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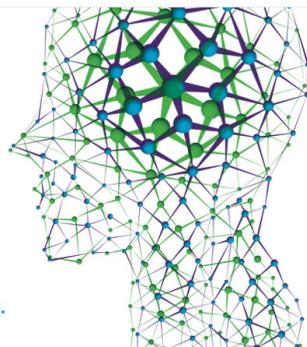
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The cluster model of a hot dense vapor

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We explore thermodynamic properties of a vapor in the range of state parameters where the contribution to thermodynamic functions from bound states of atoms (clusters) dominates over the interaction between the components of the vapor in free states. The clusters are assumed to be light and sufficiently “hot” for the number of bonds to be minimized. We use the technique of calculation of the cluster partition function for the cluster with a minimum number of interatomic bonds to calculate the caloric properties (heat capacity and velocity of sound) for an ideal mixture of the lightest clusters. The problem proves to be exactly solvable and resulting formulas are functions solely of the equilibrium constant of the dimer formation. These formulas ensure a satisfactory correlation with the reference data for the vapors of cesium, mercury, and argon up to moderate densities in both the sub- and supercritical regions. For cesium, we extend the model to the densities close to the critical one by inclusion of the clusters of arbitrary size. Knowledge of the cluster composition of the cesium vapor makes it possible to treat nonequilibrium phenomena such as nucleation of the supersaturated vapor, for which the effect of the cluster structural transition is likely to be significant. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919114>]

I. INTRODUCTION

The methods used for construction of the equation of state and description of caloric properties of nonideal gases are well-known, among them, phenomenological approaches, which imply construction of the fundamental equation for the Helmholtz energy including up to a hundred number of terms. For example, such equations were obtained by Jacobsen, Stewart, and Jahangiri for nitrogen,¹ by Jahangiri *et al.* for ethylene,² and by Stewart and Jacobsen for argon.³ Other approaches utilize the pressure expansion in powers of the density (virial expansion, see, e.g., the works of Tegeler, Span, and Wagner⁴ and Maitland *et al.*⁵), the expansion in powers of the activity, etc. Estela-Uribe and Jaramillo⁶ recovered the intermolecular interaction potential from the phenomenological virial expansion. In the work of Vargaftik, Voljak, and Stepanov,⁷ the phenomenological virial expansion including seven terms was employed to calculate the heat capacity and the sound velocity for the nonideal gaseous state of cesium in sub- and supercritical regions; Fokin, Popov, and Naurzakov⁸ used the virial expansion to calculate the equation of state and caloric properties of mercury saturated vapors.

In these phenomenological approaches, a very high accuracy is attained, so that the calculation results are commonly used as reference data. On the other hand, a set of experimental data required for calculation of the gaseous phase thermodynamic functions includes typically the *PVT*-data, the temperature dependences of the saturated vapor pressure and density, the triple and critical temperatures, and the parameters of the dimer molecule. This renders impossible to predict thermodynamic properties of a substance in the region of state

parameters, where such experimental data are not available. Also within this approach, a real structure of the fluid remains obscure since the interatomic interactions are included merely formally. Hence, it is impossible to treat nonequilibrium phenomena such as the interaction of a vapor with the electromagnetic field or the nucleation of supersaturated vapor.

One can classify all intermolecular interactions in a nonideal gas (vapor) as occurring with and without formation of bound states that are commonly called the clusters. Under certain conditions, the fraction of atoms bound in the clusters is sufficiently high so that the contribution to the thermodynamic functions from the interaction between the atoms in free states is negligibly small as compared to that from the interaction of atoms bound in the clusters. Such conditions are realized for a vapor near the saturation line between the melting and critical temperatures and even above the critical point. Thus, one can treat a nonideal gas as a mixture of clusters of different sizes. This model could not be applicable in the region of state parameters where clusters are almost absent or where the dissociation of monomers at sufficiently high temperature results in the emergence of additional gas components (e.g., in the region of atom ionization or of the chemical dissociation of the molecular monomers). Band^{9,10} proposed to consider a nonideal gas as a mixture of clusters of arbitrary size. However, modeling the cluster partition functions was rather qualitative so that an acceptable accuracy could not be attained. The simplest reduction of this approach is the allowance only for the atoms and dimers. For example, for the cesium vapor, this approximation was used in Refs. 11 and 12. However, the neglect of all clusters heavier than a dimer imposes too strong limitations on its limits of validity. A good correspondence with the reference data can be attained solely in the region where a gas is almost ideal. Therefore, an urgent problem is

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a correct description of the clusters consisting of more than two atoms.

As shown in Ref. 13, the clusters comprising less than ten atoms undergo the structural transition as the temperature is increased. The “hot” clusters prove to change their structure from the close packed to the chainlike one. The thermodynamic perturbation theory developed by Wertheim^{14–16} predicts polymerization of the monomers with highly directional attraction into the chain clusters. Similar phenomenon can occur even for the spherically symmetric pair additive interatomic potential.¹³ However, in this case, the chainlike clusters are formed via the transformation of the close packed ones rather than by polymerization of the monomers. The approximation of the minimum number of bonds between the atoms comprising a cluster is a clue for calculation of the cluster partition function, which was expressed in terms of the equilibrium constant of the dimer formation. Then, a gas was treated as an ideal mixture of different size clusters, and this made it possible to calculate the size distribution of the clusters comprising more than two atoms and the compressibility factor of the vapor. The latter quantity calculated for cesium and water¹⁷ appeared to reproduce well its temperature and density dependences, which were observed experimentally. An obvious shortcoming of this model is the inaccessibility of the unit compressibility factor due to neglect of the interaction between the monomers and clusters in free states. However, its advantage is the possibility to deduce concise analytical results.

An objective of this study is to extend such an approach to the caloric quantities of a nonideal gas (vapor). Based on the approximation of the minimum number of bonds along with the treatment of the gas as an ideal mixture of clusters, one can derive explicit expressions for the isobaric and isochoric heat capacities and for the velocity of sound. Within this approach, an exact analytical solution of the thermodynamic problem, which includes solely the information on the equilibrium constant of the dimer formation, can be used as a guide in collection of the thermodynamic data for poorly investigated substances. Obviously, the limits of validity of this model are restricted by the requirement that the temperature is above the point of the structural transition. Therefore, it is necessary to estimate the structural transition temperature for metals with the nonadditive interatomic potentials. We demonstrate that if the binding energy of a dimer is much greater than the temperature, the structural transition occurs well above the melting point for the bulk substance. Then the model was extended by consideration of arbitrary size clusters on the basis of the notion of a cluster as a core of the internal atoms surrounded by a layer of the surface atoms. This makes it possible to reach a good correlation with experiment up to the neighborhood of the critical point. This extended model can be used for treatment of a nonequilibrium process, namely, the homogeneous nucleation of supersaturated vapor. A comparison with the experimental data reveals the effect of the structural transition on the critical size clusters.

The paper is organized as follows. In Sec. II A, the size distribution is derived for the clusters with the minimum number of bonds, and the resulting compressibility factor for an ideal mixture of such clusters is derived. In Sec. II B, we calculate the heat capacities and the velocity of sound for

this system; the temperature range of the cluster structural transition is defined in Sec. II C. In Sec. II D, we compare the calculated caloric properties of nonideal gases with the reference data. In Sec. III, we extend the model by inclusion of arbitrary size clusters and check the resulting equation of state. This model is applied for the calculation of the critical supersaturation ratio for the cesium vapor in Sec. IV. The paper ends with a discussion of results (Sec. V).

