# A rare gas mixture: From rigid to gas-like fluid by a mutual concentration change

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For a number of mixtures of rare gases at high pressures, sound speed minima are experimentally observed depending on the concentration. This behavior has not yet been explained. We have studied the behavior of a mixture of argon and helium using computer simulation. Sound speed minima have been discovered at a certain concentration, which is in good agreement with experimental data. It is shown that this behavior is due to the fact that the P and T parameters for gas mixtures are near the Frenkel line, separating the states of "rigid" and quasi-gas fluid.

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### INTRODUCTION

Speed of sound  $c_s$  is an important thermodynamic characteristic of a substance, which is relatively easily measurable experimentally. It allows obtaining other thermodynamic properties, first of all an equation of state, i.e. the density as a function of pressure at given temperature. A speed of sound also demonstrates different behavior in a dense liquid and in a gas: while in the former case it decreases upon isobaric heating, in the latter it increases. Some other properties of fluid also demonstrate qualitatively different behavior in liquid and gas states, for instance, shear viscosity. As a result, it also demonstrates a minimum. In our recent works a special line separating liquid-like and gas-like regimes of fluid (the Frenkel line) was proposed [1-4]. It is remarkable that the minima of all quantities with different behavior in liquid and gas states are close to the Frenkel line.

Although the speeds of sound of pure fluids are sufficiently well documented, much less is known about the speed of sound in mixtures, especially at elevated pressures. Three types of concentration dependence of the speed of sound in mixtures are reported [5]: (i) with a minimum of  $c_s$  as a function of the component concentration; (ii) with a maximum and (iii) with a bend. However, up to now there is no firm theoretical understanding of the reasons for different behavior of  $c_s$  in mixtures.

The minimum of concentration dependence of the speed of sound is reported even in very simple systems, like mixtures of noble gases. For instance, in Ref. [6, 7] a minimum of  $c_s$  in a mixture of argon and helium at high pressure was reported. The same authors also performed measurements of a speed of sound in mixtures of some other gases at high pressure (carbon dioxide - helium, nitrogen - methane and some others [8–11]) and found minima of  $c_s$  as a function of concentration of the com-

ponents in some of these mixtures (carbon dioxide - helium), but not in others (nitrogen - methane). Moreover, in the latter case it was found that the speed of sound in a mixture at high pressure can be relatively precisely described by an expression for the speed of sound in a mixture of ideal gases [11]. At the same time the authors do not give any explanations of the nature of different behavior of a speed of sound in mixtures of different gases.

The goal of the present paper is to find the reasons of minima of the concentration dependence of a speed of sound in mixtures of noble gases at high pressure.

### SYSTEM AND METHODS

In the present work we simulate a mixture of argon and helium at three different values of pressure: 200, 300 and 400 MPa at T = 298 K by means of the molecular dynamics method. These thermodynamic conditions are taken from Ref. [6] in order to compare the results of simulation with experimental data. The molar concentration of helium is varied from x = 0.0 (pure argon) to x = 1.0 (pure helium) with step  $\Delta x = 0.1$ . In all cases a system of 32000 particles with a given concentration of species placed in a cubic box with periodic boundary conditions is considered. We simulate the system under constant pressure conditions, i.e. constant number of particles N, pressure P and temperature T. The time step is set to 1 fs. The equilibration period is 200 ns and further 300 ns are used for calculation of the properties of the system.

We calculate the adiabatic speed of sound as  $c_s = \left(\gamma \frac{\partial P}{\partial \rho}\right)^{1/2}$ , where  $\gamma = c_p/c_V$ . In order to evaluate the pressure derivative on density we calculate two points with slightly higher density and two more at slightly smaller one from the minimum. The pressure at these five points is fitted to a straight line, the slope of which gives the derivative. Analogously, by calculating two points at higher and lower temperatures either along the isochor,

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FIG. 1: The speed of sound in the mixture of argon and helium as a function of helium concentration at P = 200 MPa. The experimental data are taken from Ref. [6]. The inset enlarges the region near the minimum of the curves.

or along the isobar we calculate the heat capacities at a constant volume or at constant pressure.

