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Mesoscopic phase transition in molecule-cluster mixture of argon

Kassymov A.B., Kurlapov L.I.

Kazakh National Technical University after K.I.Satpaev, Almaty, Kazakhstan
[1]festland2@yandex.kz, [2]lkurlapov@yandex.com

Key words: mesoscopic phase transition, molecule-cluster mixture, viscosity, thermal diffusion, centrifuge.

Abstract. Calculations of concentrations of cluster components in molecule-cluster mixture of argon were shown. Pressure and temperature ranges where mesoscopic phase transition is observed are found on the example of viscosity, thermal diffusion and in centrifuge. Phenomenon of mesoscopic phase transition in molecule-cluster mixture lies in the fact that in certain area of macroparameters properties of gases correspond to the properties of liquids.

Мезоскопический фазовый переход в молекулярно-кластерной смеси аргона

Касымов А.Б., Курлапов Л.И.
[1]festland2@yandex.kz, [2]lkurlapov@yandex.com

Казахский Национальный Технический Университет имени К.И.Сатпаева,
Алматы, Казахстан

Ключевые слова: мезоскопический фазовый переход, молекулярно-кластерная смесь, вязкость, термодиффузия, центрифуга.

Аннотация. Приведены расчёты концентраций кластерных субкомпонентов в молекулярно-кластерной смеси аргона и выявлены области давлений и температуры, в которых наблюдается мезоскопический фазовый переход на примере вязкости, термодиффузии, а также в центрифуге. Мезоскопический фазовый переход в молекулярно-кластерной смеси проявляется в том, что в определённой области макропараметров свойства газов соответствуют свойству жидкости.

Introduction.Argon is usually used as a test substance in the investigations of gas properties and in different technologies, which is connected to the relative simplicity of monatomic molecules and inertness. In this paper we present calculations of some properties of argon at temperatures and pressures (in near-critical region) where mesoscopic phase transition takes place [1-4]. In this area of macroparameters molecular collisions lead to the formation of multimolecular formations – clusters, containing up to ten molecules of argon. Such large clusters impose some properties of liquid on gas, and molecule-cluster mixture is considered as a mesoscopic system that occupies an intermediate position between the two phases of matter. Mesoscopic phase transition takes an intermediate position between the phase transitions of the first kind and the second kind and has the properties of these transitions. Mesoscopic phase transition has some properties of the phase transition of the first kind (release/absorption of latent energy takes place in the system) and some properties of the phase transition of the second kind: it takes place in the entire system without the formation of the phase boundary. This phenomenon can be used in practice in the calculations of thermal phenomena. But the main application of it can be found in the theory for the clarification of features of liquid and gaseous states.

Method. In this paper we use method based on a physical model, in which every gas is considered as a multi-component mixture consisting of clusters of different sizes – molecule-cluster mixture. The physical properties of this mixture is largely determined by the concentration of cluster components, for the calculations of which schemes based on dynamic equilibrium distribution of cluster sizes in the space were used:

$$C_g^{(c)} = C_1^{(c)} \exp\left[-\beta(g-1)\right], \qquad (1)$$

where g – number of molecules in the cluster,

$C_g^{(c)}$ – concentration of clusters containing g molecules,

$C_1^{(c)}$ – concentration of molecular sub-component, which is considered as a one-dimensional cluster,

β – dimensionless factor that depends on the conditions (pressure, temperature and individual characteristics of the gas).

Calculations of the thermal diffusion coefficient and formula of distributions of clusters in the field of external forces are determined by solving the kinetic equation for the multicomponent mixture of dense gases, which in this model has the following form [1-4]:

$$\frac{\partial f_\alpha}{\partial t} + \vec{\xi}_\alpha \cdot \vec{\nabla} f_\alpha + \vec{\Xi}_\alpha \cdot \frac{\partial f_\alpha}{\partial \vec{\xi}_\alpha} = \sum_{\beta=1}^{s} \int \left(f'_\alpha f'^{0}_\beta - f_\alpha f^{0}_\beta \right) Y b\, db\, g_{\alpha\beta}\, d\varepsilon\, d^3\xi_\beta, \qquad (2)$$

where f_α – non-equilibrium distribution function of test particles,

f_β^0 – spatially uniform function of the velocity of field particles,

$\vec{\xi}_\alpha$ – velocity of test particles in the primary inertial reference system,

$\vec{\Xi}_\alpha$ – acceleration of particles of mass m_α by external force

Y – correlation function in a dense gas.