II. THERMODYNAMICS OF AN IDEAL MIXTURE OF THE LIGHTEST CLUSTERS

A. Size distribution and compressibility factor

We will treat the vapor as an ideal mixture of clusters with different size k . Here, we will confine ourselves to the lightest clusters comprising $k \lesssim 10$ atoms. In so doing, we assume that the gas nonideality is solely due to the formation of physical clusters. Obviously, this model, which neglects the repulsion between the mixture components (monomers and clusters), must underestimate the overall repulsion between molecules (however, the repulsion is partly included in the cluster formation). Band¹⁰ proposed to take repulsion into account as the volume exclusion introduced by monomers and clusters. On the other hand, analysis of the cesium vapor¹⁸ shows that the volume exclusion is partly compensated by attraction between atoms in unbound states so that, solely, the repulsion between free atoms should be included, and this is only appreciable in the vicinity of the critical point, while the excluded volume of the clusters is always negligibly small. Apparently, one can assume that for most substances, the contribution from the repulsion in free states is small everywhere but in the vicinity of the critical point, where the validity of the cluster model becomes questionable. Indeed, in this region, the difference between the gas and liquid vanishes, which obviously makes a definition of a cluster problematic. In any case, within the framework of the model of an ideal mixture of clusters, it is possible to obtain concise analytical formulas for all essential thermodynamic quantities of the system.

The basic characteristic of the cluster vapor is the equilibrium size distribution of clusters. In absence of the information concerning the interaction between the monomers, we will utilize the assumption of Ref. 19 that the surface energy of a cluster is proportional to the number of its surface atoms. The lightest clusters with $k \lesssim 10$ cannot include internal atoms, and therefore, they consist solely of the surface atoms. Thus, the chemical potential of a cluster comprising k atoms μ_k ($k = 1$ denotes the atom) can be written in the form,

$$\mu_k = T \ln p_k + \zeta_k(T), \quad \zeta_k(T) = A(T)k + B(T), \quad (1)$$

where T is the temperature, p_k is the partial pressure of corresponding clusters, and $\zeta_k(T)$, $A(T)$, and $B(T)$ are functions of temperature. We write (1) for $k = 1, 2$ to derive $A(T) = \zeta_2(T) - \zeta_1(T)$ and $B(T) = 2\zeta_1(T) - \zeta_2(T)$. The mass action law for the reaction of dimer formation $K_p(T) = p_2/p_1^2$, where $K_p(T)$ is the equilibrium constant for this reaction, makes it possible to find $\zeta_2(T) = -T \ln K_p(T) + 2\zeta_1(T)$.

Therefore,

$$\mu_k = T \ln p_k + k\zeta_1(T) - (k-1)T \ln K_p(T). \quad (2)$$

With the mass action law for the reaction of the k -mer formation, $\mu_k = k\mu_1$, we arrive at the sought equilibrium size distribution of partial pressures¹⁹

$$p_k = p_1^k K_p^{k-1}(T), \quad (3)$$

which can be written as the distribution of the cluster number densities $n_k = p_k/T$: $n_k = n_1^k [TK_p(T)]^{k-1}$. Here and in what follows, we set the Boltzmann constant to unity and measure the temperature in energy units.

If the potential of the interaction between molecules is known, then linearity assumption (1) can be validated. As was shown in Ref. 13, the lightest clusters of atoms interacting via the short-range pair additive potential undergo the structural transition: at sufficiently high temperature, the cluster structure changes from the close packed to the loosely bound one. The basic assumption of this model defining the loosely bound state is that the number of atomic pairs with the nonzero interaction energy (the number of bonds) is equal to its minimum $k-1$; the interaction between other atoms pertaining to the same cluster as well as to different clusters is assumed to vanish. Thus, a cluster can be represented as a set of intersecting chains of atoms (Fig. 6 of Ref. 13). In the simplest case of a single chain, for each atomic configuration, one can enumerate the cluster atoms in such a way that the nearest neighbors for each i th atom are the $(i-1)$ th and $(i+1)$ th ones, and the first and the last ones have only one neighbor. In contrast to a rigid polymer chain, the ordering of atoms is *not fixed* so the atoms change their positions in the chain; however, at any instant, the number of bonds in the cluster remains minimal. Hence, treated chains are rather the virtual than the real ones. Manifestation of the structural transition is, e.g., a sharp change in the temperature dependence of the cluster average potential energy (Fig. 3 of Ref. 13). If the number of bonds is $k-1$ then the partition function of a cluster $Z_c^{(k)}$ can be factorized as

$$Z_c^{(k)} = \lambda^{-3k} \int \cdots \int' \exp \left[-\frac{U_c(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k)}{T} \right] d\mathbf{r}_1 \cdots d\mathbf{r}_k \\ = \frac{V}{\lambda^3} [Z_c^{(2)}]^{k-1}, \quad (4)$$

where $Z_c^{(2)} = (V/\lambda^6) \int' \exp[-u_2(r)/T] d\mathbf{r}$ is the partition function of a dimer and the integral with prime means that the integration is performed over the phase space region, where only physically different states are realized. Here, $\lambda = (2\pi\hbar^2/MT)^{1/2}$ is the thermal wavelength, M is the monomer mass, V is the system volume, $U_c(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k)$ is the potential energy of a cluster as a function of the atom coordinates, and $u_2(r)$ is the potential energy of the interaction between two monomers at the distance r . Since $\mu_k = T \ln N_k - \ln Z_c^{(k)}$, where N_k is the number of clusters comprising k atoms, we readily derive from the mass action law for the reaction of cluster formation distribution (3).

It is worth comparing this result with the Wertheim approach as applied to the gas of chain clusters.^{14–16} In our approach, the short-range potential is also implied. In addition, cluster partition function (4) is similar to that of a rigid chain due to elimination of the physically identical states. However,

the differences between the two approaches are essential. First, no more than two bonds per a monomer (a single bond per attraction site) are allowed in the Wertheim theory. On the contrary, any number of bonds per atom is allowed in the virtual chain (see, e.g., Fig. 6 of Ref. 13). Due to this, at $k \gtrsim 10$, an atom can form many bonds. Then, the increase in the potential energy cannot be dominated by the increase in the entropy, and this suppresses the formation of a chain. Second, in the Wertheim approach, chains emerge as the temperature is decreased.²⁰ On the contrary, in our approach, the virtual chains emerge as the temperature is increased. The latter is a consequence of the different types of bonds, highly directional and spherically symmetric, respectively.

Based on Eq. (3), one can calculate the compressibility factor,¹⁹

$$Z = \frac{pV}{NT} = \frac{\sum_{k=1}^{\infty} p_k}{\sum_{k=1}^{\infty} k p_k} = \frac{1}{1 + pK_p(T)}, \quad (5)$$

where $p = \sum_{k=1}^{\infty} p_k$ is the total pressure and $N = \sum_{k=1}^{\infty} N_k$ is the total number of monomers. In Eq. (3), we assume a fast convergence, which allows one to extend summation to infinity. Equation (5) can be rewritten in the form of the equation of state,

$$pM = \frac{\rho T}{1 + pK_p(T)}, \quad (6)$$

where $\rho = MN/V$ is the density.

