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Citation: The Journal of Chemical Physics **140**, 014502 (2014); doi: 10.1063/1.4855656
View online: http://dx.doi.org/10.1063/1.4855656
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Is there a third order phase transition for supercritical fluids?

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(Received 5 September 2013; accepted 4 December 2013; published online 3 January 2014)

We prove that according to Molecular Dynamics (MD) simulations of liquid mixtures of Lennard-Jones (L-J) particles, there is no third order phase transition in the supercritical regime beyond Andrew's critical point. This result is in open contrast with recent theoretical studies and experiments which instead suggest not only its existence but also its universality regarding the chemical nature of the fluid. We argue that our results are solid enough to go beyond the limitations of MD and the generic character of L-J models, thus suggesting a rather smooth liquid-vapor thermodynamic behavior of fluids in supercritical regime. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4855656]

INTRODUCTION

When pressure and temperature increase beyond Andrew's critical point[1,2] a fluid enters in the so-called supercritical regime. Supercritical fluids are particularly convenient as solvents in a wide variety of applications, for example, for production of pharmaceutical powders.[3] However, despite their existence is known for more than a century, its potentiality started to be explored only in the last decades. In this context, the experimental[4–11] as well as theoretical[2,12–16] investigation of the fluid's behaviour around the critical point represents a mandatory task in order to clarify the essential features of superfluidity and explore its potentiality. In recent years, the work of Koga *et al.* claims the existence of the so-called "Koga-Line" in supercritical regime, that is a collection of foci of anomalies in some third-order derivatives of the Gibbs function.[11] The natural consequence is the prediction of a third-order phase transition beyond Andrews critical point; this latter, later on, was claimed in a theoretical work by Ma and Wang.[2] In Ref. 2, using a mean-field approach, not only is proved the existence of such a transition but it is also claimed its universality regardless of the specific molecular chemical structure. If such conclusions can be proved true, then the physics of superfluidity will become by far more clear: it would imply that by external manipulations of temperature and pressure, thermodynamics quantities related to the second order derivatives of Gibbs free energy, for example, the heat capacity c_P or the isothermal compressibility κ, will have abrupt variations which in turn may be programmed to change physical properties, e.g., of solutes, on demand. However, the interpretation of experimental results lies on the analysis of data according to ideal models whose constraints may not be fully met by the experimental conditions. On the other hand, theoretical models based on mean-field approaches cannot properly characterize the instantaneous fluctuations of the particle number density which are instead a key characteristic of fluids and whose accurate description is mandatory in order to predict the correct behaviour of second order derivatives of the Gibbs free energy, among which, for example, the isothermal compressibility. In this perspective it becomes mandatory to describe a fluid as a particle based liquid and as a consequence the treatment of the problem via molecular simulation. Unfortunately, at the current state of the art, in general, computationally affordable chemically detailed models for the supercritical regime are scarce[17,18] and even for those few available the capability of describing phase transitions is highly questionable (this is true even in standard thermodynamic conditions).[19] However, generic Lennard-Jones liquids may be sufficient for a satisfactory description of the mean features of the supercritical state. The fact that a supercritical fluid has both liquid and gas behaviour suggests that the specific chemical structure and its consequent bonding network are not as relevant as in ambient conditions and thus a generic spherical (L-J) model may be able to capture the essential thermodynamic features; this is a point that we will treat more specifically in the light of our results later on. In general, simulations of L-J fluids have been for long employed to understand the thermodynamic behaviour around the critical point,[14,16] however the exciting question of the possibility of the existence of a third-order phase transition has never been addressed. Instead in a previous paper, some of the authors of the current work have addressed explicitly this question with extended numerical simulations and it was proven that for a one-component L-J fluid a third-order phase transition does not occur.[20] Unfortunately, this answer cannot be considered satisfactory because the experimental conditions are rather different and imply the use of (at least) a two-component fluid.[11] In this perspective, here we have treated a much general condition, that is we considered (I) a L-J fluid solvating L-J particles of larger size, to mimic a situation of solvation, and (II) a binary mixture of L-J particles with similar molecular size. Moreover, since the critical point occurs at high pressure where the interaction between L-J particles of different nature becomes more

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TABLE I. The tested controlling parameters of system I and II. E_{AB} and R_{AB} are the ratios of the interaction strength and diameter of molecule type B over those of type A, respectively. C_B is the number density of type B, defined by $C_B = N_B/(N_A + N_B)$.

