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On the existence of a third-order phase transition beyond the Andrews critical point: A molecular dynamics study

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The possibility of the existence of a gas-liquid third order phase transition for fluids is becoming a subject of growing interest. Experimental work suggests its existence for specific systems while recent theoretical models claim its universality. In this work, we employ Molecular Dynamics and investigate the third-order phase transition beyond the Andrews critical point by treating a system of Lennard-Jones particles along three isotherms. Two partial derivatives of the Gibbs free energy are measured, namely the molar constant pressure heat capacity and isothermal compressibility. The convergence of these simulations with respect to the system size as well as the cut-off radius is carefully checked. The obtained results show that partial derivatives certainly do not present sharp cusp singularities at the maxima, and actually suggest that there are no singularities at all. On these basis we then conclude that a third-order phase transition in the considered temperature region: $T^* \geq 1.36$ may indeed not exist. © 2011 American Institute of Physics. [doi:10.1063/1.3666848]

I. INTRODUCTION

Phase transitions represent specific signatures of macroscopic systems' behavior generated by the detailed specific molecular chemistry (see, e.g., the key role of hydrogen bond into the phase behavior of water). However there is a universal behavior (independent of the specific molecular chemistry) for a large class of systems on a P - T phase diagram. The gas-liquid coexisting line goes from the lower temperature and pressure side to the higher temperature and pressure side, and ends at the Andrews critical point. The gas-liquid phase transition is first order, because the first-order derivatives of the Gibbs free energy, such as molar volume and internal energy, are discontinuous at the transition. The Andrews point is a second-order phase transition point, because the second-order derivatives of the Gibbs free energy, such as the compressibility and heat capacity, diverge to infinity. Beyond the Andrews critical point, all phase transitions lower than the second-order disappear. The gas and liquid phases are indistinguishable, and both of them change into the supercritical phase.

The most favorable property of the supercritical fluid is the fast change of the solubility with respect to the small change of thermodynamic parameters. K. Nishikawa and her coworkers extensively studied the density fluctuation of various fluids in the supercritical region by means of the small-angle X-ray scattering (SAXS).¹⁻⁶ They found a "ridge" that is defined by the maxima of the density fluctuation on isothermal lines. This ridge was also confirmed by small angle neutron scattering (SANS) experiments,⁷ which also investigated the fluctuation structures of the gas-like and liquid-like supercritical CO₂. These maxima of the density fluctuation as well as the maxima and minima of some other quantities, such as heat capacity and thermal expansion, can be explained as

anomalies of the second-order derivatives of the Gibbs free energy.⁸ Despite the experimental evidence a clear interpretation in terms of basic principles of thermodynamics and statistical mechanics is not yet available. Of course this is highly needed given the relevance of the subject for a better understanding of supercritical fluids. Recently a theoretical approach was proposed by T. Ma and S. Wang.⁹ This was built on the mathematical basis of the dynamics of phase transitions applied to the Landau mean field model for studying the gas-liquid phase transition¹⁰ of the physical-vapor transport system. Their study successfully reproduced the first-order phase transition at the gas-liquid co-existing line and the second-order phase transition at the Andrews critical point, which were derived from the classical research by van der Waals. However the innovative and surprising discovery was the prediction of a third-order phase transition line, which is a natural extension of the gas-liquid coexisting line, beyond the Andrews critical point. If this corresponds to physical reality, then it would represent a powerful contribution to the understanding of the supercritical state in fluids on the basis of statistical fundamental principles. However, possible limitations of the model and practical approximations employed could have led to artificial results, of this point one should be well aware. For example, the fact that they do not consider the spacial fluctuation of ρ and S because the system is homogeneous does not really apply to realistic fluids. In fact local fluctuations of quantities which are constant in average play a major role in the thermodynamic behavior of the system. A constant average temperature does not hinder local thermal fluctuations which in turn may induce large local density fluctuations. These, for instance, play a major role in the thermodynamics of water solvation (see, e.g., Ref. 11 and references therein). Despite mean field models can still capture the basic correct behavior, a crosscheck is needed using an approach which does not suffer or does not need the approximations

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above. In this context, molecular dynamics (MD) provides a powerful tool to address the problem. In MD, the specific chemistry of the single molecule is directly linked to the thermodynamic behavior of a large collection of particles. Their dynamical evolution, according to Newton's equations of motion, on long trajectories for statistical large samples allows to characterize with local details the thermodynamic of the system and thus overcome the limitations and the simplifications of a mean field approach.