The equilibrium constant of the dimer formation in Eq. (3) has the form $K_p(T) = CT^{-1/2} \exp(D/T)$, where the pre-exponential factor C depends on the vibration quantum and the moment of inertia of the dimer and D is the dimer binding energy. At high temperatures when $T \sim D$, a correction for finiteness of the number of vibration levels $D/\hbar\omega$ proves to be effective in the reproduction of the equation of state for dense vapors. If we neglect the anharmonicity, then the form of the equilibrium constant is transformed to¹⁷

$$K_p(T) = \frac{C}{T^{1/2}} \left[\exp \left(\frac{D}{T} \right) - 1 \right]. \quad (7)$$

It follows from Eq. (7) that at high temperatures, $TK_p(T) \propto T^{-1/2}$, i.e., Z must weakly depend on T at constant N and V . Note that Eqs. (5) and (7) include no adjustable parameter, and $K_p(T)$ can, in principle, be calculated *ab initio*.

It is noteworthy that in the used approximation, the rotational and vibration parts of the virtual chain partition function are not explicitly isolated. In this meaning, the chain vibration partition function is not the product of dimer vibration partition functions.

At moderate densities, the compressibility factor calculated along the isotherms using (5) and (7) is in a good agreement with the equations of state for cesium and water measured in experiment.¹⁷ The effect of clusters is most pronounced for cesium vapor, for which Z is appreciably lower than unity. The model discussed above reproduces the *PVT* data rather accurately up to the density $\rho \approx 0.04 \text{ g/cm}^3$, and the difference between this model and the calculation neglecting the clusters larger than the dimers is significant (see Sec. III, Fig. 7).

B. Heat capacity and velocity of sound

Consider the most important caloric properties of a mixture of the lightest clusters. In Ref. 21, the isobaric heat capacity was calculated for an ideal mixture of atoms and dimers. The objective of this section is the generalization of this result to the mixture of infinite number of clusters.

Our approach is based on distribution (3). In addition, we have to know the ground state energy and the heat capacity of the cluster comprising k atoms. Obviously, if the cluster is a set of virtual chains, then its binding energy is $(k-1)D$; therefore, the cluster ground state energy is $\varepsilon_k = k\varepsilon_1 - (k-1)D$, where ε_1 is the ground state energy of an atom. Also in this approximation, we can use partition function (4) to reduce the average potential energy of a cluster \bar{u}_k to the average potential energy of a dimer \bar{u}_2 : $\bar{u}_k = (k-1)\bar{u}_2$.¹³ Hence, the internal energy per one molecule of an ideal gas of the k -atom clusters $e_k = 3kT/2 + \bar{u}_k$ is

$$\begin{aligned} e_k &= \frac{3T}{2} + (k-1) \left(\frac{3T}{2} + \bar{u}_2 - D \right) + k\varepsilon_1 \\ &= \frac{3T}{2} + (k-1)T \left(c_{V_2} - \frac{3}{2} - \frac{D}{T} \right) + k\varepsilon_1, \end{aligned} \quad (8)$$

where $c_{V_2} = 7/2$ is the isochoric heat capacity per one molecule of an ideal gas of dimers. Therefore, the isochoric heat capacity of an ideal gas of k -atom clusters per one cluster is $c_{V_k} = de_k/dT = 3/2 + 2(k-1)$, and the isobaric heat capacity of this gas is

$$c_{p_k} = \frac{5}{2} + 2(k-1). \quad (9)$$

Formula (9) can be interpreted as follows. If a cluster is a set of chains, then it must have three translational degrees of freedom and four (two rotational, one vibration in the coordinate space, and one vibration in the momentum space) degrees of freedom per a chain dimer, i.e., $3 + 4(k-1)$ total degrees of freedom. With due regard for the equipartition theorem and the relation $c_{p_k} - c_{V_k} = 1$, we arrive at result (9).

We use the mass action law for the reaction of cluster formation $\mu_k = k\mu_1$ to write the entropy of the cluster vapor in the form

$$S = \sum_{k=1}^{\infty} N_k \left[c_{p_k} - (k-1) \frac{D}{T} \right] - \frac{\mu_1 - \varepsilon_1}{T} \sum_{k=1}^{\infty} kN_k. \quad (10)$$

Knowledge of isobaric and isochoric heat capacities (14) and (18) makes it possible to calculate the sound velocity

$$\begin{aligned} c_s^2 &= \left(\frac{\partial p}{\partial \rho} \right)_S = \gamma(p, T) \left(\frac{\partial p}{\partial \rho} \right)_T = \frac{3c_{id}^2}{5} \frac{\gamma(p, T)}{1 + 2pK_p(T)} \\ &= \frac{3c_{id}^2}{5} \frac{\gamma Z}{2 - Z}, \end{aligned} \quad (20)$$

where $c_{id}^2 = 5T/3M$ is the sound velocity for an ideal gas.

Then, we represent the chemical potential of an atom in the form,²¹ $\mu_1 = T \ln p_1 + \varepsilon_1 - c_{p_1} T \ln T - T\chi_1(T)$, where c_{p_1} is the isobaric heat capacity of a monomer and $\chi_1(T)$ is a function of temperature, to rewrite (10) as

$$S = N \left[2 - \frac{D}{T} - \ln p_1 + \frac{5}{2} \ln T + \chi_1(T) + \left(\frac{D}{T} + \frac{1}{2} \right) Z(p, T) \right]. \quad (11)$$

Equation (3) allows one to relate p_1 and p . Since

$$p = p_1 \sum_{k=1}^{\infty} [p K_p(T)]^{k-1} = \frac{p_1}{1 - p_1 K_p(T)}, \quad (12)$$

we have $p_1 = pZ(p, T)$. Then, the entropy is represented in the form

$$S = N \left[\frac{5}{2} \ln T - \frac{D}{T} - \ln Z(p, T) + \left(\frac{D}{T} + \frac{1}{2} \right) Z(p, T) \right]. \quad (13)$$

The derivative of (13) defines the *isobaric* heat capacity of a cluster vapor per atom,

$$\frac{c_p}{N} = \frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_p = 2 + \frac{Z}{2} + (1-Z)[\delta + (Z\delta - 1)\delta_1], \quad (14)$$

where

$$\delta = \frac{D}{T} + \frac{1}{2}, \quad \delta_1 = \frac{D}{T} \left[1 - \exp \left(-\frac{D}{T} \right) \right] + \frac{1}{2}. \quad (15)$$

We use the relation between the isochoric and isobaric heat capacities²¹

$$\frac{c_p - c_v}{N} = -\frac{T}{N} \frac{\left(\frac{\partial V}{\partial T} \right)_p^2}{\left(\frac{\partial V}{\partial P} \right)_T}, \quad (16)$$

to derive

$$\frac{c_p - c_v}{N} = \frac{Z}{2-Z} [1 + (1-Z)\delta_1]^2. \quad (17)$$

Hence, the *isochoric* heat capacity of the cluster vapor per atom is

$$\begin{aligned} \frac{c_v}{N} &= 2 + \frac{Z}{2} + (1-Z)[\delta + (Z\delta - 1)\delta_1] \\ &\quad + Z(Z-2)^{-1}[1 + (1-Z)\delta_1]^2, \end{aligned} \quad (18)$$

and we can write the heat capacity ratio $\gamma(p, T) = c_p/c_v$ as

$$\gamma(p, T) = \frac{2 + \frac{Z}{2} + (1-Z)[\delta + (Z\delta - 1)\delta_1]}{2 + \frac{Z}{2} + (1-Z)[\delta + (Z\delta - 1)\delta_1] + Z(Z-2)^{-1}[1 + (1-Z)\delta_1]^2}. \quad (19)$$

C. Assessment of the structural transition temperature

The discussed model is valid if the temperature is sufficiently high to transform a compact solid-like cluster to a set of chains. The temperature of such transition was estimated in Ref. 13 for the pair additive short-range potential. Objective of this section is a similar estimate for the metal clusters. However, the interaction between atoms is still assumed to be of the short-range type, at least, for the metals treated below.

