

Boiling line and near-critical maxima of propane-nitrogen mixturesYu. D. Fomin *Vereshchagin Institute of High Pressure Physics, Russian Academy of Sciences, Kaluzhskoe shosse 14, Troitsk, Moscow 108840, Russia*

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It is well known that some thermodynamic quantities demonstrate maxima in the vicinity of a critical point. The lines of these maxima in the density-temperature or pressure-temperature planes are called “Widom lines.” The behavior of Widom lines of one-component fluids has already been well studied in a number of papers by different authors. However, up to now the understanding of Widom lines in binary mixtures is still lacking. In this paper we study the boiling curve and the near-critical maxima of mixtures of nitrogen and propane by means of molecular dynamics simulation. We calculate the boiling curves and estimate the critical temperatures in a set of concentrations from pure nitrogen to pure propane. The influence of the composition of the mixture on the Widom lines of the system is evaluated. We find that the mixture of propane and nitrogen behaves as a type I mixture in the van Konynenburg–Scott classification, i.e., when the concentration is changed, the critical point and the corresponding Widom lines continuously shift in the density-temperature plane.

DOI: [10.1103/PhysRevE.106.064102](https://doi.org/10.1103/PhysRevE.106.064102)**I. INTRODUCTION**

Propane is a natural gas widely used as a fuel. It is often liquified for transportation purposes, which makes knowledge of the boiling curve of propane of crucial importance. The situation becomes even more complex since natural gas usually contains nitrogen contamination, which may shift the phase equilibrium points. For this reason, investigation of the properties of propane-nitrogen mixtures becomes of great importance.

Propane-nitrogen mixtures have been widely studied both experimentally and theoretically. For instance, in Ref. [1] the solubility of nitrogen in propane at low temperatures (from 91.9 to 128.4 K) was studied. The vapor-liquid equilibrium of propane-nitrogen mixtures at temperatures from 114.1 to 122.2 K was reported in Ref. [2]. There is still a lack of experiments at high temperatures, which are closer to the propane critical temperature ($T_c = 369.9$ K).

Phase diagrams of binary mixtures can demonstrate rather rich behavior. A classification of phase diagrams of binary mixtures was introduced in a seminal paper by van Konynenburg and Scott [3]. They studied possible phase diagrams of a binary mixture of van der Waals gases and found that six types of diagrams can take place. In the case of type I mixtures, only a gas-liquid transition takes place, and critical points of mixtures form a continuous line in the P - T plane connecting the critical points of the pure components. In type II mixtures a liquid-liquid transition appears in addition to the gas-liquid one. In the case of type III mixtures, gas-liquid and liquid-liquid transitions take place. Two critical lines are present in the system, one of which starts at the critical point of the component with higher critical temperature T_c and goes to infinite pressure and the other of which starts at the critical

point with lower T_c and ends at the upper critical end point. Three critical lines take place in the case of type IV mixtures, one of which goes into infinite pressure. If the later curve does not take place in the system, then it corresponds to a type V mixture. The last type, type VI mixtures, which are not possible in van der Waals mixtures and were not observed in Ref. [3], are characterized by a gas-liquid transition and a liquid-liquid one which starts at the lower critical end point and ends at the upper critical end point [4].

Nitrogen-alkane phase diagrams were widely discussed in the frame of equation-of-state approaches. The dew-bubble curves of mixtures of several alkanes with nitrogen obtained on the basis of the Peng-Robertson equation of state with the addition of some group contribution method were reported [5,6].

Although the equation-of-state-based methods are powerful in the prediction of the phase equilibrium of the system, they do not give any insight into the microscopic nature of the processes. Such a view can be obtained by the methods of molecular simulation. One of the methods of simulation of vapor-liquid coexistence is the so-called two-phase method [7]. In this method a drop of liquid surrounded by a vacuum is simulated by the molecular dynamics method at constant volume and temperature and with a constant number of particles. If the temperature is high enough, some of the particles evaporate from the drop. Calculating the density profiles of the system, one can determine the coexisting densities at a given temperature. This method was successfully employed for the calculation of boiling curves of water [7], one-component hydrocarbons [8], and butane-nitrogen mixtures [9].

Another important question involves near-critical maxima in the vicinity of a gas-liquid (or liquid-liquid) critical point, also known as Widom lines [10]. As was shown in Ref. [10], in the vicinity of a critical point several quantities such as correlation length, isobaric heat capacity, isothermal compressibility, thermal expansion coefficient, etc., demonstrate

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maxima. These maxima fall on a master curve in close vicinity to the critical point. However, if the system goes far from the critical point, either increasing temperature or increasing pressure, the maxima of all quantities become spread out and rapidly disappear [11–13]. In an original paper [10] it was proposed to define a “Widom line” as a line of maxima of the correlation length. However, in the same paper the authors pointed out that measurement or calculation of the correlation length is a hard task and proposed using the line of maxima of the isobaric heat capacity instead. In this paper we use a kind of generalized view of the Widom line and refer to a line of maxima of any quantity in the vicinity of a critical point as a Widom line with respect to this quantity. We refer to a set of lines of maxima of several quantities as Widom lines. Widom lines close to a liquid-gas critical point were reported for a wide variety of systems including a van der Waals gas [11], a Lennard-Jones system [12], a square-well model [13], carbon dioxide [14,15], water [16,17], etc. Several publications reported Widom lines in the vicinity of a liquid-liquid transition in computer models of supercooled water [18,19]. In Ref. [20], a Widom line in a system with a magnetic phase transition is given.