In this context, our purpose is to study the existence of the theoretically predicted third-order phase transition by MD simulations. A straightforward way is to calculate the third-order partial derivatives of the Gibbs free energy and to study their continuity. However, the physical meaning of the third-order derivatives is not clear, thus we study the second-order partial derivatives instead. If there were a third-order phase transition, all second-order derivatives would present obvious cusps (namely continuous but not differentiable). This is our criterion. The system we choose is a Lennard-Jones fluid. Despite its "chemical" simplicity this would represent a test as a necessary condition to the existence of a gas-liquid third order phase transition which is universal for fluids. If already for this system a clear cusp in the second-order derivative is not detected, then one may safely conclude that a third order phase transition is not (at least) universal. Actually, one may conclude that the transition does not exist at all in general. In fact, one could argue that the gas-liquid transient identity of the system beyond Andrews point, may suggest that specific molecular chemistry (structure) does not play a major role. In fact if it was not so, then the chemistry specific bonding motif of standards liquids would be too dominant to allow the system to mutate spontaneously in gas-like behavior and vice versa. This suggests that, at the thermodynamic conditions at which we work, spherical molecular models, without specific chemical structures, may indeed be sufficient to model the problem and thus Lennard-Jones models are ideal general test cases.

II. OBSERVABLES

We consider two partial derivatives of the Gibbs free energy, namely the molar constant pressure heat capacity c_P and isothermal compressibility κ :

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

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

where β is the inverse temperature, namely $1/(k_B T)$, G denotes the Gibbs free energy, P is the external pressure and V is the instantaneous volume. From (1) and (2), it is not difficult to prove c_P and κ are related to the thermodynamic fluctuation of the instantaneous properties of the system by

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

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

where H is the instantaneous enthalpy, given by $H = \mathcal{H} + PV$. Here \mathcal{H} denotes the Hamiltonian. We adopt equations (3) and (4) to calculate c_P and κ in the MD simulations.

III. SIMULATION RESULTS

The MD simulations contain 4000 particles interacting via the Lennard-Jones 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 , σ , m and τ ($\tau = \sigma \sqrt{m/\epsilon}$), respectively. All quantities are written in the unitless form by adding the superscript "****". For example, $r^* = r/\sigma$, $T^* = k_B T/\epsilon$ and $P^* = P\sigma^3/\epsilon$. The MD time step is $\Delta t^* = 0.002$. The simulations last for 1×10^8 time steps. The first 2.5×10^7 steps are discarded. The quantities of interest are sampled every 100 time steps. The commonly used blocking average method¹² is applied to estimate the statistical uncertainty of the autocorrelated data. The NPT ensemble is generated by the Nosè-Hoover thermostat^{13,14} coupled with the Parrinello-Rahman barostat.^{15,16} We use a cut-off radius of $r_c^* = 8$. The reliability of this cut-off radius and the finite size effect are discussed later. The internal energy and the pressure contributions from the particles falling out of the cut-off radius are included by the standard long-range correction.

The Andrews critical point and the gas-liquid coexisting line of the pure untruncated Lennard-Jones fluid have been well studied in the past 20 years, some examples are Refs. 17–21. One of the most modern studies of the Andrews critical point²¹ reported a critical temperature of $T_c^* = 1.3123$. We plot the simulation measurements of the mentioned second-order derivatives on three isothermal lines located at $T^* = 1.36, 1.38, 1.42$ in Fig. 1 and 2, where the