As was shown in Ref. 13, the ratio of the probabilities P_{vc} and P_{sol} to find a light cluster in the chain-like and the solid-like state, respectively, can be estimated as

$$\frac{P_{vc}}{P_{sol}} = \frac{\pi^{k-1}}{C_r C_v} \left(\frac{a}{r_0} \right)^{2k-5} \left(\frac{2D}{\pi T} \right)^{k-5/2} \exp \left(-\frac{\Delta E_k}{T} \right), \quad (21)$$

where C_r and C_v are the geometric factors corresponding to the rotational and vibration degrees of freedom defined by the close packed structure of a cluster and ΔE_k is the ground state energy difference between the chain-like and the solid-like states. The potential is assumed to be a short-range one with the typical equilibrium distance between the atoms in a dimer a and the potential width r_0 . The characteristic temperature of a transition between these two states is defined by the equality $P_{vc} = P_{sol}$, which we represent in the form

$$\frac{2D}{T} \exp \left(-\frac{2\Delta E_k}{(2k-5)T} \right) = \pi^{3/(5-2k)} (C_r C_v)^{2/(2k-5)} \left(\frac{r_0}{a} \right)^2. \quad (22)$$

Since we are interested in the transition in the structure of the largest possible light clusters, we set formally $k \rightarrow \infty$. Then Eq. (22) is transformed to

$$e^\tau = \frac{\tau}{\varepsilon} \left(\frac{a}{r_0} \right)^2, \quad (23)$$

where $\tau = 2D\varepsilon/T$ and $\varepsilon = \lim_{k \rightarrow \infty} [\Delta E_k/(2k-5)D]$. At $\tau > 0$, Eq. (23) has two roots if $(a/r_0)^2 > \varepsilon e$. The smaller root $\tau \approx 1/[(a/r_0)^2 \varepsilon^{-1} - 1] \ll 1$ has no physical meaning because bound states are absent if the temperature is so high. The bigger root $\tau > 1$ defines the sought characteristic temperature of the structural transition. The latter occurs in a smeared temperature region, whose halfwidth can be estimated as $\Delta T = 2D\varepsilon(1/\tau - 1/\tau')$. Here, τ' is the root of the equation

$$e^{\tau'} = \frac{10\tau'}{\varepsilon} \left(\frac{a}{r_0} \right)^2, \quad (24)$$

which corresponds to the temperature when solid-like configurations are more probable than the chain-like ones and $P_{sol}/P_{vc} = \sqrt{10}$. For the Lennard-Jones potential ($\varepsilon = 1$ and $a/r_0 = 6$), Eqs. (23) and (24) yield $T/D = 0.382$ and $(T - \Delta T)/D = 0.251$. These estimates are in a good agreement with the molecular dynamics simulation.¹³ However, Eqs. (23) and (24) can also be applied for the interatomic interactions, which are not pair-additive.

Next, we estimate T and ΔT for cesium. The data concerning the parameters of cesium dimer reported in different studies vary in a relatively wide range.^{22–26} The dimer binding energy D varies from 0.34 eV^{22,26} to 0.452 eV,²⁵ the equilibrium distance a from 4.62×10^{-8} cm²³ to 5.35×10^{-8} cm,²⁶ and the vibrational quantum $\hbar\omega_e$ from 0.0036 eV²⁶ to 0.0052 eV.²⁴ We adopted the values $D = 0.44$ eV, $a = 5.3 \times 10^{-8}$ cm, and $\hbar\omega_e = 0.0051$ eV. The potential width r_0 can be estimated from the relation $D = M\omega_e^2 r_0^2/4$, whence it follows that

$$\left(\frac{r_0}{a} \right)^2 = \frac{4\hbar^2}{MD} \left(\frac{D}{\hbar\omega_e} \right)^2 = \frac{8m_e}{M} \frac{\text{Ry}}{D} \left(\frac{D}{\hbar\omega_e} \frac{a_0}{a} \right)^2, \quad (25)$$

where m_e is the electron mass and a_0 is the Bohr radius. Thus, $(r_0/a)^2 \approx 0.0747$, i.e., the interatomic interaction can be treated as a short-range one.

For $3 \leq k \leq 8$, the binding energy of a solid-like cluster can be estimated as $(3k-6)D_k$,¹³ where D_k is the binding energy per bond for such cluster. According to Bahadur and McClurg,²⁷ the energy of a trimer per one bond (0.444 eV) almost coincides with D . Therefore, if the cesium atom has one or two bonds then the interatomic potential is little different from a pair additive one and it is steadily saturated for three or more bonds. Hence, for the chain-like cesium cluster, the binding energy is $(k-1)D$. Since $3D_k \rightarrow 0.8$ eV, i.e., $D_k \approx 0.606D$ at $k \rightarrow \infty$,²⁷ we have

$$\varepsilon = \lim_{k \rightarrow \infty} \frac{0.606(3k-6) - k + 1}{2k-5} = 0.409. \quad (26)$$

Corresponding solutions of Eqs. (23) and (24) are $\tau = 5.12$ and $\tau' = 7.62$. This yields the characteristic temperature of the structural transition $T = 816$ K and the temperature of its onset $T - \Delta T = 548$ K, respectively. Thus, the entire region where the difference of the compressibility factor from unity can be experimentally resolved ($T \geq 950$ K)⁷ lies above the transition temperature and the proposed approximation of chain-like clusters is valid. In contrast, the experimental data concerning the cesium vapor nucleation are available for the region of considerably lower temperatures that only partly intersects with the region of structural transition (Sec. IV). The difference in the position of the transitional temperatures for the Lennard-Jones system and cesium (below and well above the bulk melting points, respectively) is a consequence of the fact that the ratio D/T is noticeably higher for cesium. Apparently, one can expect a similar situation for most metals but mercury.

The mercury dimer has a low binding energy $D = 504$ K²⁸ and the van der Waals type bond. The lightest clusters up to $k = 20$ have the same bond type,²⁸ then cluster metallization starts. Hence, we can set $\varepsilon = 1$ similarly to the Lennard-Jones clusters. We borrow the dimer parameters for mercury from Ref. 28 and use Eq. (25) to obtain $a/r_0 = 4.34$. Thus, the estimated temperature of the structural transition amounts to 228 K, which is below the melting point of a bulk material.

Apparently, since a noticeable error is likely to be involved in the above-discussed estimates for metals, the obtained temperatures should be treated just as a guide for more exact calculations in the transitional region.