From the list above, one can see that the phenomenon of near-critical maxima is very general. It is also of wide importance for thermodynamic properties of a system in the vicinity of the critical point. Surprisingly, to the best of our knowledge, there is only one publication which reports a study of the Widom lines of a binary mixture [21]. Widom lines of equimolar mixtures of argon and krypton and of neon and krypton are studied by means of molecular simulation in that paper. The argon-krypton mixture is a type I mixture in the classification of van Konynenburg and Scott [3]. In this case the behavior of the near-critical maxima is qualitatively identical to that in a one-component system. The behavior of the neon-krypton system is more complex. This mixture belongs to type III in the van Konynenburg–Scott classification, i.e., a liquid-liquid transition appears in a system in addition to the boiling line. As a result the authors of Ref. [21] observe two regions of near-critical maxima in the neon-krypton mixture.

Mixtures of propane and nitrogen should belong to type III [22], which makes the investigation of the properties of this system more complex.

II. SYSTEM AND METHODS

In this paper we calculate the boiling curve and near-critical maxima of a propane-nitrogen mixture at different concentrations of the components. We employ molecular dynamic simulation with the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field [23].

The boiling lines were determined by means of the two-phase simulation technique [7]. In this method a system of a condensed phase surrounded by a vacuum is simulated. In our study we used a system of 200 molecules of both species (in the case of pure nitrogen an 8000-molecule system is used; otherwise, the system appears to be too small) initially located on sites of a square crystal surrounded by a vacuum. The total length of the box in the Z direction is 120 Å. The molecules occupy about 1/3 of this length. Periodic boundary conditions

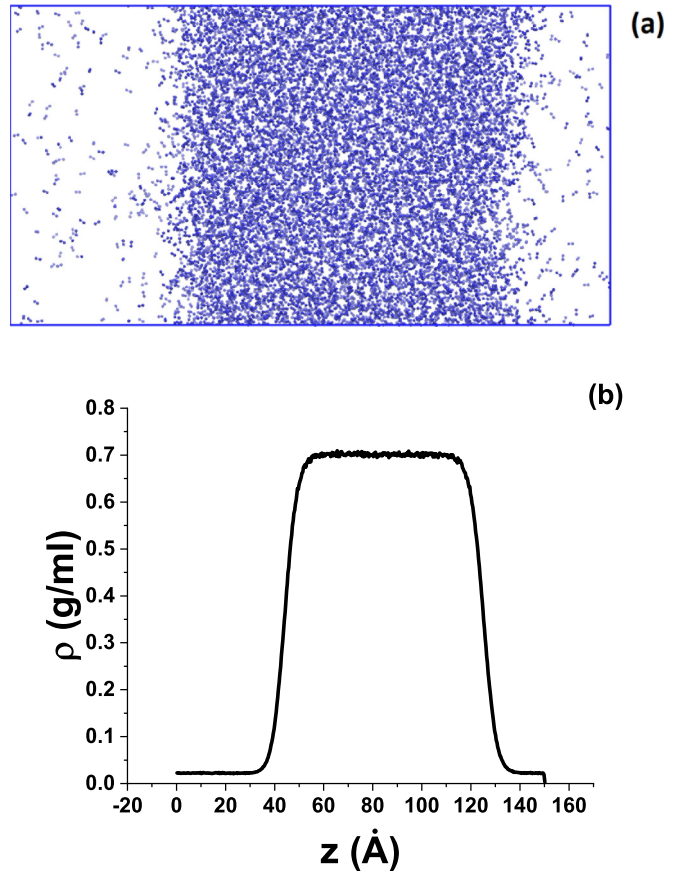


FIG. 1. (a) A snapshot of the system of pure nitrogen at $T = 80$ K. (b) Density profile of the same system.

are used in all three directions. We simulate the system in the canonical ensemble (constant number of particles N , volume V , and temperature T). In the course of simulation we see that some of the molecules evaporate from the initial condensed phase, while others stay in the drop, which becomes liquidlike. We determine the densities of the liquidlike and gaslike regions, which are the densities at coexistence.