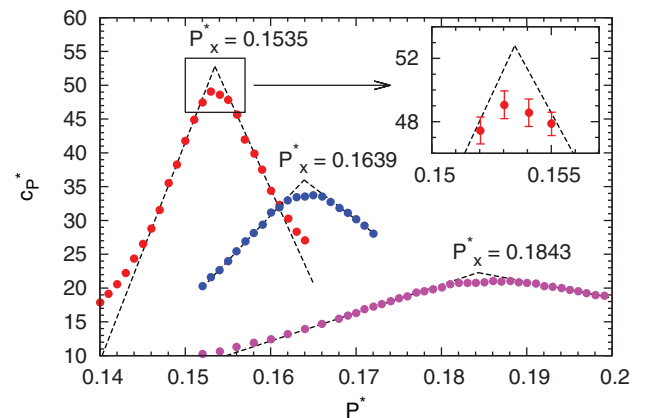


FIG. 1. The molar constant pressure heat capacity as a function of pressure on three isotherms. In the main plot, the three peaks from left to right correspond to $T^* = 1.36, 1.38,$ and 1.42 , respectively. The error bars are not shown because most of them are smaller than the size of the dots. Two dashed straight lines are shown with each peak, presenting the linear regression of data points on the higher and lower pressure branch of each peak, respectively. The pressure of the line intersections are denoted by P_x^* . The insertion shows the enlarged maximum of c_P^* at $T^* = 1.36$, with error bars (indicating the confidence interval with 95% confidence level) plotted on each data point.

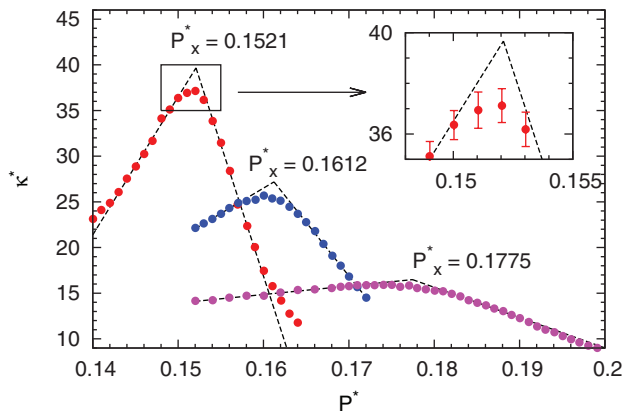


FIG. 2. The isothermal compressibility as a function of pressure on three isotherms. In the main plots, the three peaks from left to right correspond to $T^* = 1.36, 1.38, 1.42$, respectively. The error bars are not shown because most of them are smaller than the size of the dots. Two dashed straight lines are shown with each peak, presenting the linear regression of data points on the higher and lower pressure branch of each peak, respectively. The pressure of the line intersections are denoted by P_X^* . The insertion shows the enlarged maximum of κ^* at $T^* = 1.36$, with error bars (indicating the confidence intervals with 95% confidence level) plotted on each data point.

data points are colored by red, blue and pink, respectively. Only the P^* range of special interest, where the derivatives present a peak, is plotted for clarity. At the Andrews critical point, second-order derivatives diverge to infinity. It is natural to consider these peaks as extensions of the critical point divergence, with a much weaker singularity. The peak is sharper near the critical point ($T^* = 1.36$), while it is comparatively blunter far from the critical point ($T^* = 1.42$). With each peak, we present two dashed lines that are linearly regressed from the MD data points on the higher and lower pressure branches. If there were a third-order phase transition, the intersection of the lines would predict the location of the phase transition on the corresponding isotherm, and all MD simulation results would overlap with the lines around the intersection. However, in Fig. 1 and 2, we find obvious deviations of the MD results from the lines around the intersections. To show the deviations clearly, we insert in Fig. 1 and 2 two enlarged plots of the intersection regions at $T^* = 1.36$. Taking into consideration the statistical uncertainty, presented by the error bars with 95% confidence level in the inserted plots, we conclude that the deviations are systematic. The deviations at $T^* = 1.38$ and 1.42 are similar, so they are not enlarged.

It is interesting to find that the pressure of intersections, denoted by P_X^* in Fig. 1 and 2, are different for different partial derivatives. When $T^* = 1.36$, it is $P_X^* = 0.1535$ for c_p^* versus $P_X^* = 0.1521$ for κ^* ; when $T^* = 1.42$, it is $P_X^* = 0.1843$ for c_p^* versus $P_X^* = 0.1775$ for κ^* . The higher the temperature, the larger the discrepancies are. This observation contradicts the existence of an ideal third-order phase transition, because the location of the phase transition should be the same for both c_p^* and κ^* . In other words, the pressure of the intersections P_X^* should be the same for different second-order derivatives.

