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Description of liquid–gas phase transition in the frame of continuum mechanics

Abstract A new method of describing the liquid–gas phase transition is presented. It is assumed that the phase transition is characterized by a significant change of the particle density distribution as a result of energy supply at the boiling point that leads to structural changes but not to heating. Structural changes are described by an additional state characteristics of the system—the distribution density of the particles which is presented by an independent balance equation. The mathematical treatment is based on a special form of the internal energy and a source term in the particle balance equation. The presented method allows to model continua which have different specific heat capacities in liquid and in gas state.

Keywords Liquid–gas phase transition · Cluster · Chemical potential · Source term

1 Introduction

The problem of description of phase transitions is a matter that attracts attention of researches working in different areas of science: physics, thermodynamics, nonlinear mechanics, etc. [2–4,6,16,17,23,26,32,36,40,45,44]. In spite of the difference in approaches and methods, all investigations are based on the opinion that phase transitions are the result of structural modifications of substance under consideration and the nature

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of interactions at a microlevel. At present time several approaches to mathematical implementation of this concept are developed. Each of them is used to solve certain problems. One of the conventional approaches is based on the assumption of a sharp interface separating different phases. The local interfacial velocity is then calculated from the driving force for the interface motion. The second approach which is based on the theory of mixtures is developed in relation to the description of chemical reactions [11,20,48]. The basic assumption of this approach is that there are several constituents at each point of continuum. Depending on various conditions, these constituents can interact or not. The percentage of each constituent is determined by the concentration, which is one of the basic variables. A third approach is based on the diffuse-interface description developed by van der Walls [46] and Cahn [12]. The microstructural evolution is described by the Cahn-Hilliard nonlinear diffusion equation [13] and the time-dependent Ginzburg-Landau equation [19]. This approach is developed primarily in relation to the description of phase transitions associated rather with the change of various physical properties of the substance than with the change of aggregate state, see [31]. The key point of third approach is the use of so-called order parameters. Sometimes the order parameters really play the role of parameters in the sense that they take one of two values depending on the phase state of the substance. For example, the vector of the electric polarization or magnetization can be order parameters. In some cases, the order parameters are used as independent variables characterizing the process of phase transition. Of course, the above classification is weak in the sense that, for example, the movement of the phase boundary can be described within the framework of both the second and the third approaches, and the concentration of the substance in a mixture can be considered as the order parameter. Nevertheless, the classification seems to be useful because it gives an idea of the differences between the known approaches and allows us to evaluate the place that our approach occupies among other studies.

In this paper we consider a model describing the liquid–gas phase transition. The phase transition problem of liquid–gas is a classical and the simplest one which is presented in the classical textbooks on the equilibrium thermodynamics. The conventional view is that this problem can be solved by using the van der Waals model. However, not all details are very well investigated that is the reason for various publications, for example [1,9], in this field. One direction of research is related to the improvement in the constitutive equations using models of interaction of particles on the microlevel, see [7,10,22,49] among others. A simple analysis of the van der Waals model results in the conclusion that there are problems which are not discussed in textbooks. For example, if the parameters of the van der Waals model given in the classical books on thermodynamics for the case of the water vapor phase transition are used then the compressibility of water calculated by using the van der Waals equation turns out to be negative. This fact shows the inapplicability of the van der Waals model for description of water. One can assume that a modification of the van der Waals equation can be a solution of the problem. However, there is another problem. It is well known that during the liquid–gas phase transition both the average value of the specific heat at constant volume and the character of its dependence on temperature change significantly. The van der Waals model does not describe these facts. These disadvantages of the van der Waals model are the motivation for the research presented below. The purpose of the investigation is to propose a model which correctly describes the mechanical and thermodynamic properties of the liquid and the gas and also the process of phase transition.

The proposed approach to the description of the liquid–gas phase transition is similar to the methods using the order parameters as independent variables. We start with the data given in [33,39] where it is shown that the molecules of water and liquids based on water can create clusters that have properties of large molecules. When the temperature increases the clusters begin to disintegrate and the clusters fully disappear when the liquid transforms to a gas. The cluster microstructure model was introduced by various authors. In the case of phase transitions examples are given in [28–30,37,38,43]. In [37], for example, the phase transition gas–liquid description is based on the introduction of clusters which are composed of hundreds of atoms or molecules. Then, an explicit boundary between the phases is introduced and the balance equation is presented for the activated molecules in the clusters. The main idea of our approach to the description of the liquid–gas phase transition is that we consider the matter as a one-component medium which can be either in the liquid state or in the gaseous state. We introduce the additional variable to indicate the number of clusters in a given point of the medium, the value of which allows us to determine whether the substance is a liquid or a gas. In fact, this additional variable can be considered as the order parameter. We suppose that the phase transition should be accompanied by fast changing of the number of particles per unit mass (the ratio of the density of particle distribution to the density of mass) that is due to the fact that at the boiling point the input energy is necessary for the modification of the structure instead of heating. The mathematical formalization of the proposed approach is as follows. To describe structure modifications we introduce the density of the particle distribution as an independent characteristic, and for this quantity we formulate an additional balance equation

[5,50]. The special choice of the form of the source term in the particle balance equation allows us to obtain the desired behavior of this additional variable during the phase transition.

The implementation of the approach outlined above is impossible without a clear idea of what is mentioned by a particle in the cluster model of the liquid. There are two possible interpretations. According to one viewpoint the particles are either single molecules or clusters consisting of several molecules. Thus, when the clusters break up, the number of particles increases. Consequently, in a gas the number of particles per unit mass is greater than in a liquid. According to another viewpoint, the particles are molecules and hybridized electron clouds by means of which the molecules are held in clusters. Thus, the cluster consists of several molecules (particles having mass) and several massless particles simulating links between the molecules in the cluster. A system consisting of mass points which are connected by massless springs can be considered as analog of such model of cluster. According to this viewpoint, when the clusters break up, the links disappear, i.e. the number of particles decreases. Hence, in a gas the number of particles per unit mass is smaller than in a liquid. Adoption of one of the viewpoints is a matter of principle, because it has an effect on both the interpretation of the results and the construction of a mathematical model. Therefore, the preference of one point of view is not a question of taste or intuitions. Choosing one or another model it is important to take into account the problems that arise or do not arise in implementation of the mathematical model. In what follows the implementation of the two interpretations of the conception "particle in the cluster model of liquid is considered and a comparative analysis of two mathematical models is carried out.