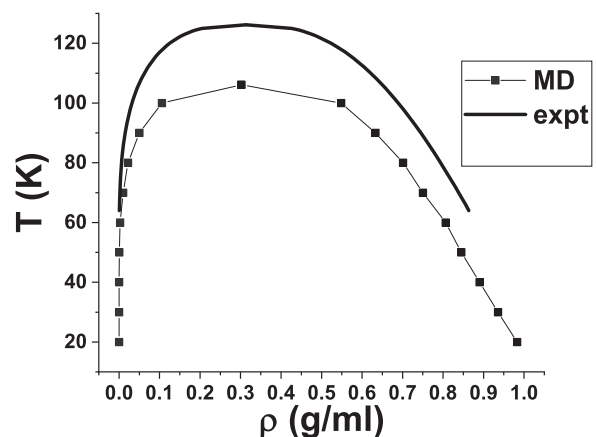


FIG. 2. Boiling curve of nitrogen. MD, the data of this study; expt, experimental data from Ref. [27].

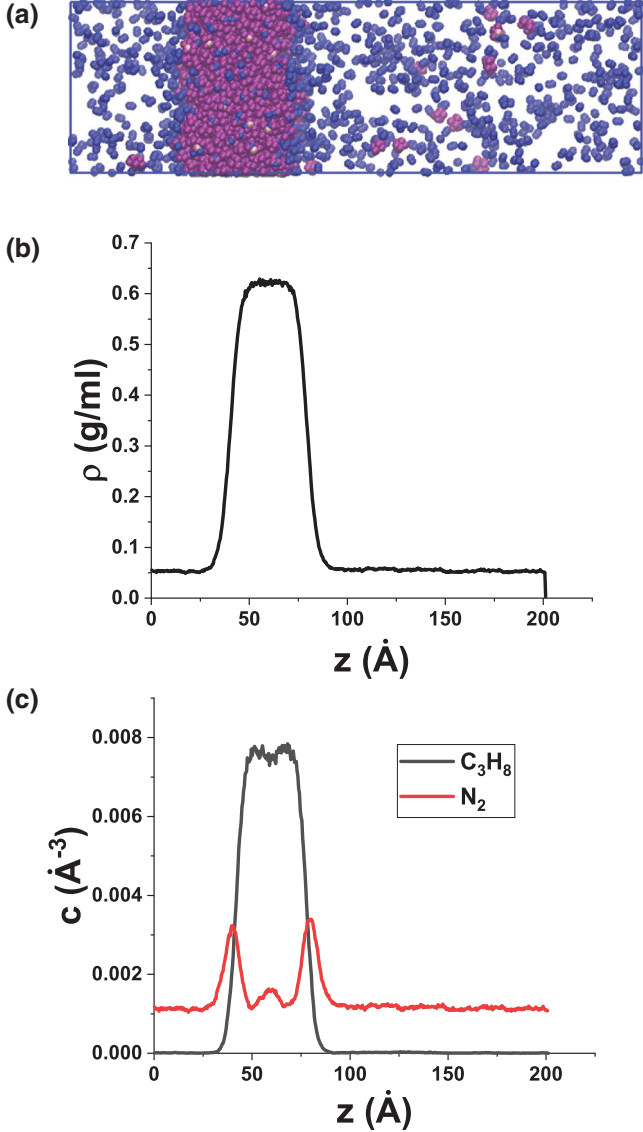


FIG. 3. (a) A snapshot of the equimolar system at $T = 260$ K. (b) Mass density profile of the same system. (c) Number density profile of nitrogen and propane in the same system.

Apparently, this method fails in the vicinity of the critical point. For this reason we use the law of rectilinear diameters to find the critical parameters [24]. The law of rectilinear diameters is written as

$$\frac{\rho_l + \rho_g}{2} = \rho_c + A(T - T_c), \quad (1)$$

where ρ_l and ρ_g are the densities of the liquid and the gas, respectively. A is a fitting constant. The second fitting equation is the difference between the density of the liquid and the density of the gas:

$$\rho_l - \rho_g = B(T - T_c)^\beta, \quad (2)$$

where $\beta = 1/8$ [25]. Fitting the data to these two equations, we obtain the critical temperature and critical density.

In the second part of this paper we simulate the near-critical maxima of a propane-nitrogen mixture. We employ

the same systems of 200 molecules with a given concentration of species (8000 molecules for pure nitrogen) placed in a cubic box with periodic boundary conditions. We simulate the systems from temperatures slightly below the critical temperature to ones about 100–150 K above T_c . The densities vary from 0.1 to 0.5 g/ml (up to 0.58 g/ml for pure nitrogen). We calculate the equation of state (pressure as a function of temperature and density), the internal energy, and the enthalpy of the system. The internal energy and pressure are approximated by a polynomial function and are used for further development of the data. From these data we evaluate the critical points from the equations $(\frac{\partial P}{\partial V})_T = 0$ and $(\frac{\partial^2 P}{\partial V^2})_T = 0$. By numerical differentiation of the obtained polynomials we obtain the response functions: isobaric heat capacity $c_P = (\frac{\partial H}{\partial T})_P$, where H is the enthalpy of the system, thermal expansion coefficient $\alpha_P = -\frac{1}{\rho}(\frac{\partial \rho}{\partial T})_P$, and isothermal compressibility $\beta_T = \frac{1}{\rho}(\frac{\partial \rho}{\partial P})_T$. We evaluate the maxima of these quantities and place their positions (Widom lines) on the phase diagrams.