Since the MD simulations deal with much smaller systems than typical macroscopic experiments ($N \sim 10^{23}$), the finite system size can be a serious artificial effect, particularly near phase transitions. A number of studies have been devoted to the finite-size scaling studies of the first-order phase

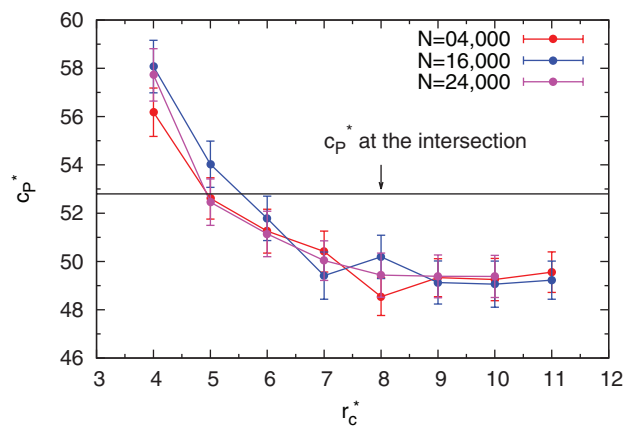


FIG. 3. $T^* = 1.36, P^* = P_X^* = 0.1535$, the convergence of the molar constant pressure heat capacity c_p^* with respect to the cut-off radius r_c^* and system size N . The c_p^* at the intersection is added to show the discrepancy between the converged MD simulation results and the intersection of the dashed lines in the insertion of Fig. 1.

transition and the critical point properties, some of them are reported in Refs. 22–26. Moreover, the cut-off radius of the Lennard-Jones potential is another source of the artificial effect. Therefore, to ensure the reliability of the MD results in our study, the convergence of the c_p^* and κ^* with respect to the system size and the cut-off radius is carefully checked. The considered thermodynamic parameters are $\{T^* = 1.36, P^* = P_X^* = 0.1535\}$ for c_p^* and $\{T^* = 1.36, P^* = P_X^* = 0.1521\}$ for κ^* . Since the singularity at $T^* = 1.36$ is stronger than $T^* = 1.38$ and $T^* = 1.42$ (see Fig. 1 and 2), the convergence check at $T^* = 1.36$ is representative. We are mostly concerned about the fact that MD simulation results overlap the dashed lines around the intersections, therefore the convergence check at the intersection pressure is representative for other values of the pressure.

In Figs. 3 and 4, simulation results of system size $N = 4000, N = 16000$ and $N = 24000$ are compared. The results show no observable dependence on the size of the system which in turns implies that the finite size effects in our

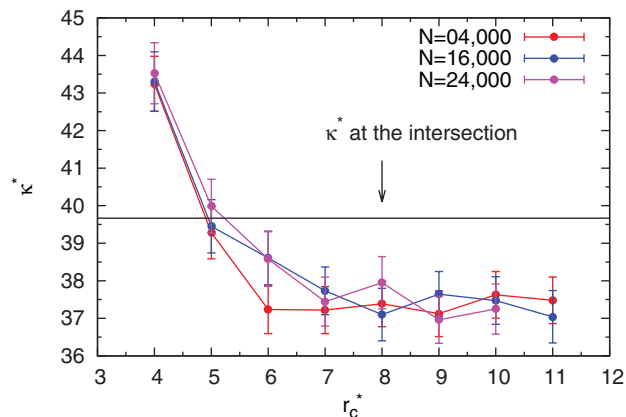


FIG. 4. $T^* = 1.36, P^* = P_X^* = 0.1521$, the convergence of the isothermal compressibility κ^* with respect to the cut-off radius r_c^* and system size N . The κ^* at the intersection is added to show the discrepancy between the converged MD simulation results and the intersection of the dashed lines in the insertion of Fig. 2.

simulations are negligible. When the cut-off radius is smaller than $r_c^* = 6$, c_p^* and κ^* show obvious dependence on r_c^* . When the cut-off radius is larger than 7, both the derivatives satisfactorily converge, despite the fluctuations that are smaller than the size of the error bars. Therefore, we use $r_c^* = 8$ for all of our MD simulations in order to be in a fully safe simulation regime.