2 Thermodynamic quantities in continuum mechanics

The liquid–gas phase transition is traditionally studied in classical thermodynamics, where equilibrium processes (homogeneous in all points of the space) are considered. In equilibrium thermodynamics all assumptions are fulfilled with reference to one mole of the substance under consideration. Both the first and the second law of thermodynamics are generally accepted. In what follows we use the methods of continuum mechanics that allow us to describe both equilibrium and non-equilibrium processes, including fast dynamical processes. Since we consider liquid and gas we use the spatial description. As a result, all differential equations contain material derivatives.

Let us choose an inertial reference system and observe the volume V (control volume) fixed in the reference system. The first law of thermodynamics (the energy balance equation) states that there is a function of state U (called internal energy) satisfying the equation

$$\frac{\mathrm{d}}{\mathrm{d}t}(K + U) = N^{\mathrm{e}} + Q, \tag{1}$$

where $\mathrm{d}/\mathrm{d}t$ is the total time derivative, K is the kinetic energy of the substance in the control volume, N^{e} is the power of external forces, Q is the energy supply from external sources per unit time.

The kinetic energy is assumed to be a quadratic form of velocities. As usual it is an additive function of the mass and thus can be written in terms of the mass density of the kinetic energy κ

$$K = \int_V \rho \kappa \, \mathrm{d}V.$$

The definition of internal energy is less formal than that of the kinetic energy. As a matter of fact, the internal energy is the energy of motion on degrees of freedom which are ignored in the model under consideration. In other words, the sense of the internal energy depends on the mathematical model used for the description of the system. For example, in classical equilibrium thermodynamics the internal energy of the ideal gas is an additive function of the number of particles and proportional to the temperature. In statistical thermodynamics the internal energy is determined by the elastic interactions of the particles, and for the ideal gas it is equal to zero. The difference of the approaches cannot give a cause for doubts about their correctness. The fact is that the internal energy is an immeasurable quantity, and so there are no physical experiments which let us know what the internal energy of the system under consideration is.

In many continuum mechanics applications the internal energy is an additive function of the mass [45]. Here we intend to take into account the formation and the decomposition of clusters, i.e. a change of the

number of particles in the medium. Therefore, we suppose that the internal energy is an additive function of the number of particles [50], and we will study the consequences of our supposition. Now we accept

$$U = \int_V \eta u \, dV,$$

where u is the specific internal energy, η is the density of particle distribution.

The energy supply per unit time is determined due to adding (vanishing) of new particles to (out of) the control volume and by the heat supply per unit time Q which is the sum of the heat supply per unit time in the volume V and through the boundary of volume V

$$Q = \int_V \eta q \, dV + \int_\Omega \mathbf{n} \cdot \mathbf{h} \, d\Omega,$$

where q is the energy supply per unit time into the particles of the medium, $\mathbf{h}$ is the heat flow, Ω is the boundary of the control volume, $\mathbf{n}$ is the unit vector normal to the boundary.

The local form of the balance of mass and linear momentum can be written as:

– mass balance

$$\frac{\delta \rho}{\delta t} + \rho \, \nabla \cdot \mathbf{V} = 0. \tag{2}$$

Here $\mathbf{V}$ is the velocity of the particles in the given point, $\delta/\delta t$ is the material derivative

$$\frac{\delta}{\delta t} \Lambda = \frac{d}{dt} \Lambda + \mathbf{V} \cdot \nabla \Lambda.$$

Λ is a field, ∇ is nabla operator.

– linear momentum balance

$$\rho \frac{\delta}{\delta t} \mathbf{V} = \nabla \cdot \mathbf{T} + \rho \mathbf{F}. \tag{3}$$

Here $\mathbf{F}$ presents the specific action of external forces, $\mathbf{T}$ is the stress tensor. From the angular momentum balance it follows that, if there are no couple stresses and specific external moments the stress tensor should be a symmetric tensor.

By the standard transforms taking into account (2) and (3), the equation of energy balance (1) can be reduced to the following local form

$$\frac{\delta(\eta u)}{\delta t} = W + \frac{\eta u}{\rho} \frac{\delta \rho}{\delta t} + \nabla \cdot \mathbf{h} + \eta q.$$

Here W is the power of the internal interactions. For an ideal liquid or gas W can be expressed in terms of the pressure p

$$W = \frac{p}{\rho} \frac{\delta \rho}{\delta t}.$$

Consequently, the energy balance equation takes the form

$$\frac{\delta(\eta u)}{\delta t} = \frac{p + \eta u}{\rho} \frac{\delta \rho}{\delta t} + \nabla \cdot \mathbf{h} + \eta q. \tag{4}$$

The energy balance equation (4) should be transformed to a special form called reduced equation of energy balance [5,50]. Let us denote

$$\eta T \frac{\delta S}{\delta t} = \nabla \cdot \mathbf{h} + \eta q. \tag{5}$$

The quantities T and S defined by Eq. (5) are the absolute temperature and entropy related to one particle, respectively. At the same time, the temperature T is considered to be some characteristic of the medium that is

measured by a thermometer, and entropy S is introduced as a quantity conjugate with the temperature. Since we suppose that the internal energy is an additive function of the number of particles it can be assumed that the entropy is also an additive function of the number of particles. Note that this definition of entropy is different from the definition used, for example, in classical thermodynamics and physics, where an inequality is introduced. In particular, the proposed definition does not coincide with the concept of an equilibrium process. Substituting Eq. (5) into Eq. (4) we obtain the reduced equation of the energy balance

$$\frac{\delta(\eta u)}{\delta t} = \frac{p + \eta u}{\rho}\frac{\delta\rho}{\delta t} + \eta T\frac{\delta S}{\delta t}. \tag{6}$$

Note that Eqs. (5), (6) neglect the fact that a part of the energy supply can be used for the structure transitions. Later it will be specified by introducing chemical potential as a quantity conjugate with the density of particle distribution.