Both argon and helium were simulated with the Lennard-Jones (LJ) potentials. The potential parameters for both helium and argon are taken from Ref. [12]:  $\varepsilon_{He} = 10.9$  K,  $\sigma_{He} = 2.64$  Å and  $\varepsilon_{Ar} = 119.8$  K,  $\sigma_{Ar} = 3.405$  Å. The cross-interaction parameters were taken from the Lorentz-Berthelot rules.

All simulations were performed using the LAMMPS simulation package [13].

#### **RESULTS AND DISCUSSION**

The speed of sound of the argon - helium mixture at P = 200 MPa is shown in Fig. 1. We see that  $c_s$  from simulation demonstrates a minimum, but it is less pronounced compared with the experimental curve. It is seen that the speed of sound of pure argon from simulation is in perfect agreement with the experimental one  $(c_s = 1012.52 \ m/s \text{ from MD} \text{ and } c_s = 1019.64 \ m/s \text{ from}$ the experiment), while the speed of sound of pure helium in molecular dynamics is higher than the experimental one. The speed of sound of the mixture obtained in simulation is also higher than the experimental one at the same concentration, which should be related to overestimation of the speed of sound of helium. As a result, the minimum of  $c_s$  from the simulation is less pronounced than that from the experiment. However, the location of the minimum at concentration  $x_{He} \approx 0.3$  is the same for both experiment and simulation.

Figures 2 (a) and (b) show the heat capacities and the density derivative of the pressure of the argon-helium mixture at P = 200 MPa. It is seen that both isobaric and isochoric heat capacities monotonically decrease with



FIG. 2: (a) The isobaric and isochoric heat capacities of the mixture of argon and helium as a function of helium concentration at P = 200 MPa (in the units of  $k_B$ ). (b) The density derivative of pressure of the same system. The inset enlarges the region of the minimum.

an increase in the helium concentration. At the same time the derivative  $\left(\frac{\partial P}{\partial \rho}\right)_T$  demonstrates a minimum at concentration  $x_{He} \approx 0.2$ , which is smaller than the concentration for the minimum of  $c_s$ . It means that the minimum is related to the shape of the derivative of compressibility, while the heat capacity only shifts the minimum, but does not change the qualitative shape of the curve.

Figure 3 shows the speed of sound in the Ar-He mixture at pressures 300 and 400 MPa. The experimental results are qualitatively similar to the case of 200 MPa, while the minimum of  $c_s$  from the simulation becomes less pronounced and is hardly visible at P = 400 MPa.

It is known that mixtures can demonstrate much more complex phase diagrams than pure substances (see, for instance, [14]). In particular, a mixture of argon and helium belongs to the III type in the van Konynburg -Scott classification [15], i.e. in addition to a usual gas liquid transition it also demonstrates a liquid-liquid one at high pressures. There are several works where the



FIG. 3: The speed of sound in the mixture of argon and helium as a function of helium concentration at (a) P = 300 MPa and (b) P = 400 MPa. The experimental data are taken from Ref. [6]. The insets enlarge the region near the minimum of the curves.

phase diagram of an Ar-He mixture is reported [16–18]. An empirical equation of state for this mixture is constructed in Ref. [19] and the phase diagram of the mixture is calculated. However, all these data belong to either much lower pressures, or much lower temperatures. To the best of our knowledge, no data for phase behavior of an Ar-He mixture at T = 300 K and pressures above 200 MPa are reported in the literature. Figure 4(d) of Ref. [19] reports the phase diagram of the mixture up to very high pressure P = 10 kbar and temperature up to 180 K. Extrapolation of the data of this figure leads us to the conclusion that the points of interest (T = 300)K and P = 200, 300 and 400 MPa) belong to one phase region, and should be far from the phase transition lines. Therefore, no influence of phase transitions is expected at these points.