IV. CONCLUSION AND DISCUSSION

We have addressed the question of the existence of a third-order phase transition beyond the Andrews critical point by performing MD simulations on three isotherms ($T^* = 1.36, 1.38$ and 1.42) and calculated two partial derivatives of the Gibbs free energy, namely c_p^* and κ^* . We have shown that the second order derivatives do not present sharp cusps, thus we conclude that the theoretically predicted third-order phase transition¹⁰ may not exist on the mentioned isotherms. Since the higher the temperature, the weaker the singularity, it is reasonable to extend our conclusion to $T^* \geq 1.36$. For $T^* < 1.36$, our simulation is not precise enough to reach any deterministic conclusion, due to the statistical uncertainty. This work contributes to the understanding of thermodynamic behavior of fluids in supercritical regime, posing a clear question about the existence of anomalies of the second and third derivatives of thermodynamic potentials recently proposed by experimental as well as theoretical work.

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- ¹K. Nishikawa and I. Tanaka, *Chem. Phys. Lett.* **244**, 149 (1995).
- ²K. Nishikawa and T. Morita, *J. Supercritical Fluids* **13**, 143 (1998).
- ³T. Morita, K. Kusano, H. Ochiai, K. I. Saitow, and K. Nishikawa, *J. Chem. Phys.* **112**, 4203 (2000).
- ⁴K. Nishikawa and T. Morita, *Chem. Phys. Lett.* **316**, 238 (2000).
- ⁵K. Nishikawa, K. Kusano, A. A. Arai, and T. Morita, *J. Chem. Phys.* **118**, 1341 (2003).
- ⁶A. A. Arai, T. Morita, and K. Nishikawa, *Chem. Phys.* **310**, 123 (2005).
- ⁷T. Sato, M. Sugiyama, K. Itoh, K. Mori, T. Fukunaga, M. Misawa, T. Otomo, and S. Takata, *Phys. Rev. E* **78**, 51503 (2008).
- ⁸Y. Koga, P. Westh, Y. Moriya, K. Kawasaki, and T. Atake, *J. Phys. Chem. B* **113**, 5885 (2009).
- ⁹T. Ma and S. Wang, *Indiana Univ. Math. J.* **57**, 2861 (2008).
- ¹⁰T. Ma and S. Wang, *AIP Advances* **1**, 042101 (2011).
- ¹¹B. P. Lambeth, C. Junghans, K. Kremer, C. Clementi, and L. Delle Site, *J. Chem. Phys.* **133**, 221101 (2010).
- ¹²H. Flyvbjerg and H. G. Petersen, *J. Chem. Phys.* **91**, 461 (1989).
- ¹³S. Nosé, *Mol. Phys.* **52**, 255 (1984).
- ¹⁴W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
- ¹⁵M. Parrinello and A. Rahman, *Phys. Rev. Lett.* **45**, 1196 (1980).
- ¹⁶M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).
- ¹⁷A. Lotfi, J. Vrabec, and J. Fischer, *Mol. Phys.* **76**, 1319 (1992).
- ¹⁸B. Smit, *J. Chem. Phys.* **96**, 8639 (1992).
- ¹⁹A. Z. Panagiotopoulos, *Int. J. Thermophys.* **15**, 1057 (1994).
- ²⁰J. J. Potoff and A. Z. Panagiotopoulos, *J. Chem. Phys.* **109**, 10914 (1998).
- ²¹J. Pérez-Pellitero, P. Ungerer, G. Orkoulas, and A. D. Mackie, *J. Chem. Phys.* **125**, 054515 (2006).
- ²²P. Nightingale, *J. Appl. Phys.* **53**, 7927 (1982).
- ²³K. Binder and D. P. Landau, *Phys. Rev. B* **30**, 1477 (1984).
- ²⁴N. B. Wilding and A. D. Bruce, *J. Phys.: Condens. Matter.* **4**, 3087 (1992).
- ²⁵N. B. Wilding, *Phys. Rev. E* **52**, 602 (1995).
- ²⁶J. M. Caillol, *J. Chem. Phys.* **109**, 4885 (1998).