Let us assume that there are no massless particles in the system. Then, taking into account the relation $\eta u = \rho u_*$ (where u_* is the mass density of the internal energy) the energy balance equation (6) can be rewritten in the form

$$\frac{\delta u_*}{\delta t} = \frac{p}{\rho^2}\frac{\delta\rho}{\delta t} + \frac{\eta}{\rho}T\frac{\delta S}{\delta t}. \tag{7}$$

When the density of mass and the density of particle distribution are linearly dependent functions ($\rho = m_0\eta$, where $m_0 = $ const), Eq. (7) can be reduced to the standard form

$$\frac{\delta u_*}{\delta t} = \frac{p}{\rho^2}\frac{\delta\rho}{\delta t} + T\frac{\delta S_*}{\delta t}, \tag{8}$$

where $S_* = S/m_0$ is the mass density of the entropy. The energy balance equation (8) allows us to determine the arguments on which the internal energy depends on and to obtain the Cauchy–Green relations

$$p = \rho^2\frac{\partial u_*}{\partial\rho}, \qquad T = \frac{\partial u_*}{\partial S_*}, \qquad u_* = u_*(\rho, S_*). \tag{9}$$

The notation $u_*(\rho, T)$ is widely used in classical thermodynamics. But keeping up mathematical stringent we should write

$$u_*(\rho, S_*) = u_*(\rho, S_*(\rho, T)) = \tilde{u}(\rho, T).$$

It should be noted that the definition of the temperature and entropy by Eq. (5) is arbitrary in some sense. Formally, Eq. (5) can be replaced, for example, by the following definition

$$T\frac{\delta(\eta S)}{\delta t} = \nabla\cdot\mathbf{h} + \eta q. \tag{10}$$

However, in this case the temperature and entropy will appear in the Cauchy Green relation for the pressure. When $m_0 = $ const the Cauchy Green relation for the pressure takes the form

$$p + TS_* = \rho^2\frac{\partial u_*}{\partial\rho}.$$

That means that the Eqs. (5), (10) define not only the temperature and entropy, but also the internal energy. These three quantities are always interdependent, and they should be defined simultaneously. With other words, it is not possible to introduce at first the internal energy and then the temperature and the entropy. If in addition to the temperature and entropy the density of the particle distribution and the chemical potential (responsible for the fragmentation) are introduced, then all five quantities are defined simultaneously.

3 Classical thermodynamics and continuum mechanics: comparison of the approaches by the example of van der Waals Gas

Constitutive equations of gases are well known; they represent equations relating pressure, volume and temperature. Among these equations some are based on theoretical investigations, others are pure empirical relations. One of the best known constitutive equations describing the behavior of a real gas is the van der Waals equation which is linked with the kinetic theory [8]. In classical thermodynamics this equation is just postulated. At the same time, the specific heat under constant volume of the van der Waals gas is considered to be independent of temperature and coincides with the specific heat of an ideal gas. It is an essential disadvantage of the model which must describe the phase transition, as it is well known that the specific heat grows drastically near the boiling point. In this context the question arises: is the constancy of the specific heat under constant volume a consequence of the van der Waals equation or is this an independent statement? To answer this question we will use the methods of continuum mechanics; by using the Cauchy Green relations we obtain the most general form of the internal energy being in agreement with the van der Waals equation, and then, we find the expression for the specific heat under constant volume. It is evident that the expression for the specific heat obtained in this way does not contradict to the van der Waals equation. Before we present the solution of the problem we discuss briefly the properties of the van der Waals equation in the same way as in classical thermodynamics.

The van der Waals equation is obtained for the model of a gas representing a set of spherical solid particles interacting by forces

$$p = -a\rho^2 + \frac{RT\rho}{1 - b\rho}, \qquad R = \bar{R}/M. \tag{11}$$

Here $\bar{R}$ is the universal gas constant, M is the molar mass. Parameters a and b are determined from the experimental estimated $p - V - T$ data; by the parameter a attracting forces are taken into account, the parameter b is related to the size of each molecule.

The van der Waals equation approximates not only real gases and vapors, but also liquids and transition between them. To be sure, at constant parameters a and b the model is not good enough for any real substance but gives a good heuristic value for qualitative investigations. Phase diagrams corresponding Eq. (11) at different values of temperature are shown in Fig. 1.

At $T > T_{cr}$ the medium can be only in one (gas) state. If $T < T_{cr}$ three states are possible: two stable states—liquid $1/\rho_1$ and gas $1/\rho_g$—and one unstable $1/\rho_*$. In the critical point K the gas and the liquid phases cannot be distinguished. Their temperature, pressure and density have values, which are characteristic for each
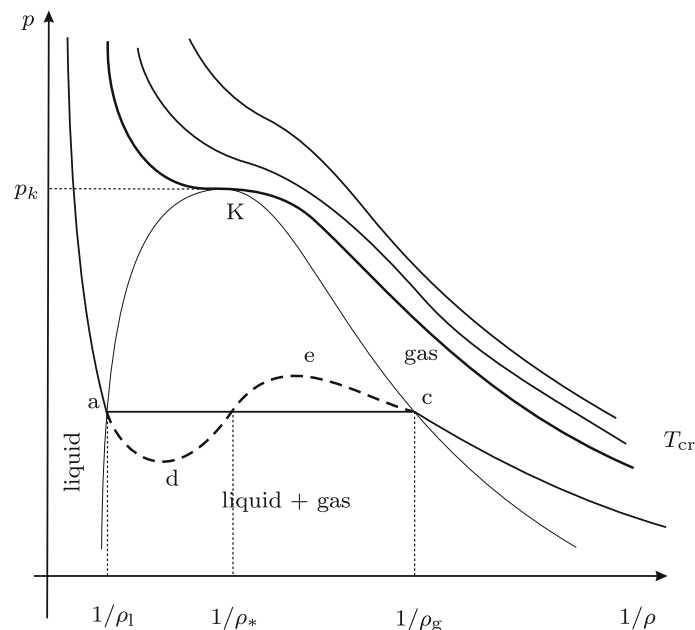

Fig. 1 Isotherms near the critical point of the equilibrium

phase. Points on the line ac are responsible for the equilibrium of the liquid and the saturated vapor. At low pressure the isotherm presents the properties of the gas. On the left hand side the approximately vertical part of the isotherm is responsible for the very small compressibility of the liquid. The parts ad and ec are responsible for the overheated liquid and the overcooled vapor (metastable state). The part ae is physically not admissible, since here at increasing pressure the volume is also increasing.