In all cases the time step of the simulation was set to 0.1 fs.

All simulations were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) simulation package [26].

III. RESULTS AND DISCUSSION

A. Two-phase simulation

We start the discussion from the results for pure nitrogen. Figure 1(a) shows a snapshot of a system at $T = 80.0$ K. One can see that the system separated into two regions: gas and liquid. The density profile of the system is given in Fig. 1(b). From this figure we extract the density of both phases at the given temperature.

Figure 2 shows the boiling curve of nitrogen obtained in this paper in comparison to the experimental data from Ref. [27]. One can see that the employed model reproduces the experimental data only qualitatively. The experimental curve is systematically above the one from the simulation. Our estimation of the critical point gives $T_c = 106.1$ K (the experimental value is $T_{c,\text{expt}} = 126.192$ [27]) and

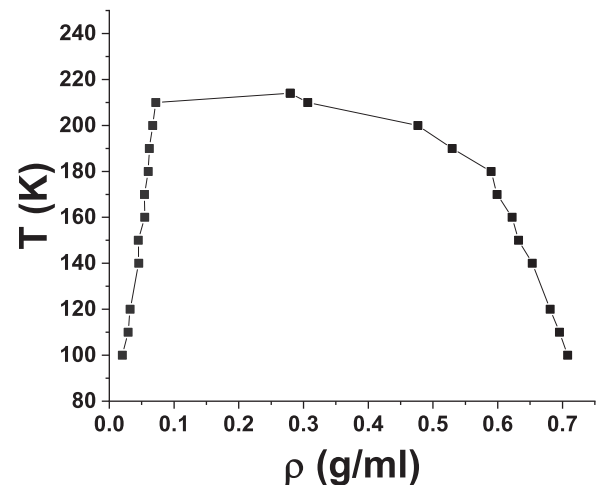


FIG. 4. Boiling curve of the equimolar system.

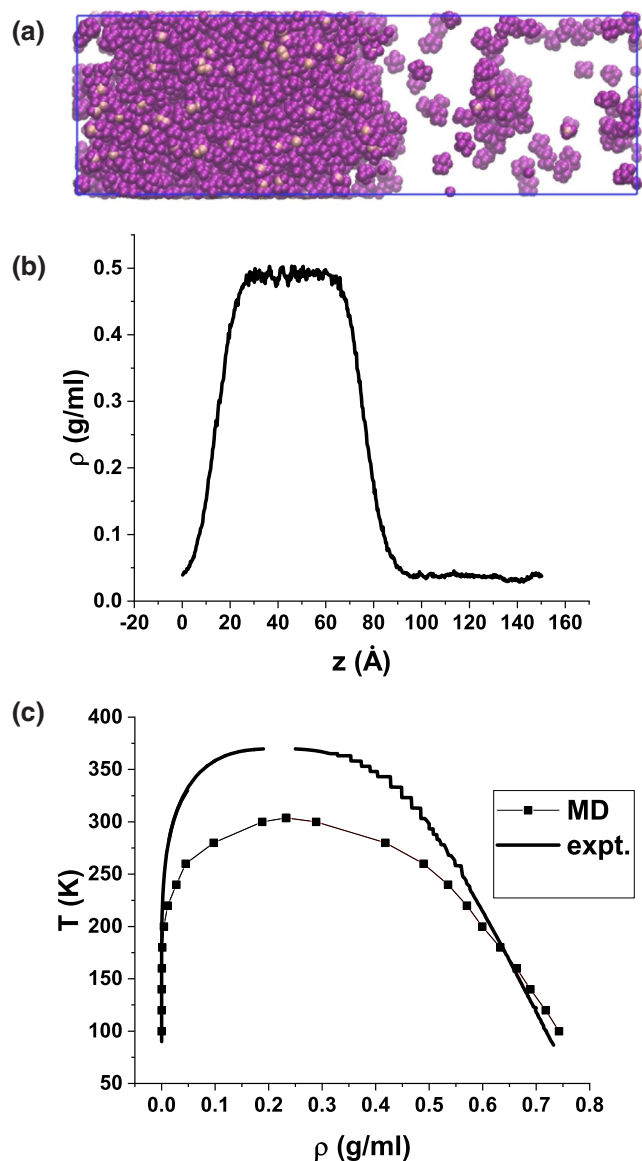


FIG. 5. (a) A snapshot of the pure propane system. (b) Mass density profile of the same system. (c) Boiling curve of pure propane in comparison to experimental data.