The surface density of particle flux $\vec{\Gamma}_\alpha$ as a first-order moment of non-equilibrium distribution function found by solving of (2) has the following form [4]:

$$\vec{\Gamma}_\alpha = n_\alpha \vec{W} - D_\alpha \vec{\nabla} n_\alpha + n_\alpha (D_\alpha^T - D_\alpha) \vec{\nabla} \ln T + n_\alpha D_\alpha \frac{m_\alpha}{k_B T} \vec{\Xi}_\alpha, \qquad (3)$$

since $$f_\alpha = f_\alpha^0 \cdot \left[1 + \Phi_\alpha\right]; \quad \vec{W} = \frac{1}{n_\alpha} \int \vec{\xi}_\alpha f_\alpha^0 d\vec{\xi}_\alpha, \quad \vec{\Gamma}_\alpha = \int \vec{\xi}_\alpha f_\alpha d\vec{\xi}_\alpha;$$

where n_α – partial number density of component of the mixture under the number α,

$\vec{W}$ – velocity of ordered motion (convection velocity, which is the same for all components of mixture, since it is defined as a first-order moment with locally equilibrium function f_α^0),

D_α – intrinsic diffusion coefficient,

D_α^T – thermal diffusion coefficient.

As seen from (3), flux of the particles of each component of the mixture under number α consists of three components: convection, diffusion (conventional and thermal) and force drift.

In the one dimensional case this expression transformed into the following equation for one component of the gradient of the partial number density:

$$\frac{dn_\alpha}{d\mathrm{x}} = n_\alpha\left[-\frac{m_\alpha\Xi_\alpha}{k_BT} + \frac{W}{D_\alpha} + \left(\frac{D_\alpha^T}{D_\alpha} - 1\right)\frac{d\ln T}{d\mathrm{x}}\right] - \frac{\Gamma_\alpha}{D_\alpha}. \qquad (4)$$

Selecting size of the device L as length scale, and numerical density n_α, corresponding to the origin of coordinates $n_\alpha(0)$ as scale, in isothermal conditions equation (3) can be reduced to dimensionless form:

$$\frac{dN}{dX} = -NB - Q\,, \qquad (5)$$

where $X \equiv \frac{\mathrm{x}}{L}$; $\quad N \equiv \frac{n}{n(0)}$; $\quad B \equiv L\left(\frac{m\Xi}{k_BT} - \frac{W}{D}\right)$; $\quad Q \equiv \frac{L\Gamma}{n(0)D}$.

As can be seen from (4) and (5), for the simple case of an ideal gas in gravitational field integration of (4) gives well-known barometric formula. During the description of gas in the field of centrifugal forces in centrifuge in the form of closed tube solution of equation (5) gives the known formula [3]:

$$\frac{n(\mathrm{x})}{n(0)} = \exp\left(-\frac{m\omega^2\mathrm{x}^2}{2k_BT}\right), \qquad (6)$$

where ω – angular velocity.

For comparisons with the barometric formula, in the last formula axis $0\mathrm{x}$ directed from the periphery toward the rotation axis of the tube.

The following section presents calculations of the thermal diffusion coefficient of argon in the region of mesoscopic phase transition, as well as the results of the solutions of equation (5), taking into account the impact of addition and removal of particles, i.e. $Q \neq 0$.

Discussion

Concentration of cluster components is necessary for the calculations of the properties of molecule-cluster mixture.

Figure 1 shows the calculations of the concentrations on the basis of formula (1) and using the parameters of argon under appropriate conditions [5].

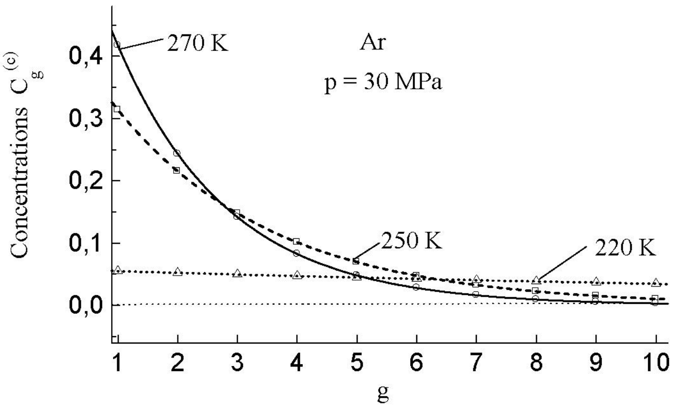

Fig. 1. Concentration distribution of argon clusters by their size at different temperatures.