It is well known that a speed of sound shows a minimum along isobars. Sometimes this minimum is considered as a boundary of liquid-like (the speed of sound decreases with temperature) and gas-like (the speed of 3

sound increases with temperature) regimes in supercritical fluid. Interestingly, the minimum of the speed of sound is located close to the Frenkel line of the fluid (although not exactly on the Frenkel line). This minimum of the speed of sound takes place at relatively high temperature. For instance, in the case of argon at P = 200 MPa the speed of sound demonstrates a minimum at  $T_m = 681$ K [20]. The minimum of the speed of sound of helium at the same pressure corresponds to  $T_m = 188.5 \text{ K} [20]$ . The phase diagrams of argon and helium are very close to the phase diagram of the LJ system [24]. Figure 4 shows the phase diagram of the LJ system in the units of  $P/P_c$  and  $T/T_c$ . We show the Frenkel line and the locations of minima of the speed of sound in the mixture obtained in the present work. For the sake of comparison, we also show the location of minima of  $c_s$  along the isobars of pure argon and pure helium taken from the NIST database [20]. One can see that at large  $P/P_c$  the line of minima of  $c_s$  becomes roughly parallel to the Frenkel line in the double logarithmic coordinates. At the same time for pure substances, it is always slightly above the Frenkel line.

The point with given thermodynamic variables (P,T) corresponds to different points for argon and helium in the plane  $(P/P_c,T/T_c)$ , since these gases have strongly different critical parameters. The points corresponding to the mixtures should belong to a line connecting those of pure components at the same pressure. As is seen from Fig. 4 this line (the dotted line) should be located not far from the Frenkel line of the LJ system and even cross it. Thus, trajectories corresponding to the minima of the speed of sound under the change of the concentration of the components near the border between gas-like and liquid-like regimes of fluid, appear on the phase diagram of the LJ system. One should expect similar behavior for the other properties of fluid demonstrating minima at the isobars (shear viscosity, heat conductivity, etc.).

As it was discussed in a number of works [1, 4, 23], the properties of liquid in the vicinity of the Frenkel line can be optimal for some technological applications. At the same time the thermodynamic parameters of the Frenkel line can be hardly achievable for many industrial fluids, since they involve rather high pressures. From the results of the present paper, we can conclude that the Frenkel line of a particular fluid can be shifted by mixing it with light components with a low critical point. This conclusion opens a window for novel methods of design of fluids with a given position of the Frenkel line on the phase diagram. It is also desirable to perform investigation of concentration dependence of other properties of fluid mixtures in the vicinity of the Frenkel line.



FIG. 4: The phase diagram of the LJ system in reduced units. The points 'Ar' show the points of pure argon at T = 300 K and P = 200, 300 and 400 MPa, i.e., the thermodynamic conditions studied in this paper. The points denoted as 'He' show the same for helium. Line  $c_V = 2.0$  shows the location of the Frenkel line. The points 'Ar NIST' and 'He NIST' show the location of minima of the speed of sound along the isobars in pure argon and helium taken from the NIST database [20]. The boiling line is taken from. Ref. [21] and the melting line from Ref. [22].

## CONCLUSIONS

A minimum of the speed of sound in a mixture of the noble gases argon and helium was established experimentally a long time ago. In the present paper we perform a molecular dynamics study of this system based on a simple LJ model of the gases. We show that this simple model also demonstrates a minimum of the speed of sound as a function of the concentration of helium. The location of the minimum is in good agreement with the experiment. We assume that this minimum might be related to the proximity to the Frenkel line of the mixture.

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- V V Brazhkin, A G Lyapin, V N Ryzhov, K Trachenko, Yu D Fomin, E N Tsiok, Where is the supercritical fluid on the phase diagram?, Physics Uspekhi 55 (11) 1061 - 1079 (2012)
- [2] V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, and K. Trachenko, Two liquid states of matter: A dynamic line on a phase

diagram, Phys. Rev. E 85, 031203 (2012)