$\rho_c = 0.30193$ g/ml (the experimental value is $\rho_{c,\text{expt}} = 0.3133$ g/ml [27]). Although the agreement between the simulation and the experiment is rather poor, we believe that our work can give interesting insight into the concentration behavior of the phase diagram of a propane-nitrogen mixture.

Figure 3(a) shows a snapshot of an equimolar system (50% nitrogen and 50% propane) at $T = 160$ K. Phase separation into gas and liquid phases is observed. Moreover, one can clearly see that the gas phase consists mostly of nitrogen. Although some propane molecules are visible in the gas phase, the concentration of propane is nearly zero.

Figure 3(b) shows a mass density profile, while Fig. 3(c) shows the profiles of the densities of nitrogen and propane. From these plots we estimate that the molar concentration of nitrogen in the liquid phase is 0.17, while the gas phase contains 0.998 molar parts of nitrogen.

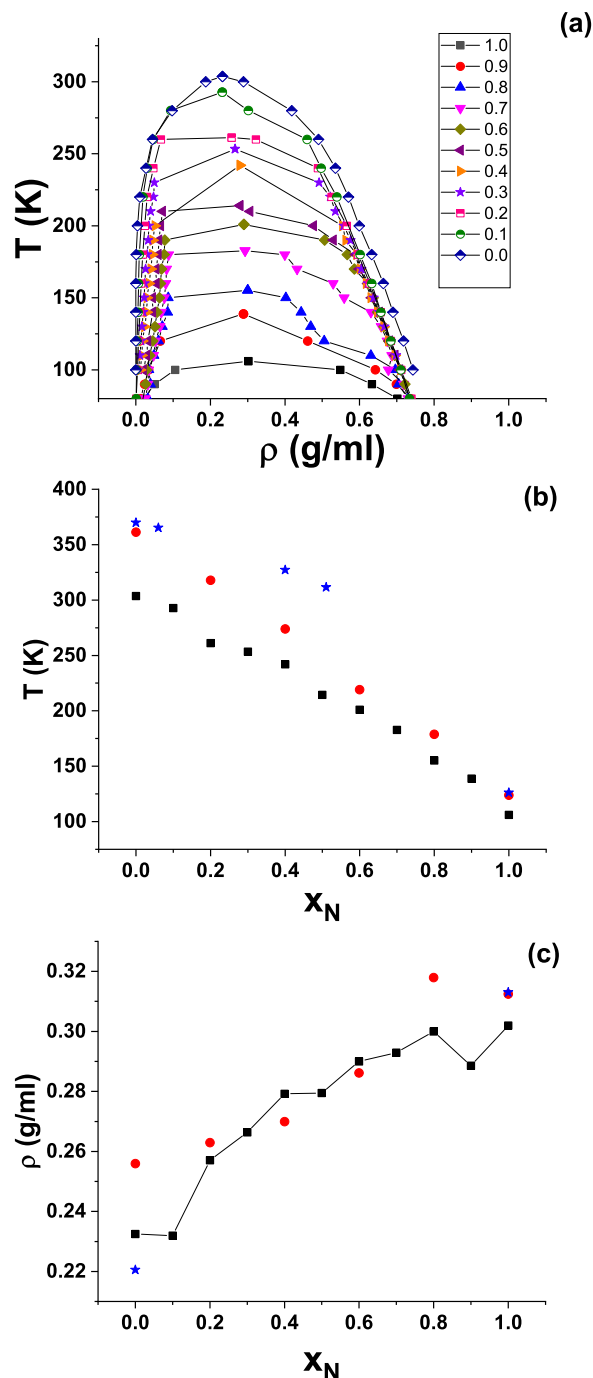


FIG. 6. (a) Boiling curves of all simulated systems (from pure nitrogen to pure propane). (b) Critical temperatures of all systems. (c) Critical densities of all simulated systems. In (b) and (c) the black squares are obtained from two-phase simulations, and red circles are obtained from near-critical maxima. Blue stars are experimental data. The experimental data for pure propane and nitrogen are taken from the NIST database, where the data can be obtained either from a particular paper or as a kind of “averaging” over available experimental data. The data for the critical temperature of mixtures are taken from Ref. [29].

The boiling curve of the equimolar system is given in Fig. 4. The critical temperature is estimated to be $T_c = 214$ K, and the critical density $\rho_c = 0.28$ g/ml.