D. Calculation results

We compare the caloric properties of an ideal mixture of the lightest clusters calculated using Eqs. (14), (19), and (20) with the reference data available in the literature. These data were obtained by processing the equation of state along with the experimentally determined temperature dependence of the saturation pressure. The strongest effect of clusters on the vapor properties takes place for cesium because of the relatively high dimer binding energy (Figs. 1–3). A typical dependence of the isobaric heat capacity on temperature for the isobars is shown in Fig. 1 and on the density along the isotherms, in Fig. 2. For the calculation, we used the analytical dependence $K_p(T)$ borrowed from Refs. 11 and 12. For Fig. 2, we utilized equation of state (6) to calculate ρ . It is seen in Fig. 1 that the heat capacity calculated for a mixture of the

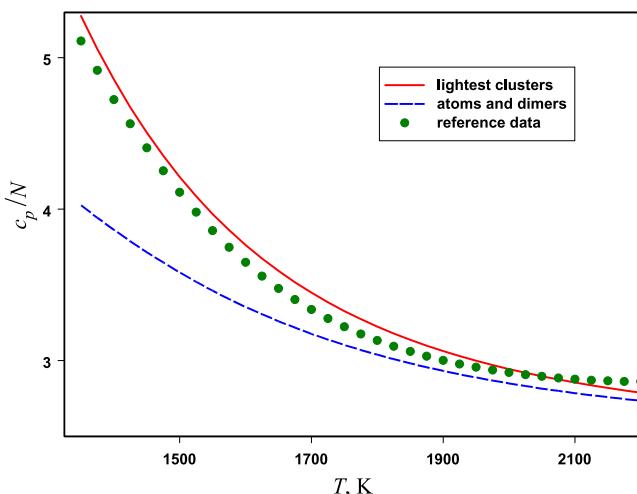


FIG. 1. Isobaric heat capacity for cesium in the gaseous state for the isobar $p = 1.5$ MPa. Solid line indicates the mixture of lightest clusters [Eq. (14)]; dashed line, of atoms and dimers;²¹ dots indicate the reference data.⁷

lightest clusters, which are treated as sets of chains, is in a good agreement with the reference data,⁷ despite the fact that the theory includes no adjustable constant. In contrast, if we confine ourselves to the treatment of atoms and dimers, then the agreement takes place only in a narrow range of high temperatures. Hence, the contribution from the clusters comprising more than two atoms to the heat capacity is quite noticeable, as it is for the compressibility factor.¹⁷ Also, Fig. 1 shows that at $T > 2200$ K, our model underestimates the heat capacity, which is an increasing function of temperature in this region. Apparently, this is due to ionization of atoms, which is not allowed for in our model. Note that the compressibility factor is still in a good agreement with experiment in the supercritical region, e.g., at $T = 2500$ K.¹⁷ This is not surprising because the contribution from k -atom clusters to the heat capacity is proportional not only to the concentration of such clusters but also to an additional factor $I_k/T \gg 1$, where I_k is the cluster ionization potential.

Figure 2 demonstrates a good correlation between heat capacity (14) as a function of the density calculated along

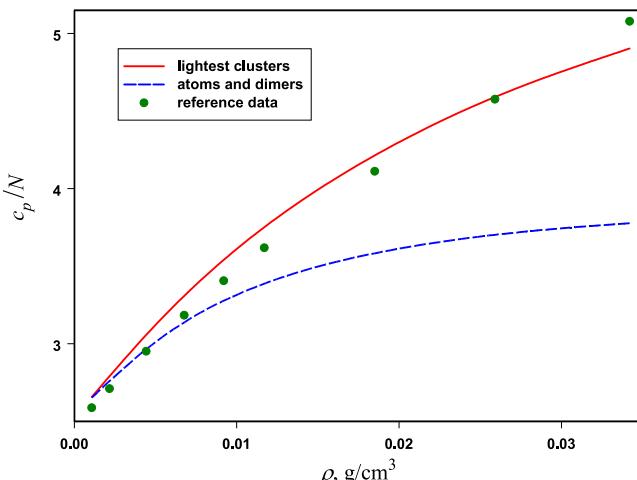


FIG. 2. Isobaric heat capacity for cesium along the isotherm $T = 1500$ K. Notation is the same as in Fig. 1.

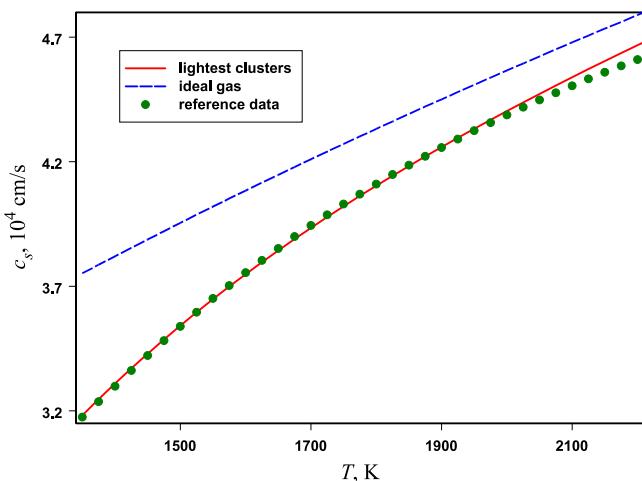


FIG. 3. Velocity of sound for cesium in the gaseous state for the isobar $p = 1.5$ MPa. Solid line indicates the mixture of lightest clusters [Eq. (20)]; dashed line, an ideal gas; dots indicate the reference data.⁷

a typical isotherm and the reference data.⁷ As is seen, the clusters with $k > 2$ should be taken into account already at $\rho > 0.01$ g/cm³, i.e., the “atoms plus dimers” model flaws, if the vapor is noticeably nonideal. At $\rho > 0.04$ g/cm³ (this approximately corresponds to $p \gtrsim 6$ MPa), our model underestimates the heat capacity. As shown in Sec. III, at high densities in the neighborhood of the critical point, convergence of series (5) is not sufficiently fast to ignore the fact that at $k \gtrsim 10$, size distribution (3) does not mimic a real one. Noted discrepancy can be removed by proper account of the heavier clusters.

Note that a good correlation with the reference data takes place for the heat capacities that are much higher than that of an ideal gas at relatively low temperatures and high densities (intersection points of the axes in Figs. 1 and 2 correspond to the heat capacity of an ideal gas). The sound velocity (Fig. 3) calculated along the isobar using Eq. (20) demonstrates the most accurate correspondence to the reference data.⁷ Even for high densities along the saturation line, for which inaccuracy of the theory is expected to be higher, a satisfactory agreement for the sound velocity is seen (Fig. 4), and the effect of the gas nonideality is quite pronounced. For Fig. 4, the temperature dependence of the saturation pressure necessary for the calculations was borrowed from Ref. 29. For the cesium vapor, formula (20) has the same limits of validity as those discussed above for the heat capacity.