The critical temperature and density are determined by the conditions

$$-2a\rho + \frac{RT}{(1-b\rho)^2} = 0, \qquad -2a + \frac{2RTb}{(1-b\rho)^3} = 0. \tag{12}$$

Hence,

$$T_{\text{cr}} = \frac{8a}{27bR}, \qquad p_{\text{cr}} = \frac{a}{27b^2}.$$

For ordinary water $T_{cr} = 647.096$ K, $p_{cr} = 22.064$ MPa. Then,

$$a = 1705.219862 \, \text{Hm}^4 \, \text{kg}^{-2}, \ b = 0.001692 \, \text{m}^3 \, \text{kg}^{-1}.$$

From the conditions Eq. (12) for the critical temperature and density it follows

$$\rho_{cr} = \frac{1}{3b} = 197 \, \text{kg m}^{-3}.$$

Note that it does not coincide with the critical density of water $\rho_{cr} = 322 \, \text{kg m}^{-3}$.

Now we consider the van der Waals equation from the point of view of continuum mechanics. Let us find the most general form of the internal energy corresponding to the van der Waals equation. In accordance with Eq. (9) the specific internal energy is a function of density and entropy, and the temperature is found as the derivative of the internal energy with respect to the entropy. Since the constitutive equation (11) depends on the temperature we must pass on to another thermodynamic potential for which the temperature is an independent variable. Introducing the specific free energy $f_* = u_* - TS_*$ we reduce the energy balance equation (8) to the form

$$\frac{\delta f_*}{\delta t} = \frac{p}{\rho^2} \frac{\delta\rho}{\delta t} - S_* \frac{\delta T}{\delta t}.$$

This implies the Cauchy Green relations

$$\frac{\partial f_*}{\partial \rho} = \frac{p}{\rho^2} = \frac{RT}{\rho - b\rho^2} - a, \qquad \frac{\partial f_*}{\partial T} = -S_*. \tag{13}$$

Integrating Eq. (13)$_1$ we obtain

$$f_* = -a\rho + RT \ln \frac{\rho}{1 - b\rho} + g(T).$$

From Eq. (13)$_2$ we have

$$S_* = -R \ln \frac{\rho}{1 - b\rho} - g'(T).$$

Consequently, for the van der Waals gas the specific internal energy takes the form

$$u_* = -a\rho + g(T) - Tg'(T). \tag{14}$$

In classical thermodynamics the free energy of the van der Waals gas is supposed to tend to free energy of the ideal gas when $\rho \to 0$. That is why, using the constitutive equation of the ideal gas $p = RT\rho$, the free energy of the van der Waals gas f_* can be expressed in terms of the free energy of the ideal gas f_*^{id}

$$f_* = f_*^{\text{id}} - RT \ln(1 - b\rho) - a\rho.$$
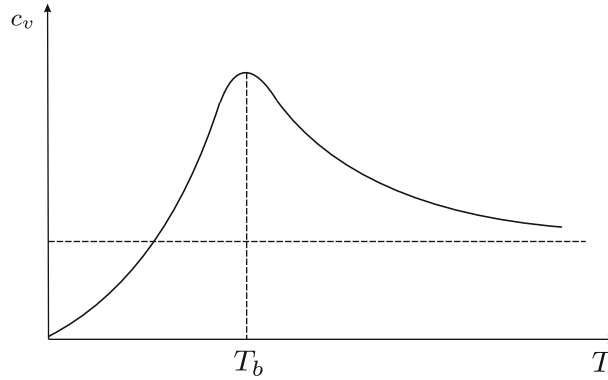
Fig. 2 Dependence of the specific heat on the temperature

Hence, by using the Gibbs–Helmholtz equation (15) the internal energy of the van der Waals gas can be expressed in terms of the internal energy of the ideal gas u_*^{id} [41]

$$u_* = -T^2 \frac{\partial (f_*/T)}{\partial T} = u_*^{\text{id}} - a\rho. \tag{15}$$

The internal energy of the ideal gas is usually considered to be a linear function of the temperature. In this case from Eq. (15) we obtain that the specific heat of the van der Waals gas under constant volume $c_v = \partial u_*/\partial T$ is constant and equal to the specific heat of the ideal gas. However, the energy supply does not lead to a temperature increase during boiling process. In the framework of classical thermodynamics this phenomenon can be explained only by a fast increase in the specific heat near the boiling point.

The expression for the internal energy (14) allows us to obtain different forms of the dependence of the specific heat on temperature. In particular, choosing the function $g(T)$ as

$$g''(T) = -\frac{c_v^{\text{id}} T^2}{(T - C)^3 + D},$$

we obtain a non-monotone dependence of the specific heat from temperature (Fig. 2). Here c_v^{id} is the specific heat of the ideal gas, and C and D are some parameters. This dependence well describes the experimental data at both the high and low temperatures, and it models also a significant increase in the specific heat near some fixed temperature. However, this temperature cannot be identified as the boiling point since the boiling point is not a constant and essentially depends on the pressure. Consequently, by means of the model of the van der Waals gas it is impossible to describe a significant increase in the specific heat near the boiling point.

At the end of the section we mention that the van der Waals equation badly describes the behavior of liquids. In particular it has a negative bulk modulus:

$$K = \rho \frac{\partial p}{\partial \rho} = \frac{R\rho T}{(1 - b\rho^2)^2} - a\rho^2 = -3 \times 10^9 \, \text{Pa}.$$

Moreover, the model does not take into account the structure transitions occurring during the process of the phase transition. Consequently, the development of an alternative model describing the liquid–gas phase transition is an actual problem.