	E_{AB}	R_{AB}	C_B
System I	1.0	2.00	0.002, 0.010, 0.020
System II	1.0	1.01–1.05	0.500

relevant, we tested our conclusions also for the case of different interaction strengths. We will show that, as for the case of a one-component liquid, there is a rather clear evidence that a third-order phase transition does not occur.

MODEL SYSTEMS

In the present work, we consider particles interacting via the standard L-J potential. The conventional notations are adopted: the interaction strength and molecular diameter are denoted by ϵ and σ, respectively. The one-component system has been already treated in our previous work[20] and thus it will be considered only as a term of comparison here, while we extend the simulation study to systems (I) and (II). We denoted the component of the mixture by molecules of type A and type B, so the interaction strength and molecular diameter are denoted ϵ_A and ϵ_B, σ_A and σ_B, respectively. Molecules of different species also interact via the L-J potential, following the Lorentz-Berthelot combination rule: $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$ and $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$. For Convenience, without loss of generality, we assume $\sigma_A \leq \sigma_B$. The parameters that control the physics of the system, beside the thermodynamic parameters, are the ratio of the interaction strength $E_{AB} = \epsilon_B/\epsilon_A$, the ratio of the molecular diameter $R_{AB} = \sigma_B/\sigma_A$, and the relative number density of B (concentration of B), denoted by $C_B = N_B/(N_A + N_B)$, where N_A and N_B denote the number of molecules of specie A and specie B, respectively. Our starting point is the one-component fluid, for which we have already proved the non-existence of the third order phase transition. We choose this system as a reference and consider (build) system (I) and (II) as increasingly larger perturbations of the one-component system (see details in Table I). For simplicity, throughout this work, we explicitly discuss the case $E_{AB} = 1$. Several tests were carried out with different values of E_{AB}, but no difference in the main conclusions was found, therefore the results are not presented here. For (I), we initially insert a small number of large L-J solutes and then increase its concentration. For (II), we mix first the reference one-component system with a fluid of molecules with very similar diameter, that is $R_{AB} = 1.01$, at equal density concentration (i.e., $C_B = 0.5$), and then progressively increase R_{AB}. The considered R_{AB} ranges from 1.01 to 1.05, which means that we explore the perturbations to the case of a one component liquid in terms of molecular size of part of the system. These combined with different interaction strengths and solute concentrations will provide a description of how, going away from a standard one component liquid, the system reacts. If mixtures are more likely to go through a third order phase transition, a trend must clearly emerge.

QUANTITIES TO CALCULATE

The molar constant pressure heat capacity c_p and isothermal compressibility κ, both second order partial derivatives of the Gibbs free energy, are the quantities of interest,

$$c_p = -\frac{k_B\beta^2}{N}\frac{\partial^2}{\partial\beta^2}(\beta G), \tag{1}$$

$$\kappa = -\frac{1}{\beta\langle V\rangle}\frac{\partial^2}{\partial P^2}(\beta G), \tag{2}$$

where $\beta = 1/(k_B T)$, G denotes the Gibbs free energy, P is the external pressure, and V is the instantaneous volume of the system. If there are anomalies in the behaviour of c_p and κ as a function of P then a third order phase transition may indeed occur.

SIMULATION SET UP

We perform simulations in the isotherm-isobaric ensemble (NPT ensemble). With this set up c_P and κ are calculated as

$$c_p = -\frac{1}{k_B T^2 N}\langle (H - \langle H\rangle)^2\rangle, \tag{3}$$

$$\kappa = -\frac{1}{k_B T}\frac{\langle (V - \langle V\rangle)^2\rangle}{\langle V\rangle}, \tag{4}$$

where H is the enthalpy, given by $H = \mathcal{H} + PV$ with $\mathcal{H}$ being the Hamiltonian of the system. Simulations are done at a certain temperature by fixing ϵ_B, σ_B, and C_B for a series of values of P. Along the isothermal line, the second-order derivatives (1) and (2) are then calculated. If there were a third-order phase transition in these mixture systems, then all second-order derivatives would present cusps (continuous but not differentiable) at the transition point.