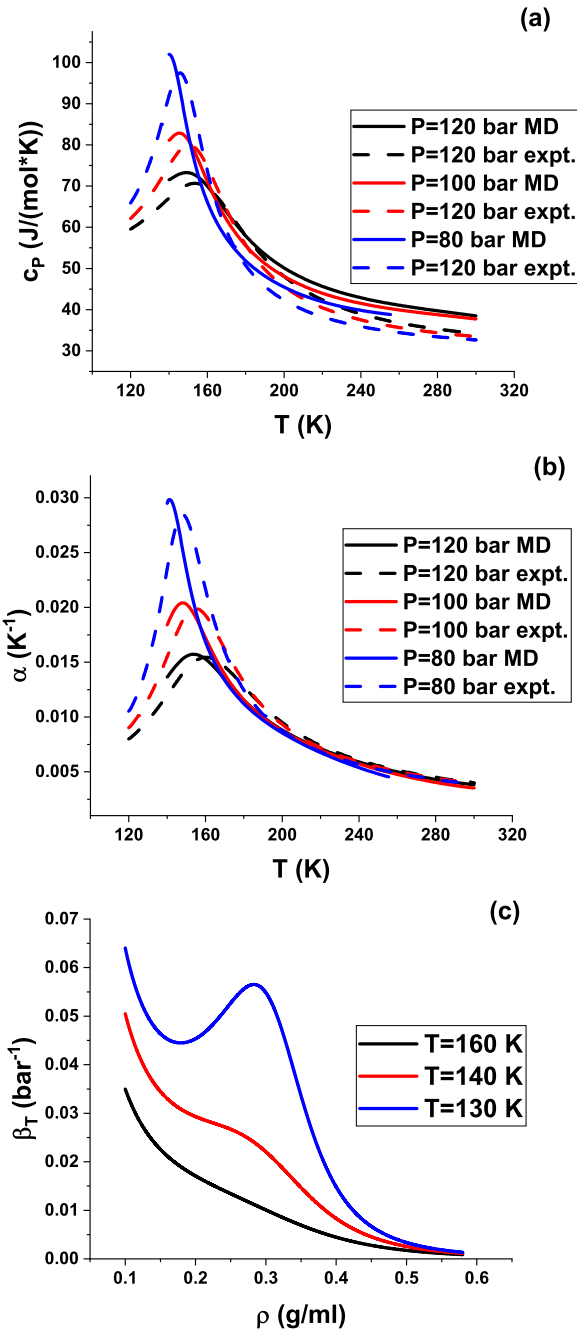


FIG. 7. (a) Comparison of isobaric heat capacities from the simulation and from NIST data for pure nitrogen. (b) The same for the thermal expansion coefficient. (c) Isothermal compressibility of pure nitrogen. NIST data are not available in this temperature range.

As a final example we consider a pure propane system. Figure 5(a) shows a snapshot of the system at $T = 260$ K. Again one observes a clear phase separation in the system. The density profile is shown in Fig. 5(b). From this profile we obtain that the density of liquid is $\rho_l = 0.49$ g/ml and the density of gas is $\rho_g = 0.045$ g/ml.

Figure 5(c) shows a comparison between the boiling curve obtained in this paper and from experiments. The experimental data are taken from Ref. [28]. One can see that the simulation highly underestimates the critical tempera-