As seen from Fig.1, in near-critical region (critical parameters for argon: T_c = 150.9 K, p_c=5.0 MPa [5]) gas may contain clusters consisting of a dozen molecules. Such heavy clusters significantly affect the properties of the gas, in particular it is they who affect the appearance of a mesoscopic phase transition, which is clearly seen from the plots of the temperature dependence of viscosity that shown in Fig.2

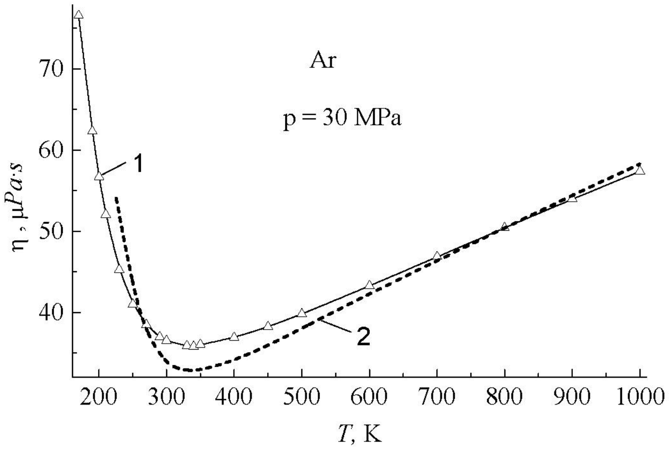

Fig. 2. Viscosity as a function of temperature:
1 – reference data [5] , 2 – calculations with the usage of cluster composition.

As expected, in the near-critical region of temperatures mesoscopic phase transition is observed. Physical meaning of it lies in the fact that below this temperature, the viscosity of the gas changes with temperature according to the characteristic of the viscosity of the liquid: when the temperature decreases the viscosity increases. This feature is related to the influence of heavy clusters, which gain advantages during the collisions with molecules and light clusters.

J.H. Jeans introduced the concept of persistence of velocities after collision to describe this phenomenon in the framework of elementary kinetic theory [4]. Equation (2) and the formulas for the transport coefficients appearing in (3) contain certain features of the elementary kinetics and mathematical apparatus also take into account this phenomenon.

Mesoscopic phase transition can be observed in the molecule-cluster mixtures in the presence of temperature gradient, under the influence of which, according to (3) there is particles flux. In this paper we used a physical model, which is basically consistent with the model of the Boltzmann known as elementary kinetic theory, in which observed phenomena is given a simple visual interpretation. In particular, within the framework of the elementary theory, flux of particles in (3) is a differential effect: during the random motion particles pass cross-section of control area in the direction of the temperature gradient and opposite direction. This difference is determined by the average value of the product of density on the thermal velocity $\langle nv \rangle$, which is more in gases in cold region, and in liquid - in hot region. According to (3) in gases particle flux is directed along the temperature gradient and the thermal diffusion coefficient is defined as a positive value, and in liquid particles flux is directed against the direction of the temperature gradient and the thermal diffusion coefficient is defined negative. In molecule-cluster mixture under certain conditions the molecule and light clusters correspond to the gas phase, and heavy clusters - the liquid phase. For example, Fig. 3 shows the thermal diffusion coefficient calculations for clusters of different sizes.

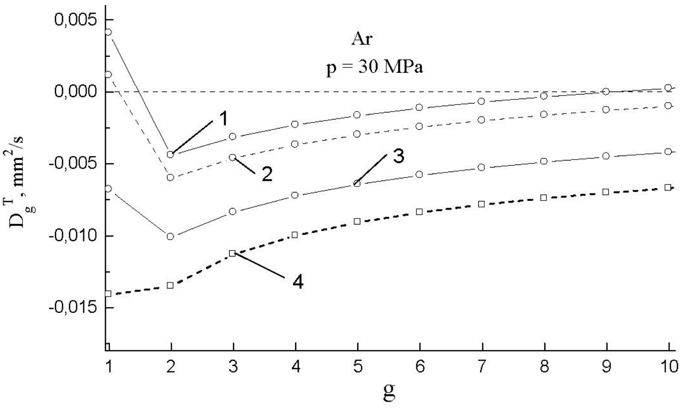

Fig. 3. Thermal diffusion coefficient of cluster components at different temperatures:
1 at T=310 *K*; 2 at T=300 *K*; 3 at T=270 *K*; 4 at T=230 *K*.