TECHNICAL SET UP

Each simulated system contains 4000 molecules interacting via the L-J 12-6 potential in a periodic simulation box. The conventional dimensionless unit system is employed. The unit of length, energy, mass, and time are denoted by ϵ_A, σ_A, m, and τ, respectively. All quantities are written in the unitless form by adding the superscript "*", e.g., $r^* = r/\sigma_A$, $T^* = k_B T/\epsilon_A$, and $P^* = P\sigma_A^3/\epsilon_A$. The MD time step is $\Delta t^* = 0.002$. Each simulation last for 1×10^8 time steps; the first 2.5×10^7 steps are then discarded to ensure that statistics is done in equilibrium. Every 100 time steps the quantities of interest are sampled. A Nose-Hoover thermostat[21,22] and a Parrinello-Rahman barostat[23,24] are employed to generate a NPT ensemble. The cut-off radius in the simulations is chosen to be $r_c^* = 8$. The internal energy and the pressure contribution from the molecules falling out of the cut-off radius are included by the standard long-range correction. All the simulation are done at the same temperature $T^* = 1.36$; such a value has been chosen based on results of our previous study for the one-component system. $T^* = 1.36$ was the lowest temperature simulated, it was found that for higher

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temperatures the behaviour of c_p^* and κ^* was much smoother and thus of no interest for the existence of a phase transition. Since current systems are progressive perturbation of the one-component system, one can expect the same behaviour; indeed tests at higher temperature confirm this trend (results are not shown). Moreover, sharp phase transitions happen only in the ideal case of thermodynamical limit; in order to give a more solid ground to our conclusions we performed several tests considering systems of 8000 particles and of 16000 particles. Results show that the behaviour of c_p^* and κ^* at the predicted point of discontinuity is not sensitive to the size of the system; moreover they are independent of the cut-off radius in the simulations. The point of discontinuity represents the most delicate situation one can study for these systems, thus these additional tests suggest that the main conclusions of the work do not change in any sensible way by increasing the size of the simulated system.

RESULTS FOR SYSTEM (I)

Figs. 1 and 2 show a clear trend: As C_B becomes larger the positions of the peaks shifts to the lower pressure side. At the same time, the peaks become sharper, which indicates the potential presence of a stronger singularity; however we have plotted two dashed lines that are linear regressions of data along the low- and high-pressure branches of each peak. If there were a third-order phase transition, then the simulation data would be consistent (within the statistical uncertainty) with the cusp predicted by the intersection of the dashed lines. It is not difficult to draw the conclusion that there is no indication whatsoever of a third-order phase transition for $C_B = 0.002$, and 0.01, because the heat capacity and compressibility, even considering the statistical uncertainty, clearly do not follow the anomalous behaviour, which the predicted cusps would suggest (see inset of Figs. 1 and 2). The same conclusion could not be made for $C_B = 0.02$ by the plot of the heat capacity (Fig. 1) due to the large statistical error. Therefore, we have carried out an additional simulation at the crossing pressure, and have proved that the cusp is clearly outside the error bar.

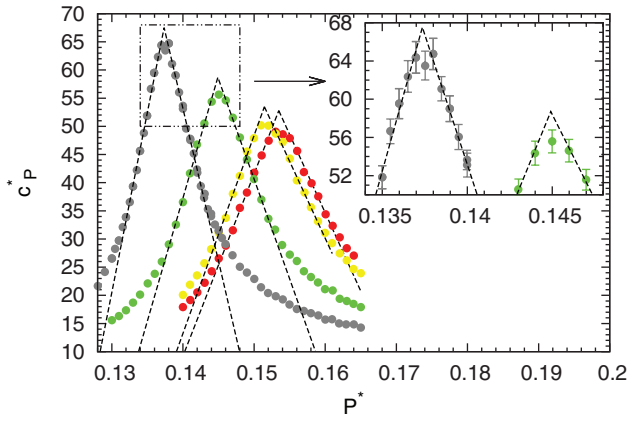

FIG. 1. The molar constant pressure heat capacity as a function of pressure of four systems at $T^* = 1.36$ and $\sigma_B^* = 2.00$. In the main plot, four peaks from left to right correspond to $C_B = 0.02$, 0.01, 0.002, 0.00, respectively. Error bars are not shown because they are smaller than the size of the dots. Two dashed straight lines are shown with each peak, presenting the linear regressing of data points on the higher and lower pressure branches of each peak, respectively. The inset shows the enlarged maximum of c_p^*, with error bars (indicating the confidence interval with 95% confidence level) plotted on each data point.