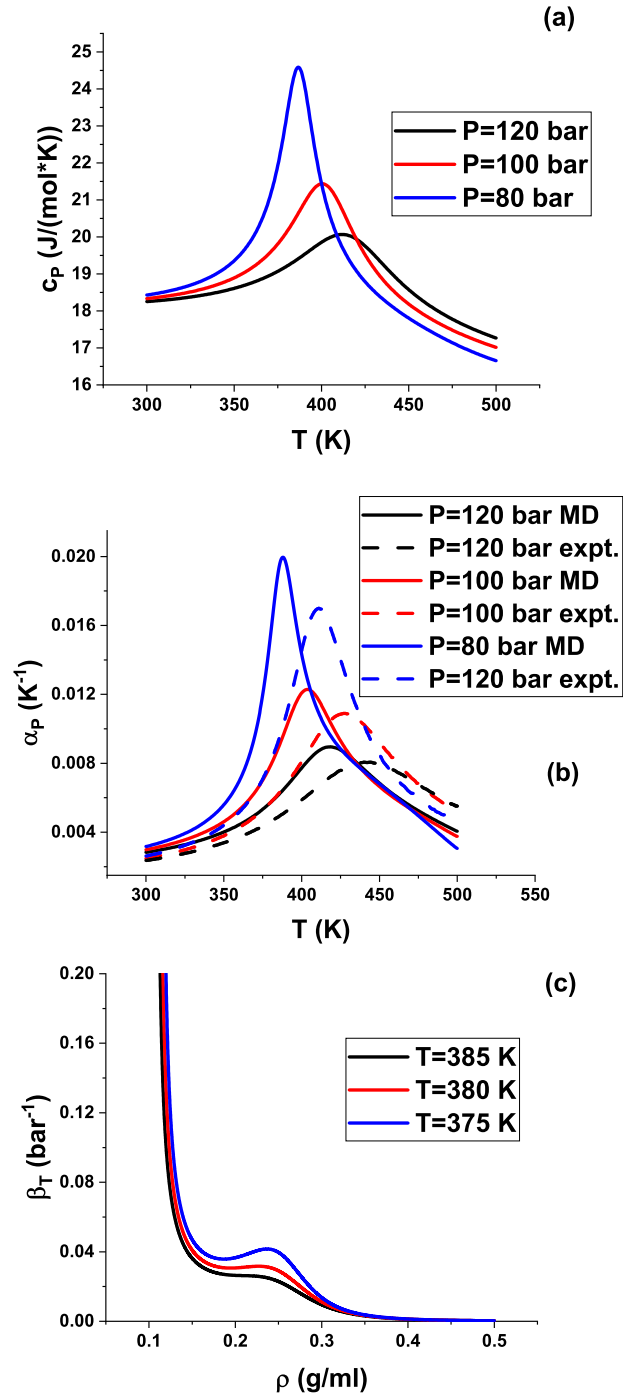


FIG. 8. (a) Comparison of isobaric heat capacities from simulation and from NIST data for pure propane. (b) The same for the thermal expansion coefficient. (c) Isothermal compressibility of pure propane.

ture of the system: $T_c = 303.7$ K in the simulation vs $T_c = 369.9$ K in experiment. At the same time the critical density obtained in the simulation appears to be in good agreement with experiment ($\rho_c = 0.23$ g/ml in the simulation and $\rho_c = 0.22$ g/ml in experiment).

From the results above, we conclude that the selected model underestimates the critical temperature of both nitrogen and propane. Therefore we expect that the critical

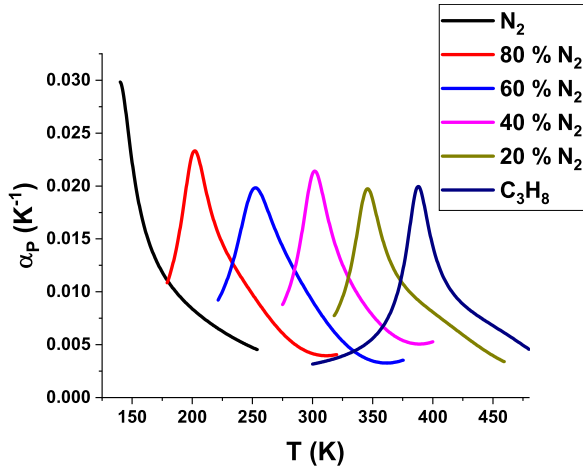


FIG. 9. Thermal expansion coefficient of the nitrogen-propane mixture at different concentrations of components.

temperatures of the mixtures are also underestimated. However, in spite of this underestimation the employed model can give valuable insight into the microscopic mechanisms of propane-nitrogen mixtures.

Figure 6(a) shows the boiling curves of the system at all concentrations under consideration, while Figs. 6(b) and 6(c) demonstrate the critical temperature and critical density as a function of the concentration. All boiling curves and examples of the density profiles are given in the Supplemental Material [30].

As was discussed above, the propane-nitrogen mixture is a type III mixture in the van Konynenburg–Scott classification [22]. However, we do not observe any complication of the phase diagram due to the presence of the liquid-liquid phase transition. We believe that this liquid-liquid phase transition is located at low temperatures and because of this it did not appear within the frame of the present study.

B. Near-critical maxima

Next we study the near-critical maxima of propane-nitrogen mixtures. Figure 7 shows isobaric heat capacities, thermal expansion coefficients, and isothermal compressibilities of pure nitrogen. Where it is possible, the data from the simulation are compared with the data from the National Institute of Standards and Technology (NIST) database [31]. One can see that for both c_P and α_P the simulation overestimates the height of the peaks. Moreover, the peaks from the simulation are shifted to slightly lower temperatures, which means that the critical temperature is again underestimated. We evaluate the critical parameters from the standard condition $(\frac{\partial P}{\partial V})_T = 0$ and $(\frac{\partial^2 P}{\partial V^2})_T = 0$. The critical point of pure nitrogen obtained by this method appears to be $T_c = 124$ K, $\rho_c = 0.3125$ g/ml, and $P_c = 42.174$ bar. Compared with the two-phase simulation, the critical temperature obtained by this method is in closer agreement with the experimental data.

Figure 8 shows the isobaric compressibility, thermal expansion coefficient, and isothermal compressibility of pure propane in comparison to the NIST data [31].