As seen in Figure 3, the thermal diffusion coefficient at relatively high temperatures (points on lines 1 and 2) has a positive value for molecules that, according to (3) corresponds to the gas. At temperatures close to the critical, thermal diffusion coefficient for all cluster components is negative, which corresponds to the liquid. Moreover, for all the considered temperatures argon is in homogeneous gaseous phase. Thus, mesoscopic phase transition is observed in the phenomenon of thermal diffusion: entire mixture has intermediate properties between gas and liquid, reason of which is the interaction of heavy clusters with molecules and light clusters.

Results of calculations of distribution of particles in centrifuge are shown in Fig.4

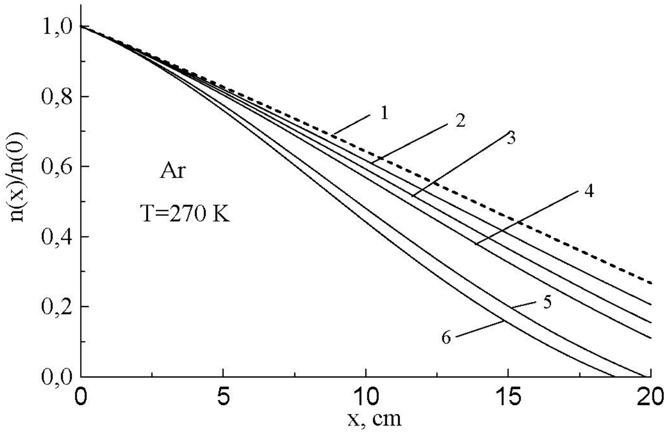

Fig. 4. Concentration distribution of clusters by their coordinate in centrifuge tube of length L = 20 cm at angular speed ω = 10 s^{-1} and at dimensionless flow of addition and removal of particles Q = -0.033: 1 – for molecules, g =1; 2 – g=2; 3 - g=3; 4 – g=4; 5 – g=8; 6 – g=10.

As can be seen from Fig. 4, heavy clusters ($g \geq 6$) are located only in the peripheral region of the centrifuge like a liquid, i.e. they represent mesoscopic particles forming the mesoscopic phase transition.

Conclusion

1. Calculated concentration of cluster components in dense gases allowed to calculate the properties that in good agree with the known experimental data in the corresponding area of macroparameters. Calculations of viscosity, thermal diffusion coefficient and distribution of heavy clusters in centrifuge for molecule-cluster mixture of argon allowed to reveal mesoscopic phase transition. According to these properties in the region of phase transition molecule-cluster mixture occupies intermediate position between gas and liquid.

2. Mesoscopic phase transition is related to the fact that heavy clusters have advantages in collisions

with molecules and light clusters that allows them to carry molecule (cluster) feature over abnormally large distance, so the properties of molecule-cluster mixture of gas acquire the characteristics of the properties of the other phases of matter, in particular – of fluid. However, the formation of a new phase with the visible phase boundary is prevented by collisions that lead to the decay of the clusters.

3. Heavy clusters are mesoscopic particles that occupy an intermediate position between the microparticles, involved in the thermal random motion as molecules, and macrobodies belonging to particular phase of matter, which is the feature of macroscopic bodies.

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Аргонның молекула-кластерлік қоспасындағы мезоскопиялық фазалық ауысу

А.Б.Касымов, Л.И.Курлапов
[1]festland2@yandex.kz, [2]lkurlapov@yandex.com

Қ.И.Сәтбаев атындағы Қазақ Ұлттық Техникалық Университеті, Алматы, Қазақстан

Тірек сөздер: мезоскопиялық фазалық ауысу, молекула-кластерлік қоспа, тұтқырлық, термодиффузия, центрифуга.

Аннотация. Аргонның молекула-кластерлік қоспасындағы кластерлік субкомпоненттер концентрациясының есептері көрсетілген, сонымен қатар тұтқырлық, термодиффузия және центрифуга үлгілерінде мезоскопиялық фазалық ауысу байқалатын қысым және температура аймақтары анықталған. Молекула-кластерлік қоспасында мезоскопиялық фазалық ауысу белгілі макропараметрлер аймағында газдың қасиеттері сұйықтыққа сәйкес келетінінде байқалады.

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