4 Particle balance equation: chemical potential: equation of structural transformations

Let us consider that during the phase transition some part of the energy supply is responsible for changing the number of particles. We are sure that this fact has to be taken into account when structural transitions are described. Therefore, instead of Eq. (5) we use a more general equation containing an additional term accounting for structural transitions. Suppose that the thermal energy supply does not only lead to temperature, entropy, pressure and mass density changes but also lead to the number of particles changes because of agglomeration or the decomposition of them. In this case the mass of a particle m_0 in the relation $\rho = m_0 \eta$ is

not a constant and depends, for example, on the temperature. Then, the functions η and ρ become independent variables. The density of particle distribution η is determined by the particle balance equation which can be written by analogy to the mass balance equation (2) with a source term. Thus, the particle balance equations takes the form [5,50]

$$\frac{\delta \eta}{\delta t} + \eta \nabla \cdot \mathbf{V} = \chi. \tag{16}$$

Here χ is the rate of particle production per unit volume.

Let us denote [50]

$$\eta T \frac{\delta S}{\delta t} + \eta \frac{\delta \psi}{\delta t} = \nabla \cdot \mathbf{h} + \eta q. \tag{17}$$

Analogous to the temperature and entropy, η and ψ appear in Eq. (17) as conjugate variables. The density of particle distribution is a measurable quantity. Thus, Eq. (17) is the combined equation of structural transitions (e.g. fragmentation) and heat conduction.

Inserting Eq. (17) into Eq. (4) we obtain the reduced energy balance equation in the sense of Zhilin's definition [50]

$$\frac{\delta (\eta u)}{\delta t} = \frac{p + \eta u}{\rho} \frac{\delta \rho}{\delta t} + \eta T \frac{\delta S}{\delta t} + \eta \frac{\delta \psi}{\delta t}. \tag{18}$$

From Eq. (18) follow the Cauchy Green relations

$$p = \rho^2 \frac{\partial}{\partial \rho} \left(\frac{\eta u}{\rho} \right), \quad T = \frac{1}{\eta} \frac{\partial (\eta u)}{\partial S}, \quad \eta = \frac{\partial (\eta u)}{\partial \psi}, \quad \eta u = \eta u(\rho, S, \psi). \tag{19}$$

It is important to notice that instead of Eq. (17) we can introduce the following equation with the material derivative of the density of particle distribution instead of $\frac{\delta \psi}{\delta t}$

$$\eta T \frac{\delta S}{\delta t} + \bar{\psi} \frac{\delta \eta}{\delta t} = \nabla \cdot \mathbf{h} + \eta q. \tag{20}$$

In this case the reduced energy balance equation takes the form

$$\frac{\delta (\eta u)}{\delta t} = \frac{p + \eta u}{\rho} \frac{\delta \rho}{\delta t} + \eta T \frac{\delta S}{\delta t} + \bar{\psi} \frac{\delta \eta}{\delta t}, \tag{21}$$

the internal energy becomes the function $\eta u(\rho, S, \eta)$, and the Cauchy Green relation for $\bar{\psi}$ is written as

$$\bar{\psi} = \frac{\partial (\eta u)}{\partial \eta}. \tag{22}$$

In thermodynamics the derivative of the internal energy with respect to the number of particles is usually called chemical potential [18,40]. Similar to (20) expressions are given in the classical textbooks [27,34,35,40]. Quantities ψ and $\bar{\psi}$ have, in general, a different sense. However, ψ being the variable conjugate to the density of particle distribution also can be treated as a chemical potential.

Which of the ways of the chemical potential introduction is more preferable? It is impossible to answer the question unambiguously because of the fact that the chemical potential as well as the entropy and the internal energy is immeasurable quantities. Immeasurable quantities are characteristics of a mathematical model, and they are necessary for obtaining some relations that connect measurable quantities. Consequently, the preference of this or that chemical potential definition is determined by specific features of the problems under consideration.[1]

Before using the proposed method for describing of processes in systems with a varying number of particles it is necessary to demonstrate that under certain choice of the internal energy the definitions (17) and (20) allow us to obtain the known constitutive equations for some simple models, in particular, for the ideal gas.

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[1] Details are presented in [24].

At first we consider the definition (17). Let us represent $\eta u(\rho, S, \psi)$ as a sum of the internal energy of the ideal gas and the term linearly depending on ψ

$$\eta u = A\rho^{R/c_v^{\text{id}}+1} e^{S/c_v^{\text{idM}}} + D\rho\psi. \tag{23}$$

From Eq. (19)$_3$ it follows that

$$\eta = D\rho, \tag{24}$$

i.e. if the internal energy is defined by Eq. (23), then the mass density and the density of particle distribution are not independent variables. Hence, the source term in Eq. (16)$_2$ equals to zero.

From Eqs. (19)$_2$ and (19)$_1$ it follows that

$$T = \frac{A}{c_v^{\text{id}} DM} \rho^{R/c_v^{\text{id}}} e^{S/c_v^{\text{id}}}, \qquad p = RDM\,T\rho \tag{25}$$

If we substitute $D = 1/M$ relation (25)$_2$ becomes the ideal gas law. If

$$A = \frac{c_v^{id} T_0}{M} \rho_0^{-R/c_v^{\text{id}}} e^{-S_0/c_v^{\text{id}}},$$

then from Eq. (25)$_1$ follows the classical expression for the entropy of the ideal gas.

$$S = S_0 + c_v^{\text{id}} M \ln T/T_0 - \bar{R} \ln \rho/\rho_0. \tag{26}$$

To determine the function ψ it is necessary to split Eq. (17) into two equations: the heat conduction equation and the equation of structural transitions

$$\eta T \frac{\delta S}{\delta t} = \nabla \cdot \mathbf{h} + \eta q + Q, \qquad \eta \frac{\delta \psi}{\delta t} = -Q, \tag{27}$$

where Q characterizes the rate of energy exchange in the processes of the heat conductivity and the structural transitions. Since according to Eq. (24) new particles in the system are not generated it may be assumed that $Q = 0$, i.e. $\delta \psi/\delta t = 0$.