For mercury, the effect of clusters is moderate due to the low binding energy of the lightest clusters. In other terms, the mercury vapor consists predominantly of atoms. For this reason, the compressibility factor is little different from unity even in the vicinity of the critical point. The same is true for the heat capacity: this quantity is little different from the ideal gas one. Since the difference seems to have the same order of magnitude as the accuracy of our model, it is inappropriate to compare the calculation results and the reference data. However, for the velocity of sound, the difference from the ideal gas is quite noticeable, and one can testify a satisfactory reproduction of the reference data⁸ by formula (20). The values of D and $\hbar\omega_e$ necessary for the calculation of $K_p(T)$ were borrowed from Ref. 28 and the temperature dependence of the

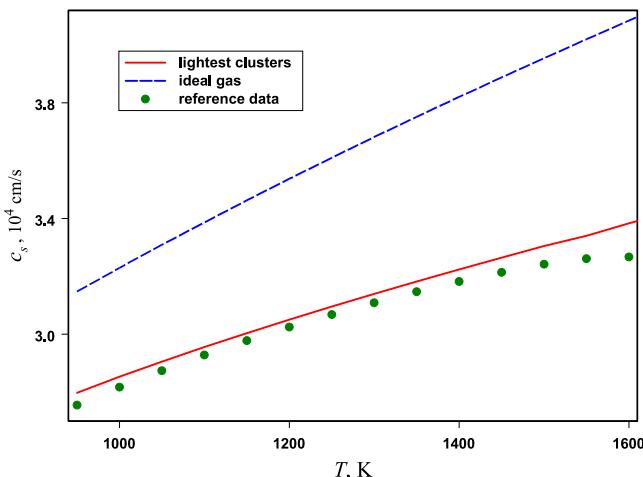


FIG. 4. Velocity of sound for cesium in the gaseous state along the saturation line. Notation is the same as in Fig. 3.

saturation pressure from Ref. 8. A considerable disagreement is visible only near the critical point (Fig. 5).

The situation is similar for argon. Nevertheless, heat capacity ratio (20) calculated for the isobars is in a satisfactory agreement with the reference data of Ref. 3 (Fig. 6). For the calculation of $K_p(T)$, the value $D = 119.8\text{ K}^{30}$ commonly used in molecular dynamics simulation was selected; the pre-exponential factor C in (7) was found from the best fit to the measured compressibility factor for the isobar $p = 0.3\text{ MPa}^3$ by Eq. (5). Note that due to absence of the atomic ionization, Eq. (20) mimics correctly the behavior of c_p/c_v not only in the subcritical but also in the supercritical region. Figure 6 shows that disagreement increases with the increase in the pressure. Apparently, this is the result of the free state repulsion of the argon atoms which must dominate at sufficiently high pressures and temperatures.

One can testify a satisfactory overall agreement between calculated caloric quantities and reference data for three considered substances. Note that the analytical expressions used in the calculations are based on the model of a nonideal

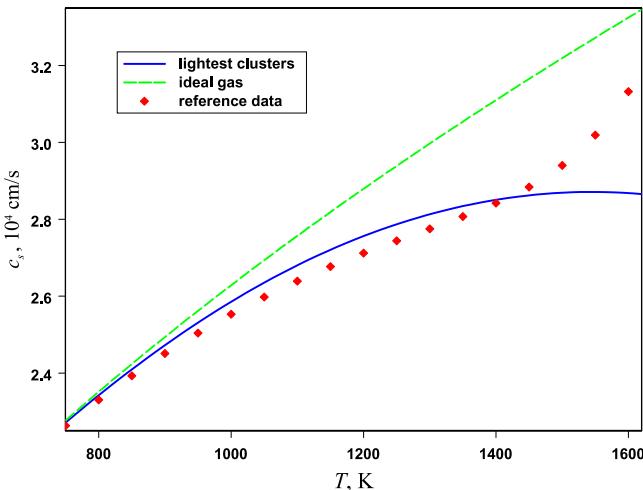


FIG. 5. Velocity of sound for mercury in the gaseous state along the saturation line. Dots indicate the reference data,⁸ other notation is the same as in Fig. 3.

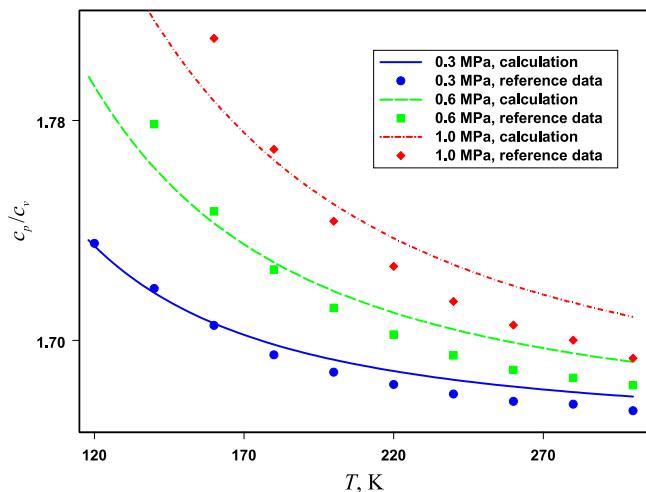


FIG. 6. Heat capacity ratio c_p/c_v for argon along the isobars. Lines indicate calculation using formula (19) for the isobars $p = 0.3$ (solid line), 0.6 (dashed line), and 1.0 MPa (dashed-dotted line); dots indicate the corresponding reference data.³

gas in which it is represented by an ideal mixture of the lightest clusters that are sets of atomic chains. Note that all the thermodynamic reference data discussed above relate to the temperature region *above* the transitional temperature estimated in Sec. II C.

III. MODEL EXTENSION: THE MIXTURE OF ARBITRARY SIZE CLUSTERS

In Sec. II D, we have demonstrated that closer to the critical point, one has to include heavier clusters with $k \gtrsim 10$ to account for the behavior of Z and c_p . Obviously, size distribution (3) is not applicable for this purpose. To include arbitrary size clusters, we utilize the model first proposed in Ref. 19 and vindicated in Refs. 13 and 31, in which a cluster is represented as a core of the internal atoms surrounded by a layer of the surface atoms. Corresponding size distribution of the partial pressures is written in the form,

$$p_k = p_1 \exp\left(-\frac{\Delta\Phi_k}{T}\right),$$

$$\Delta\Phi_k = \frac{4\pi\sigma r_\ell^2}{3\omega}(k_0 - 1) - (k - 1)T \ln \frac{p_1}{p_{1s}}, \quad (27)$$

where σ is the surface tension of a flat liquid–vapor interface; $r_\ell = (3/4\pi n_\ell)^{1/3}$ is the radius of a molecular cell in the liquid, where n_ℓ is the atom number density in a liquid phase; p_{1s} is the partial pressure of monomers at the saturation line; and the quantity

$$\omega(T) = -\frac{4\pi}{3} \frac{\sigma(T)r_\ell^2}{T \ln [p_{1s}(T)K_p(T)]} \quad (28)$$

establishes the relation between the thickness of the cluster surface layer λr_ℓ and the cluster size $q + 1$, at which the cluster has a single internal atom and q surface atoms,

$$\lambda = \left(\frac{q}{\omega} - \frac{3}{4}\right)^{1/2} - \frac{3}{2}. \quad (29)$$

In Eq. (27), k_0 is the number of surface atoms related to the total number of atoms k in the following way:

$$k_0(k) = 3\omega(k - k_0)^{2/3} + 3\omega\lambda(k - k_0)^{1/3} + \omega\lambda^2 \quad (30)$$

if $k > \omega\lambda^2$, and $k_0 = k$ if $k < \omega\lambda^2$.