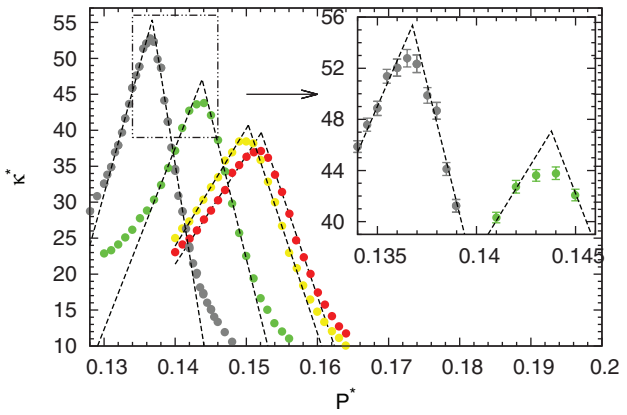

FIG. 2. Same as Fig. 1, except here the isothermal compressibility as a function of pressure is plotted.

RESULTS FOR SYSTEM (II)

In Figs. 3 and 4 we plot the simulation measurements of the mentioned second-order derivatives on the isothermal lines at $T^* = 1.36$; also in this case peaks appear along each isothermal line together with the systematic shift of the position of peaks towards the low pressure side. However, in contrast to system (I), the shapes of the peaks do not change with respect to the increasing value σ_B^*, which suggests that the possibility of having a singularity at the peaks is independent of the system treated. However, the smoothness of curves around the peaks clearly shows that also in this case there is not evidence of a phase transition.

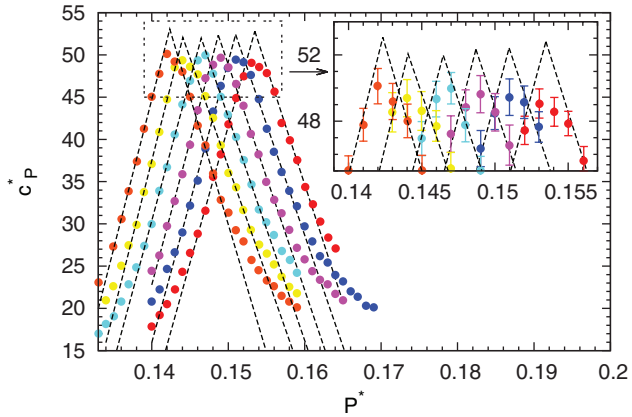

FIG. 3. The molar constant pressure heat capacity c_p^* as a function of pressure for six different systems at $T^* = 1.36$ and $C_B = 0.50$. In the main plot the six peaks from left to right correspond to $\sigma_B^* = 1.05$, 1.04, 1.03, 1.02, 1.01, 1.00, respectively. As before, the error bars are not shown because most of them are smaller than the size of the dots and the other technical details are the same of those of previous figures.

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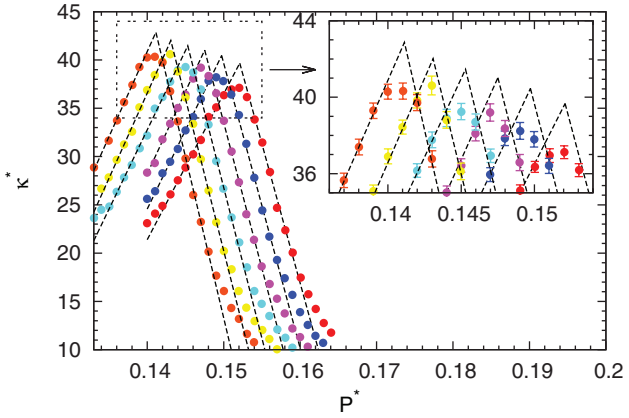

FIG. 4. Same as Fig. 3, except here the isothermal compressibility as a function of pressure is plotted.

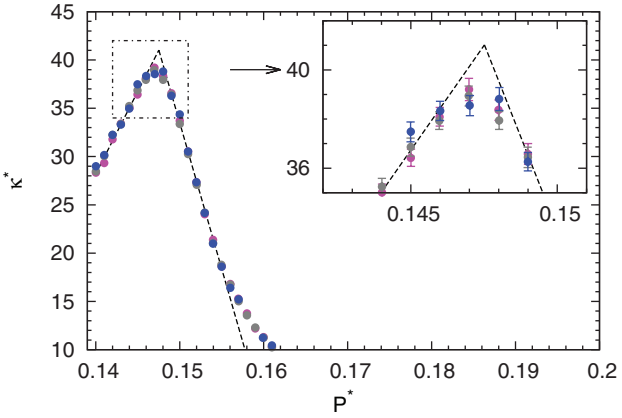

FIG. 6. Same as Fig. 5, except here the isothermal compressibility as a function of pressure is plotted.