- [3] V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, and K. Trachenko, Universal Crossover of Liquid Dynamics in Supercritical Region, JETP Letters, 2012, Vol. 95, No. 3, pp. 164–169
- [4] V. V. Brazhkin, A. G. Lyapin, V. N. Ryzhov, K. Trachenko, Yu. D. Fomin, and , E. N. Tsiok, The Frenkel line and supercritical technologies, ussian Journal of Physical Chemistry B, 2014, Vol. 8, No. 8, pp. 1087–1094.
- [5] I. G. Mikhailov, V. A. Soloviov, Yu. P. Syrnikov, Basics of molecular acoustics (in Russian), Moscow, Nauka, 1964
- [6] Yu. L. Kachanov, B. E. Kanishchev and L. L. Pitaevskaya, Velocity of sound in argon and in helium-argon and nitrogen-carbon dioxide gas mixtures at high pressures, Journal of engineering physics, 44, 1–4, (1983)
- [7] B.E. Kanishchev and L. L. Pitaevskaya, "Sound velocity and density of binary mixtures of helium with argon," Inzh.-Fiz. Zh., 399, No. 6, 1090-1094 (1980).
- [8] L. L. Pitaevskaya, A. A. Popov, Sound velocity in helium-carbon dioxide mixtures at high pressures, Dokl. Akad. Nauk SSSR, 1991, Volume 316, Number 5, 1112–1116
- [9] B. E. Kanichev, L. L. Pitaevskaya, S. L. Gutman, Speed of sound in nitrogem carbon dioxide and theirs mixtures at high pressures, Dokl. Akad. Nauk SSSR, 1981, Volume 257, Number 6, 1348-1351
- [10] L. L. Pitaevskaya, B. E. Kanichev, Speed of sound in mixtures of nitrogen and helium at high pressures, Dokl. Akad. Nauk SSSR, 1977, Volume 232, Number 1, 62-64
- [11] L. L. Pitaevskaya, B. E. Kanichev, Speed of propagation of ultrasound in mixtures of nitrogen and methane at pressures up to 4 kbar, Dokl. Akad. Nauk SSSR, 1976, Volume 229, Number 6, 1345-1346
- [12] Orhan Talu, Alan L. Myers, Reference potentials for adsorption of helium, argon, methane, and krypton in high-silica zeolites, Colloids and Surfaces A: Physicochemical and Engineering Aspects 187–188 (2001) 83–93
- [13] A. Thompson et. al., Computer Physics Communications 271, 108171 (2022)
- [14] S. Rowlinson and F. L. Swinton, Liquids and Liquid Mixtures, 3rd ed. (Butterworths, London, 1982).
- [15] P. H. Van Konynenburg and R. L. Scott, Critical Lines and Phase Equilibria in Binary Van Der Waals Mixtures, Philos. Trans. R. Soc. 298, 495 (1980).
- [16] W. B. Streett, Gas-liquid and fluid-fluid phase separation in the system helium + argon at high pressures, Transactions of the Faraday Society, 69, 696 (1969)
- [17] William B. Streett and James L. E. Hill, Phase equilibria in fluid mixtures at high pressures: the helium + argon system, Trans. Faraday Soc., 1971,67, 622-630
- [18] W.B. Streett, A.L. Erickson, Phase equilibria

in gas mixtures at high pressures: Implications for planetary structures, Physics of the Earth and Planetary Interiors Volume 5, 1972, Pages 357-366

- [19] J. Tkaczuk , I. H. Bell , E. W. Lemmon , N. Luchier , and F. Millet, J. Phys. Chem. Ref. Data 49, 023101 (2020).
- [20] https://webbook.nist.gov/chemistry/fluid/
- [21] A.Z. Panagiotopoulos, N. Quirke, M. Stapleton, and D.J. Tildesley, Phase equilibria by simulation in the Gibbs ensemble, Molecular Physics, 63, 527 (1988)
- [22] R. Agrawal and D. A. Kofke, Thermodynamic and structural properties of model systems at solid-fluid coexistence II. Melting and sublimation of the Lennard-Jones system. Molecular Physics, 85, 43-49 (1995)
- [23] C. Yang, V. V. Brazhkin, M. T. Dove, and K. Trachenko, Frenkel line and solubility maximum in supercritical fluids, Phys. Rev. E 91, 012112 (2015)
- [24] The quantum effect for helium is negligible in the range of thermodynamic parameters of this work