Now we consider the definition of the chemical potential (20). It is significant that in this case formulation (21) of the reduced energy balance equation is valid only if mass density and the density of particle distribution are independent variables. When the particle masses are constant, we should use the reduced energy balance equation in the form

$$\frac{\delta u_*}{\delta t} = \frac{p + \rho \bar{\psi}_*}{\rho^2} \frac{\delta \rho}{\delta t} + T \frac{\delta S_*}{\delta t},$$

where $\bar{\psi}_*$ is the chemical potential per unit mass. In this case the Cauchy Green relation for the chemical potential (22) loses significance, and the chemical potential is determined by the equation of structural transitions

$$\bar{\psi}_* \frac{\delta \rho}{\delta t} = -QM.$$

On the other hand, the classical expression for the entropy of the ideal gas can be obtained from Eq. (21) only in case of linear dependence of mass density on the density of particle distribution. Indeed, from Eq. (26) it follows that

$$T = C \left(\frac{\rho}{\rho_0}\right)^{R/c_v^{\text{id}}} e^{S/Mc_v^{\text{id}}}.$$

Integrating the Cauchy Green relation (19)$_2$ for the case $\eta u = \eta u(\rho, S, \eta)$ we obtain

$$\eta u = C\eta Mc_v^{\text{id}} \left(\frac{\rho}{\rho_0}\right)^{R/c_v^{\text{id}}} e^{S/Mc_v^{\text{id}}} + a_1(\rho, \eta). \tag{28}$$

For the ideal gas from Eq. $(19)_1$ it follows that

$$\frac{\partial}{\partial \rho}\left(\frac{\eta u}{\rho}\right) = R\frac{C}{\rho_0}\left(\frac{\rho}{\rho_0}\right)^{R/c_v^{\mathrm{id}}-1} e^{S/Mc_v^{\mathrm{id}}}.$$

Hence,

$$\eta u = C\rho\, c_v^{\mathrm{id}}\left(\frac{\rho}{\rho_0}\right)^{R/c_v^{\mathrm{id}}} e^{S/Mc_v^{\mathrm{id}}} + \rho a_2(S, \eta). \tag{29}$$

The expressions (28) and (29) can be equal only if $\rho = M\eta$.

Since entropy is an immeasurable quantity there is no necessity to postulate that the expression for the entropy of the ideal gas agrees with that one accepted in the equilibrium thermodynamics. If the internal energy is assigned, for example, as

$$\eta u = A\eta\rho e^{(R\rho/\eta+S)/Mc_v^{\mathrm{id}}},$$

then the constitutive equation for the pressure is the same as the equation of the ideal gas state, and

$$u = c_v^{\mathrm{id}}T, \qquad \bar{\psi} = \left(Mc_v^{\mathrm{id}} - R\frac{\rho}{\eta}\right)T, \qquad S = S_0 + c_v^{\mathrm{id}}(\ln T/T_0 - \ln \rho/\rho_0) - R\frac{\rho}{\eta}.$$

Nevertheless, the introduction of the chemical potential by means of Eq. (17) is more preferable since this allows us to pass on "standard" thermodynamic functions without any contradictions.

5 Simplest models taking into account structural transformations in liquids and gases

Before starting the study of the liquid–gas phase transition, we consider two models in which the structural transitions of the substance are taken into account. The models are very simple, and they cannot describe exactly the experimental facts. We consider these models in order to show the resources evolved from the introduction of the density of particle distribution as a new independent characteristic of the system.

The first model describes the behavior of a liquid at a temperature far from the boiling point. It is well known that the mechanical and thermodynamic parameters of liquids significantly depend on the temperature. This characteristic property distinguishes liquids from gases and solids possessing constant mechanical and thermodynamic parameters. We assume that the feature in question of a liquid is the result of structural transitions, namely the decrease in temperature is related to cluster formation, while the increase in temperature leads to the decomposition of clusters.

Let the internal energy has form

$$\eta u = A\rho e^{c\rho+BS+k\psi} + C\rho^2 + D\rho\psi$$

where A, B, C and D are parameters which should be estimated. Then, from the Cauchy Green relations $(19)_{2,3}$ it follows that

$$\eta T = AB\rho e^{c\rho+BS+k\psi}, \qquad \eta = Ak\rho e^{c\rho+BS+k\psi} + D\rho. \tag{30}$$
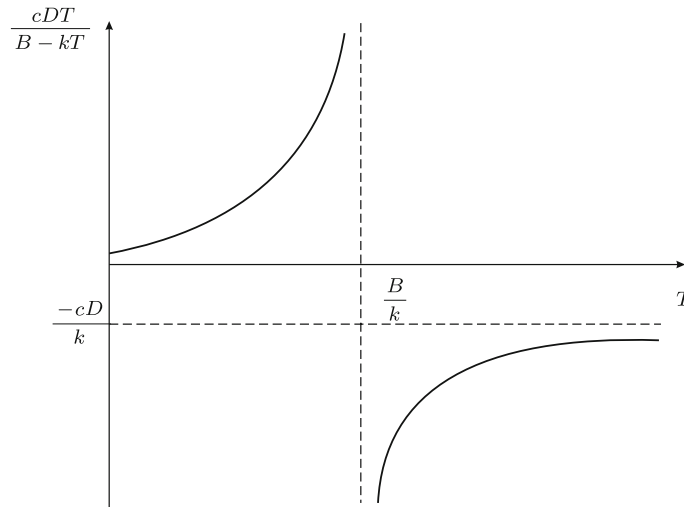
Thus, according to Eq. (30) the ratio of the density of particle distribution to the mass density is a function of the temperature

$$\frac{\eta}{\rho} = \frac{D}{1 - kT/B}. \tag{31}$$

As temperature tends to B/k the function (31) rises steeply. However, we are interested in temperatures much lower than this value.

The constitutive equation for pressure takes the form

$$p = \rho^2\left(C + \frac{cDT}{B - kT}\right). \tag{32}$$

Fig. 3 Graphical representation of Eq. (32) (note that the *right* branch will not discussed here)

Obvious that the term depending on temperature increases with increasing temperature (Fig. 3). Hence, Eq. (32) correctly describes the behavior of pressure in a liquid. Certainly, contribution of the term depending on temperature must be small in comparison with the term $C\rho^2$ that remains when $cD/k \ll C$.