Distribution (27) includes the temperature dependences $\sigma(T)$, $p_{1s}(T)$, $n_\ell(T)$, $K_p(T)$, and the quantity λ . It was shown in Ref. 32 that λr_ℓ is of the order of the distance between atoms, so that one can treat λ as a material constant independent of the temperature. Since $\sigma(T) \rightarrow 0$ at $T \rightarrow T_c$, where T_c is the critical temperature, it follows from (28) that $\omega(T)$ also vanishes as the critical point is approached. Therefore, $q(T)$ must vanish according to (29). This trend is accounted for by the fact that q is close to the number of bonds for an internal atom, and the difference between the internal, surface, and gas atoms disappears as $T \rightarrow T_c$. For example, at $T = 1700$ K, a four-atomic cluster includes one internal atom.

To calculate the compressibility factor, we first substitute (27) into the relation $p_s = \sum_{k=1}^{\infty} p_{ks}$, where the subscript s denotes a quantity at the saturation line, to derive a transcendental equation with respect to p_{1s} ,

$$\frac{p_s}{p_{1s}} = \sum_{k=1}^{\infty} (p_{1s} K_p)^{k_0(k)-1}, \quad (31)$$

where the dependence $k_0(k)$ is defined by (30). On the basis of Eq. (27), one can calculate the compressibility factor at the saturation line

$$Z = \left[\sum_{k=1}^{\infty} (p_{1s} K_p)^{k_0(k)-1} \right] \left[\sum_{k=1}^{\infty} k (p_{1s} K_p)^{k_0(k)-1} \right]^{-1}. \quad (32)$$

Given the temperature dependences of the surface tension,³³ the saturation vapor pressure,²⁹ the liquid density,³⁴ and the equilibrium constant of the dimer formation,^{11,12} we solve Eq. (31) to find $\lambda = 2.98$ from the best fit of the compressibility factor of cesium vapor at saturation line (32) to the experimental compressibility factor for the temperature interval $950 \text{ K} \leq T \leq 1600 \text{ K}$ ⁷ (Fig. 7). Note that this interval lies above the temperature of the structural transition $T = 816 \text{ K}$ (Sec. II C), so that the treatment of clusters as the sets of chains is justified. Then, given the calculated dependence $p_{1s}(T)$, we solve numerically a transcendental equation with respect to p_1 ,

$$\frac{p}{p_1} = \sum_{k=1}^{\infty} (p_{1s} K_p)^{k_0(k)-1} \left(\frac{p_1}{p_{1s}} \right)^{k-1} \quad (33)$$

for arbitrary vapor temperature and pressure. Obtained p_1 makes it possible to calculate the compressibility factor

$$Z = \left[\sum_{k=1}^{\infty} (p_{1s} K_p)^{k_0(k)-1} \left(\frac{p_1}{p_{1s}} \right)^{k-1} \right] \times \left[\sum_{k=1}^{\infty} k (p_{1s} K_p)^{k_0(k)-1} \left(\frac{p_1}{p_{1s}} \right)^{k-1} \right]^{-1} \quad (34)$$

aside from the saturation line. Compressibility factor (34) calculated for the isobars (Fig. 8) also demonstrates a satisfactory correspondence with the experiment, and the disagreement increases with the increase in the pressure.

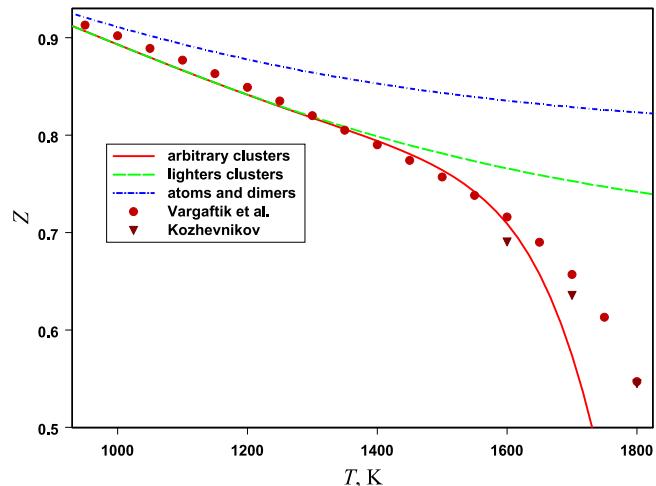


FIG. 7. Compressibility factor for cesium in the gaseous state along the saturation line. Solid line indicates the mixture of arbitrary size clusters [calculation using formulas (30), (31), and (32)]; dashed line, of the lightest clusters [calculation using formula (5)]; dash-dotted line, of atoms and dimers (see text); dots indicate the reference data of Ref. 7 (dots) and Ref. 35 (triangles).

Figures 7 and 8 show that inclusion of the arbitrary size clusters makes it possible to extend the theory toward the critical point up to the vapor density $\rho \approx 0.075 \text{ g/cm}^3$, which corresponds to the point $T \approx 1700 \text{ K}$ at the saturation line. Note that at this point, the average number of atoms in a cluster amounts to $Z^{-1} \approx 1.74$; and if we ignored the clusters with $k > 14$, Z would increase by two per cent. It is seen that the calculated compressibility factor agrees satisfactorily with the experimental data of Refs. 7 and 35. In contrast, as the critical point is approached, both the models of atoms and dimers [Eq. (32) with the upper summation limit $k = 2$ instead of ∞] and of the lightest clusters disagree with the experimental data. However, even the model of arbitrary size clusters flaws in the neighborhood of the critical point (Fig. 7). Apparently, this is due to the volume exclusion not taken into account in this model. On the other hand, even with the correction for the

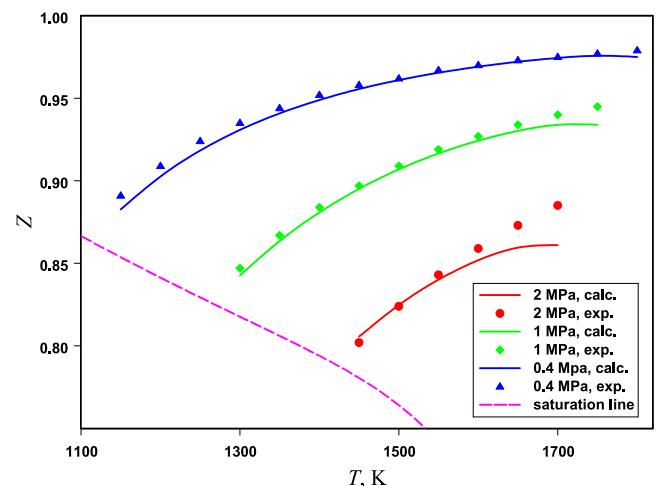


FIG. 8. Compressibility factor of cesium in the gaseous state for the isobars. Lines indicate calculation using formulas (30), (33), and (34) for the isobars $p = 2$ (red line), 1 (green line), and 0.4 MPa (blue line); dots indicate the corresponding reference data.⁷

excluded volume, the cluster model can hardly be applicable in this region because the notion of a cluster proper becomes questionable due to vanishing difference between phases. A significant difference between the cesium critical temperatures estimated in Refs. 7, 35, and 36 (about 100 K) is noteworthy. This demonstrates that the error of experimental determination of the compressibility factor can be significant in the neighborhood of the critical point.