EMPIRICAL LAW FOR THE σ_B^* VS. C_B BEHAVIOUR

We have done further simulations showing that, chosen σ_B^*, the distance (along the axis of the pressure) between the peak of a mixture system and that of the one-component system increase linearly by increasing C_B. This behaviour suggested the question of what happens if we increase linearly C_B and decrease σ_B^* or vice versa, can we obtain the same thermodynamic behaviour from different systems by systematic control of the parameters C_B (concentration) and σ_B^* (molecular size)?

Simulations show that the answer is positive, see Figs. 5 and 6. When we draw the results of $\sigma_B^* = 1.05$, $C_B = 0.20$; $\sigma^* = 1.02$, $C_B = 0.50$; and $\sigma_B^* = 1.04$, $C_B = 0.25$ on the same plot, we find that they coincide; interestingly the empirical law linking the three systems is $(\sigma_B^* - 1) \times C_B = 0.01$. Despite at this stage we do not have any deeper justification of this behaviour, however, if it is physically realistic then it would suggest the interesting opportunity of choosing either a specific fluid or a specific concentration in order to obtain the same thermodynamic behaviour.

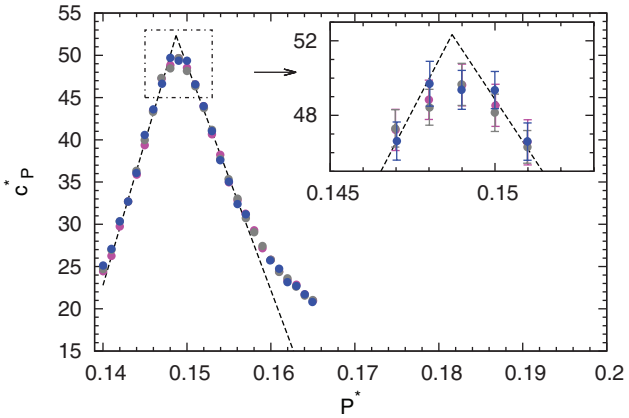

FIG. 5. The molar constant pressure heat capacity as a function of pressure at $T^* = 1.36$ for three different systems. The pink, gray, and blue dots correspond to systems $\sigma_B^* = 1.02$, $C_B = 0.50$; $\sigma_B^* = 1.05$, $C_B = 0.20$; $\sigma_B^* = 1.04$, $C_B = 0.25$, respectively. Error bars are not shown in the main plot, because of their negligible size. The inset shows the enlarged maximum of c_p^*.

DISCUSSION AND CONCLUSIONS

Supercritical fluids may indeed play a crucial role for future technology, therefore the investigation of their physical features is in this sense mandatory. The possibility of the existence of a third order phase transition beyond the Andrew's critical point is one of the most stimulating results of the last years. We have investigated this possibility with extended MD simulations of L-J mixtures, extending a previous study based on a one-component system. Our results show a rather regular behaviour of the fluid and suggest a negative response about the existence of such a phase transition. However, differently from experiments, done with fluids with specific (chemical) molecular structure, our simulations consider generic (chemically) unstructured molecules. In the first instance one may suppose that specific chemical structure may not play a major role in the supercritical regime, as suggested before in this work, however, this may not be true overall. Supposing that third order phase transitions can be shown experimentally or numerically for specific fluids, then our results implicitly show that the specific molecular chemical structure may indeed be a key factor in the thermodynamic behaviour in supercritical regime. If it was so, then this would open exciting scenarios on how to chemically design liquids with specific supercritical properties such as those related to the third order phase transition. Clearly for liquids whose molecules interact as L-J molecules, in simulation, phase transitions do not occur. In conclusion, while showing that third order phase transition are in general very unlikely on the basis of the current knowledge, this paper, if proved wrong for specific systems, suggests that the question about the relation between supercritical behaviour and chemical nature of the fluid is a key issue of supercriticality. In general, the negative response about the existence of phase transition given by us does not represent an ultimate evidence of it; on the other hand, experimental and theoretical work, which provides a positive answer to the problem, does not give conclusive evidence although firmly claims the universality of the phase transition. In this context, our work must be considered as a pilot study for future theoretical investigations (hopefully at atomistic level) and should be carefully considered in the design of future experiments.

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ACKNOWLEDGMENTS

This work was partially supported by the Deutsche Forschungsgemeinschaft (DFG) with the Heisenberg grant provided to L.D.S. (Grant Code DE 1140/5-1). The work of P.Z. is supported by grants from National Natural Science Foundation of China (Grant Nos. 50930003 and 21274005). The results described in this paper were obtained on the Deepcomp7000G of the Supercomputing Center, Computer Network Information Center of Chinese Academy of Sciences.

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