To find the specific heats we express the mass density of the internal energy in terms of temperature

$$u_* = \frac{DT}{B - kT} + C\rho + D\psi.$$

Taking into account that from Eq. $(30)_1$ it follows that

$$T'_\psi = \frac{k}{B}(B - kT)T,$$

we obtain the expression for the specific heat under constant volume

$$c_v = \frac{DB^2}{(B - kT)^2 kT} \tag{33}$$

and the expression for the specific heat under constant pressure

$$c_p = c_v + \frac{\sqrt{p}\, c^2 D^2 B^2 T}{2(B - kT)^4} \left(C + \frac{cDT}{B - kT}\right)^{-3/2}. \tag{34}$$

Analysis of Eq. (33) shows that c_v tends to infinity when T tends to zero or B/k, and c_v approaches the minimum value when $T = B/(3k)$. According to the experimental data c_v decreases with increasing temperature. Consequently, Eq. (33) correctly describes the behavior of the specific heat at constant volume when the temperature is less then $B/(3k)$ but not very low. Analysis of Eq. (34) shows that in this temperature range c_p can both increase and decrease subject to parameters of the model. This fact "agrees qualitatively" with experimental data [21,25] since the specific heat under constant pressure is known to decrease with increasing temperature in the case of most liquids and demonstrate non-monotone behavior in the case of water. Sketchy the dependence of the specific heats on temperature for two different D is shown in the Fig. 4.

Since the entropy and the chemical potential are immeasurable quantities, the equations to determine them can be excluded. In this case the system of equations describing the behavior of the medium consists of the constitutive equation for pressure (32) and Eq. (31) relating the ratio of the density of particle distribution to the mass density with the temperature. To close the system of equations we should add the equation of motion, the mass balance equation and the particle balance equation. The source term in the last equation is not equal to zero, and the constitutive equation for it should be formulated.

The second illustrative model describes the behavior of a gas when the temperature is much higher than the boiling point. It is known that a gas encloses both neutral molecules and some number of ions [42].
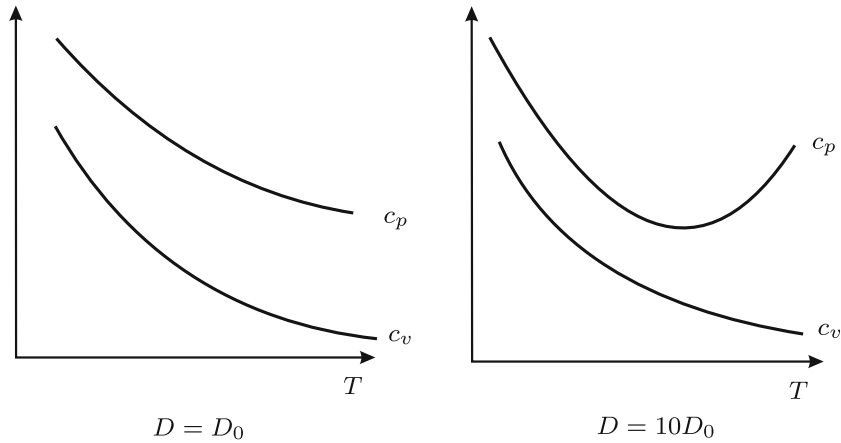
Fig. 4 Dependence of the specific heats on the temperature (D_0 is constant)

Ions are generated by means of separating electrons from the neutral molecules, and they disappear as a result of combining with electrons and producing neutral molecules.

Let the internal energy has the form

$$\eta u = A_1 \rho^{C+1} e^{BS} + A_2 \rho e^{k\psi}. \tag{35}$$

Then, using the Cauchy Green relations $(19)_{1,2}$ we obtain

$$p = A_1 C \rho^{C+1} e^{BS}, \qquad \eta T = A_1 B \rho^{C+1} e^{BS}, \tag{36}$$

and hence,

$$p = \frac{C}{B} \eta T = \frac{C}{B} \rho T \left(\frac{\eta}{\rho} \right). \tag{37}$$

From Eq. $(19)_3$ it follows that

$$\frac{\eta}{\rho} = k A_2 e^{k\psi}. \tag{38}$$

In view of Eqs. (35), (36), (38) we obtain the expressions for the specific heats

$$c_v = \frac{1}{B} \frac{\eta}{\rho} + \left(\frac{T}{B} + \frac{1}{k} \right) \left(\frac{\partial(\eta/\rho)}{\partial T} \right)_\rho,$$

$$c_p = \frac{C+1}{B} \frac{\eta}{\rho} + \left(\frac{C+1}{B} T + \frac{1}{k} \right) \left(\frac{\partial(\eta/\rho)}{\partial T} \right)_p. \tag{39}$$

It is easy to see that when $\eta/\rho = $ const the constitutive equation (37) passes into the ideal gas law, and the specific heats turn out to be constant. To correct the expressions (37), (39) for variable ratio η/ρ it is necessary to apply the mass balance equation and the particle balance equation. It is easy to show that from Eq. (16) it follows that [50]
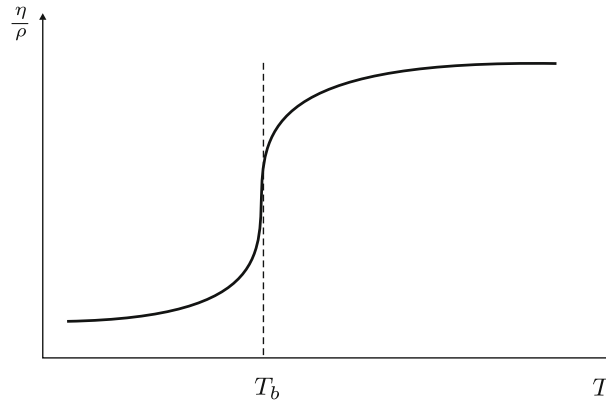
$$\frac{\delta z}{\delta t} = \frac{\chi}{\eta}, \qquad z = \ln \left(\frac{\rho_0 \eta}{\rho \eta_0} \right), \tag{40}$$

where ρ_0 and η_0 are the initial distributions of mass and particles. According to Eq. (38) linear dependence between new variable z and the chemical potential is

$$z = k(\psi - \psi_0).$$

Comparing the equation of structural transitions $(27)_2$ with Eq. (40) we obtain

$$\chi = -k Q.$$

Fig. 5 Dependence of the ratio η/ρ on temperature

Of course, the obtained relation between the exchange heat and the source term in the particle balance equation is governed by the special choice of the expression for the internal energy. However, for any form of the internal energy the constitutive equations for Q and χ cannot be independent. There are two variants. Either we formulate the constitutive equation for Q and in this case the particle balance equation allows us to determine χ, or we formulate the constitutive equation for χ, and then, the equation of structural transitions allows us to find Q. Theoretically, a third variant exists. We can arbitrarily choose the constitutive equations for Q and χ, but in this case there is no freedom in choosing internal energy.

