and the isothermal compressibility κ_c , which exhibit a large variability across all mixtures, covering almost one order of magnitude.

(ii) The loci of the liquid–liquid critical points $T_c(\rho)$, also referred to as λ -line, have been calculated within model I. This curve $T_c(\rho)$ is non-monotonic, indicating a re-entrance phenomenon upon varying the density along an isotherm (Fig. 3). In this context, for model I we have also investigated the potential occurrence of a critical end point or a tri-critical point at which the λ -line meets the liquid–vapor critical point. Our results for the isothermal compressibility (Fig. 5) indicate that this is not the case. This issue calls for additional future investigations.

(iii) The structural properties of the mixtures have been analyzed in terms of the static structure factors $S_{cc}(k)$ and $S_{\rho\rho}(k)$ of the composition and density fields, respectively (Fig. 4). As expected, long-wavelength fluctuations of the composition become dominant near the demixing transition: for small wave numbers, $S_{cc}(k \rightarrow 0)$ increases sharply as T_c is approached, at which the critical power law $S_{cc}(k) \sim k^{-2+\eta}$ is observed over one decade in k which is facilitated by the large system sizes chosen. To the contrary, $S_{\rho\rho}(k)$, which is probing density fluctuations, is almost insensitive to temperature changes in the range $T_c \leq T < 1.6T_c$; in particular, it does not display any critical enhancement at small k .

(iv) From $S_{cc}(k)$ we have determined the correlation length ξ and the order parameter susceptibility χ . For both quantities, the scaling with the corresponding critical Ising exponents is confirmed (Figs. 6 and 7), allowing us to extract the non-universal critical amplitudes ξ_0 and χ_0 . We have found that χ_0 decreases upon increasing density (model I), which we attribute to an energetically penalized particle rearrangement at denser packing. The values of χ_0 are less sensitive to changes in the strength of the AB repulsion (model II). The correlation length ξ is limited by the finite system size. Nonetheless, we have been able to achieve values of up to $\xi \approx 10\sigma$ in our simulations. Across all five binary fluid mixtures, its amplitude varies only mildly around $\xi_0 \approx 0.5\sigma$.

(v) The critical transport behavior has been studied in terms of the Onsager coefficient $\mathcal{L} = \chi D_m$ and the shear viscosity $\bar{\eta}$, the former also determining the interdiffusion constant D_m . Within model I, the Onsager coefficient and thus its critical amplitude \mathcal{L}_0 increase by a factor of 6 upon varying the density from $\rho\sigma^3 = 1$ to 0.7 (Figs. 8 and 9); concomitantly, the shear viscosity $\bar{\eta}$ decreases by a factor of 3 (Fig. 10). This trend is in line with our notion that mass diffusion is faster in a less dense fluid; it also has direct consequences for the computational efficiency of a model. The asymptotic critical enhancement of \mathcal{L} is obscured, first, by the non-universal analytic background contribution away from T_c and, second, by finite-size corrections close to T_c , which are still significant despite the large simulation boxes we used. These issues have prevented us to obtain accurate estimates of \mathcal{L}_0 . Furthermore, the critical behavior of $\bar{\eta} \sim |T - T_c|^{-\nu_{\chi\bar{\eta}}}$, $\nu_{\chi\bar{\eta}} \approx 0.043$ is difficult to assess reliably due to the smallness of the critical exponent. We have obtained the critical amplitude for 3 out of the 5 mixtures (within model I for $\rho\sigma^3 = 1, 0.8$ and within model II for $\varepsilon_{AB} = 0.25\varepsilon$).

(vi) Finally, we have computed two universal amplitude ratios, involving several static and dynamic non-universal critical amplitudes (all above T_c). One such ratio of static quantities is $R_\xi^+ R_c^{-1/3}$ [Eq. (38)], the other ratio R_D is a combination of both static and dynamic amplitudes [Eq. (39)]. For both ratios, quantitative predictions are available for the universality classes of the models H and H' based on mode-coupling and dynamic renormalization group theories, which are supported by experimental data. Across all 5 mixtures studied and including the results of Ref. 42, the simulation results for the static ratio $R_\xi^+ R_c^{-1/3}$ yield a universal value 0.70 ± 0.01 , in agreement with theoretical predictions (Fig. 12). Our results for the dynamic ratio R_D are compatible with theoretical and experimental estimates, but they are subject to large uncertainties given the difficulties in determining the dynamic critical amplitudes \mathcal{L}_0 and η_0 . A notable finding is that the dimensionless product $P_c \kappa_c$ of pressure and compressibility is remarkably constant along the λ -line in model I and with respect to variations of the strength ε_{AB} of repulsion in model II (Fig. 12).

The present study reports the first comprehensive analysis of the density dependence of the critical amplitudes. The knowledge of these amplitudes for a given simulation model facilitates the calibration of the model to a given physical binary liquid mixture. As an example we refer to the well-characterized water–lutidine mixture⁸⁰ and model I for

$\rho\sigma^3 = 0.7$: first, the measured correlation length amplitude $\xi_0 \approx 0.2$ nm implies the length scale $\sigma \approx 0.4$ nm for all of the presented simulations. Second, the relaxation rate amplitude $\Gamma_0 \approx 25 \times 10^9 \text{ s}^{-1}$ yields the critical amplitude of the interdiffusion constant $D_{m,0} = \Gamma_0 \xi_0^2 / 2 \approx 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which has to be compared with the simulation result $D_{m,0} \approx 0.09 \sigma^2 / t_0$, fixing the time scale $t_0 \approx 30$ ps. The energy scale ε is set by the critical temperature, $T_c \approx 307$ K in the experiments and $k_B T_c \approx 1.51 \varepsilon$ in the simulations, and thus $\varepsilon / k_B \approx 203$ K or $\varepsilon \approx 2.8 \times 10^{-21}$ J. Accordingly, the universal amplitude ratios fix the critical amplitudes for a number of related physical quantities such as the composition susceptibility χ_0 , the viscosity η_0 , or the surface tension.⁸¹ The coarse-grained simulation models (replacing an organic molecule and water by symmetric Lennard-Jones spheres), however, come at the price that physical quantities not linked to the critical singularities may not be captured correctly. For instance, along these lines, the pressure at criticality is predicted to be $P_c \approx 110$ MPa, which is 3 orders of magnitude larger than the ambient pressure, while the compressibility $\kappa_c \approx 25 \times 10^{-10} \text{ Pa}^{-1}$ is too high by a factor of ≈ 5 . Increasing the density ρ will reduce the compressibility, but simultaneously increase the pressure and also slow down the overall dynamics (which is computationally expensive). Quantitative agreement with actual binary liquid mixtures can be achieved with force-field-based simulation models, see Ref. 82 for a recent study. Nevertheless, the comparably simple models discussed here can correctly describe the physical behavior at long wave lengths thanks to the universality of the demixing transition. The presented compilation of results may serve as a guide to find the simulation model that is best suited to address a specific phenomenon.

This study is supposed to stimulate further computational investigations concerning critical transport in fluids. Specifically, so far there are no dedicated computations of dynamic critical amplitudes below T_c and also none for liquid–vapor transitions, neither above nor below T_c . A quantitatively reliable determination of the ratio η_0/η_b is also of significant importance, in particular in view of the difficulties associated with obtaining an accurate value of this ratio from experiments.

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