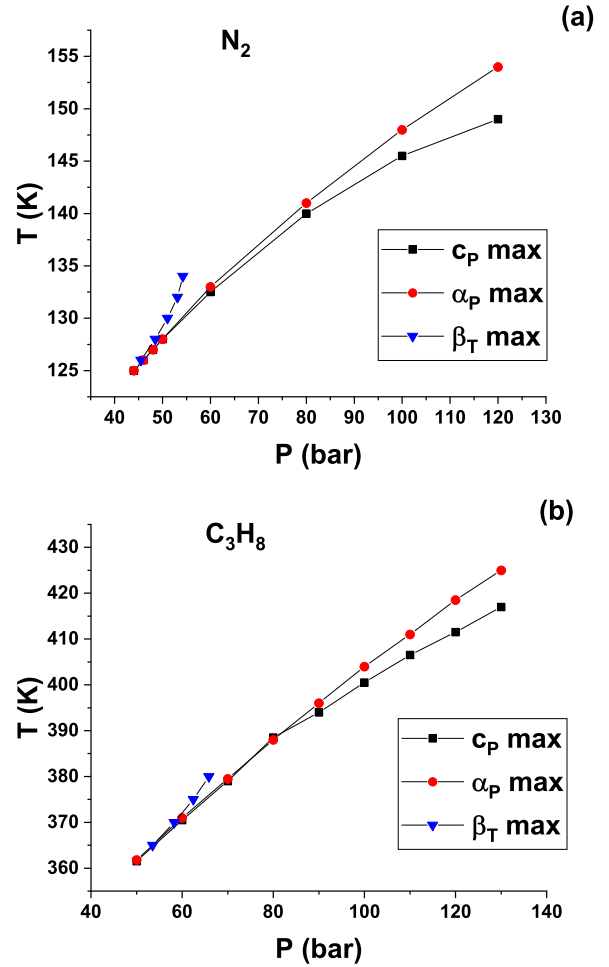


FIG. 10. (a) Location of maxima of response functions of pure nitrogen in the pressure-temperature plane. (b) The same for pure propane.

The maxima of the isobaric heat capacity, thermal expansion coefficient, and isothermal compressibility for mixtures of propane and nitrogen are given in the Supplemental Material [30].

Figure 9 shows the thermal expansion coefficient of mixtures with different concentrations of components at isobar $P = 80$ bar. One can see that the temperature of the maximum of the thermal expansion moves to higher T with increasing concentration of propane. This behavior is expected since the critical temperature of the mixture increases with an increase in the concentration of propane.

In Ref. [21], two regions of near-critical anomalies were observed in a type III mixture. In our study we observe only one region of Widom lines. We believe that the liquid-liquid critical point is located at rather low temperatures, and it appears to be beyond the range of thermodynamic parameters considered in this paper.

We evaluate the location of the maxima of different functions in the P - T plane. Figure 10 shows the location of maxima of the response functions for pure nitrogen and pure propane. Analogous plots for different concentrations of the components are given in the Supplemental Material [30]. In both the case of pure nitrogen and the case of pure propane

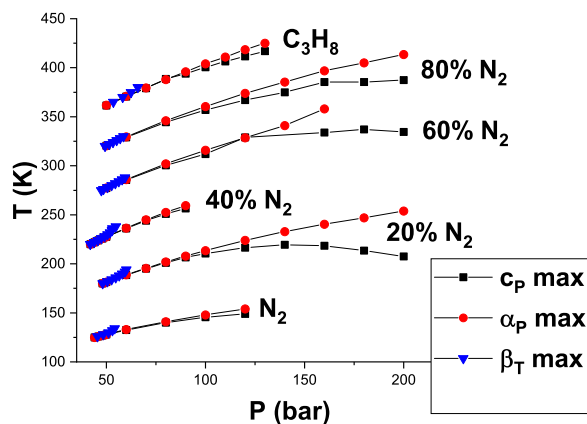


FIG. 11. Widom lines of all studied systems in the same plot.

the qualitative behavior of the Widom lines looks very similar to that of a simple liquid. The curves of the maxima of c_p and α_p have a positive slope, although at higher temperature the curve of the maxima of c_p changes to having a negative slope. The curve of the maxima of β_T rapidly disappears with temperature. The results at intermediate concentrations of the components are qualitatively similar.

Figure 11 shows Widom lines of all studied systems in the same plot. One can see that the qualitative behavior of the system at all concentrations is qualitatively similar. The only change is that the location of the curves shifts to higher temperatures as the concentration of propane increases.

IV. CONCLUSIONS

In conclusion, the boiling line of mixtures of nitrogen and propane was studied by means of molecular simulation methods. Boiling curves of the system at different concentrations of components were calculated by means of two-phase molecular simulation.

Widom lines of the mixture with different concentrations of components were also studied. The curves of the maxima of the response functions also demonstrate a continuous shift to higher temperatures moving from pure nitrogen to pure propane.

Critical parameters of the mixtures were evaluated by two different methods: two-phase simulation of gas-liquid coexistence and simulation of the disordered system from high temperatures to the temperatures below T_c and differentiation of the equation of state. The second method gives a critical temperature closer to the experimental value. This could be related to finite-size effects in two-phase simulations.

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- [31] <https://webbook.nist.gov/chemistry/fluid/>.
- [32] <http://ckp.nrcki.ru>.