IV. HOMOGENEOUS NUCLEATION OF CESIUM VAPOR

The advantage of a physical model of a nonideal vapor is that it can serve as a basis for the calculation not only of the equilibrium but also of the nonequilibrium properties. We will consider the supersaturated cesium vapor and calculate the rate of homogeneous nucleation using cluster size distributions (27) and (30) with the parameter $\lambda = 2.98$, which ensures a correct reproduction of the compressibility factor along the saturation line (Sec. III). Provided that the cluster size distribution is defined by Eq. (27), the homogeneous nucleation rate can be estimated by a direct summation,¹⁹

$$J = p_1 r_e^2 \left(\frac{\lambda}{\omega} \right)^{2/3} \left(\frac{8\pi}{MT^3} \right)^{1/2} \left(\sum_{k=1}^{\infty} \frac{1}{p_k k^{2/3}} \right)^{-1}, \quad (35)$$

where at temperatures well below the critical point, we can set $p_1 \approx p$. The factor $(\lambda/\omega)^{2/3}$ on the rhs of Eq. (35) accounts for the fact that the radius of clusters with $k < 60$ is typically defined by the surface rather than by internal atoms. This radius appears in the frequency of collisions between vapor atoms and clusters. In the supersaturated vapor, the critical size is defined as the minimum number of atoms bound in a cluster for which the cluster tends to infinite growth. The result of calculation using Eqs. (27), (30), and (35) coincides with the classical nucleation theory (CNT)^{37–39} if the critical size tends to infinity; otherwise, the size correction involved in (35) leads to a significant difference from CNT.

Equation (35) makes it possible to calculate the critical supersaturation defined as the ratio $S_{cr} = p_1/p_{1s} \approx p/p_s$ for which $J = 1 \text{ (cm s)}^{-1}$. For the vapor nucleation in supersaturated cesium vapor, this quantity was measured in Ref. 40. Unfortunately, the temperature range investigated experimentally lies below the transitional temperature estimated in Sec. II C. Nevertheless, the lower bound for the transitional range $T - \Delta T = 548 \text{ K}$ is still within this region. This means that clusters are in the intermediate state between the compact (drops) and the loose (sets of chains) structures. For the compact structure, CNT is appropriate, while for the sets of chains, Eqs. (27), (30), and (35) are more relevant. Figure 9 shows that at low temperature, the measured critical supersaturation coincides with the prediction of CNT, at high temperature, with the size-corrected model discussed in this work. At intermediate temperatures, S_{cr} passes from one line to another (corresponding critical supersaturations differ by a factor of ca. three). It is worth mentioning that one can expect a significant difference between CNT and the size-corrected theory only if the critical size is $\lesssim 100$. Since at $305 \leq T \leq 550 \text{ K}$, the cluster critical size varies from 21 to 57, i.e., it is small;

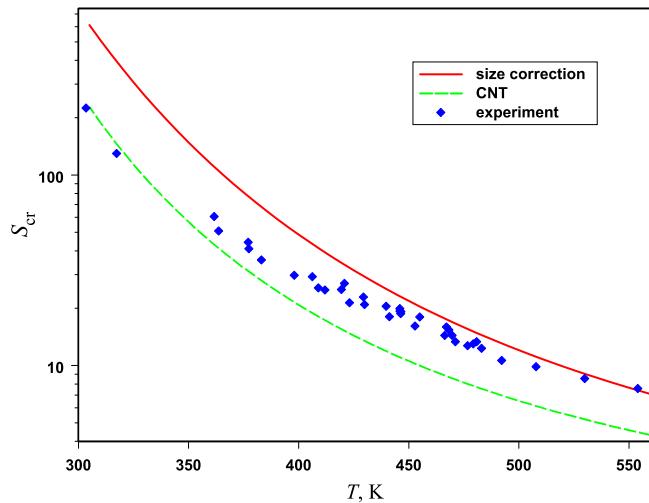


FIG. 9. Critical supersaturation for the nucleation in cesium vapor as a function of temperature. Solid lines indicate calculation using the size-corrected model [Eqs. (27) and (35)]; dashed line, CNT.^{37–39} Dots indicate the experiment Ref. 40.

Fig. 9 is likely to be a manifestation of the structural transition that the lightest cesium clusters undergo.

V. CONCLUSION

In this study, we treated an equilibrium nonideal gas as an ideal mixture of the clusters, which were represented as sets of monomer chains to calculate such thermodynamic caloric quantities as the heat capacity and the velocity of sound. The results were obtained in the form of concise analytical expressions free from adjustable parameters, which makes it possible to apply these expressions for prediction of the properties of substances below and above the critical point, for which the experimental data are lacking. In particular, obtained results allow one to calculate the shock adiabat of the nonideal fluid based solely on known equilibrium constant for the dimer formation.

In order to calculate the partition function of the lightest clusters (less than ten monomers), we explored the notion of a structural transition, which occurs as the temperature is increased. In some transitional temperature interval, the compact solid-like clusters turn into the chain-like loosely bound structures characterized by the minimum number of bonds. This transition is a result of the competition between the differences of the binding energies and entropies of two structural states: the entropy change dominates at high temperatures. Thus, the knowledge of the energy difference allows one to estimate the transitional temperature. Based on quantum calculations of the binding energies of the lightest cesium clusters available in the literature, we managed to estimate the transitional temperature as well as the width of the transitional range. In contrast to the Lenard-Jones system, cesium clusters proved to undergo the structural transition at the temperature *well above* the cesium melting temperature, while for mercury, the transitional temperature is *below* the melting point. Nevertheless, the region where a significant difference of a vapor from the ideal state can be detected experimentally

lies above both estimated transitional temperatures. This justifies the validity of proposed approach. The isobaric heat capacity, the sound velocity, and the heat capacity ratio calculated for cesium, mercury, and argon vapors both at the sub- and supercritical temperatures agree well with the available reference data in a limited range of temperatures and densities. The density upper bound is a result of emergence of the heavier clusters at low temperatures and of the effect of volume exclusion at high temperatures. An additional limitation for cesium is connected with atom ionization not taken into account in the proposed model. Note that if the excluded volume and additional vapor components (such as charged ones) were included, it would make problematic the deduction of the analytical results. Apparently for most substances, there exists a state parameter region where obtained results are literally applicable.

For the dense cesium vapor, we extended the model toward higher densities close to the critical point by inclusion of heavier clusters. On the basis of the model of an arbitrary size cluster consisting of a core of the internal atoms surrounded by a layer of the surface atoms introduced in the size-corrected theory of homogeneous nucleation, we calculated the compressibility factor using a single material constant, the thickness of the cluster surface layer. This made it possible to attain a good correspondence with experiment for the densities almost twice as high as for the model of the lightest clusters. From this calculation, one can infer that the effect of volume exclusion can be significant only in a close neighborhood of the critical point, where the notion of a cluster proper seems to be inapplicable.

As an application of our model of the vapor composition, we calculated the homogeneous nucleation rate for the super-saturated cesium vapor using the same cluster size distribution as in the calculation of the compressibility factor. According to our estimates, the experimental data on the cesium vapor nucleation were obtained at temperatures, which correspond to the onset of the structural transition. This is yet another evidence for the fact that for most substances, there exists some sufficiently wide range of state parameters, where a mixture of ideal cluster gases is a good model of a nonideal gas and even of the supercritical fluid. A comparison between the calculation and experiment is likely to be the evidence for the cluster structural transition in the cesium vapor: as the temperature is increased, the experimental data pass gradually from CNT below the transition temperature to the size-corrected theory above it. An accurate treatment of the vapor nucleation requires development of a theory applicable for the transitional temperature range.

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