6 Description of the liquid–gas phase transition in view of structure transformations: variant 1

Let us discuss a method of describing the liquid–gas phase transition based on the assumption that the particle is either a single molecule or a cluster of several molecules. According to our supposition the ratio η/ρ does not depend on the temperature at sufficiently low temperatures that corresponds to the liquid state of matter and at sufficiently high temperatures that corresponds to the gaseous state of matter. Near the boiling point the ratio η/ρ should change abruptly. That behavior of function η/ρ is shown in Fig. 5.

The behavior of function η/ρ is determined by Eq. (40) which can be rewritten in the form

$$\frac{\delta}{\delta t}\left(\frac{\eta}{\rho}\right) = \frac{\chi}{\rho}.$$

In order that the number of particles starts to change abruptly in the neighborhood of the boiling point, the source term in the particle balance equation must depend on the temperature and has the localized burst near T_b. In addition to that the change of particle number has to stop when η/ρ achieves a certain value: n_l for a liquid and n_g for a gas. It means that the source term has to be proportional to the difference $\eta/\rho - n_g$ at heating and to $\eta/\rho - n_l$ at cooling. The following function has the listed properties:

$$\chi = M e^{-\frac{(T-T_b)^2}{\varepsilon_1 T_b^2}} \left[\left(\frac{\eta}{\rho} - n_l\right) e^{\frac{\text{sign}(q+\nabla\cdot\mathbf{h})}{\varepsilon_2}} + \left(n_g - \frac{\eta}{\rho}\right) e^{\frac{\text{sign}(q+\nabla\cdot\mathbf{h})}{\varepsilon_2}}\right]. \tag{41}$$

Here the parameter ε_1 has to be small enough that the function $e^{-\frac{(T-T_b)^2}{\varepsilon_1 T_b^2}}$ could be an approximation of the Dirac delta function $\delta(T - T_b)$. The parameter ε_2 should be chosen so that $e^{-1/\varepsilon_2} \ll e^{1/\varepsilon_2}$. Parameters ε_1 and ε_2 have to be positive.

Function M determines the rate of change of η/ρ and has to depend on the heat supply velocity. We can take it in the form:

$$M = \frac{\eta q + \nabla \cdot \mathbf{h}}{\varepsilon H},$$

where H is the specific heat of vaporization.

To explain the choice let us consider the vaporization process in a homogeneous system at $T = T_b$ and suppose that the heat is supplied only into the particles of the medium. Then, $\mathbf{h} = 0$, and the source term has a form:

$$\chi = \frac{\eta q}{\varepsilon H}\left(n_g - \frac{\eta}{\rho}\right).$$

From Eq. (41) it follows that

$$\frac{\mathrm{d}(\eta/\rho)}{\mathrm{d}t} = \frac{q_*}{\varepsilon H}\left(n_g - \frac{\eta}{\rho}\right)$$

where q_* is the heat supply velocity per unit mass.

Integration of this equation with an initial condition

$$\left.\frac{\eta}{\rho}\right|_{t=t_0} = n_l$$

results:

$$n_g - \frac{\eta}{\rho} = (n_g - n_l)\exp\left(-\frac{1}{\varepsilon H}\int_{t_0}^{t} q_*\,\mathrm{d}t\right).$$

Taking into account that $\int_{t_0}^{t_1} q_*\,\mathrm{d}t = H$, where t_1 is a time when the whole liquid is vaporized, one can see that the parameter ε characterizes how close the ratio η/ρ will be to n_g with $t \to t_1$.

Now we are able to introduce an internal energy corresponding to liquid and gaseous states and phase transition between them. It has to posses a few characteristic features of the model. First, the constitutive equation for pressure must be similar the van der Waals equation in the area of gaseous state, weakly depend on temperature in the area of liquid state, and the pressure must not stepwise change in the neighborhood of the boiling point. Second, the specific heat at constant volume corresponding to the matter in liquid state must be larger than the one corresponding to the matter in gaseous state. Let us define the internal energy as

$$\begin{aligned}
\eta u &= \rho g(Y) + \rho h(X) + \rho f_3(\rho), \\
Y &= f_1(\rho)e^{BS+k_1\psi}, \qquad X = f_2(\rho)e^{k_2\psi}, \\
g(Y) &= \sqrt{A_1 + Y}, \qquad h(X) = -\sqrt{A_2 + X}.
\end{aligned} \tag{42}$$

Here A_i, k_i and B are constants that have to be identified.

Substituting Eq. (42) into the Cauchy Green relations (19) we obtain

$$T = \frac{\rho}{\eta}g'(Y)BY, \quad \eta = \rho g'(Y)k_1 Y + \rho h'(X)k_2 X \quad \Rightarrow \quad \frac{\eta}{\rho} = \frac{Bk_2}{B - k_1 T}Xh'(X),$$

$$\begin{aligned}
p &= \rho^2 g'(Y)\frac{\partial Y}{\partial\rho} + \rho^2 h'(X)\frac{\partial X}{\partial\rho} + \rho^2 f_3'(\rho) \\
&= \rho^2\left(\frac{T}{B}\left(\frac{f_1'(\rho)}{f_1(\rho)} - \frac{k_1}{k_2}\frac{f_2'(\rho)}{f_2(\rho)}\right) + \frac{1}{k_2}\frac{f_2'(\rho)}{f_2(\rho)}\right)\frac{\eta}{\rho} + \rho^2 f_3'(\rho).
\end{aligned} \tag{43}$$

Note that η/ρ has to be positive. Since $h'(X)$ is negative we assume that function $X < 0$.

Let us rewrite the constitutive equation for the pressure in a more suitable form. For that we split it into two terms in such a way that one of them is small in case of liquid and another is small in case of gas

$$p = f_4(\rho)T\frac{m_0\eta}{\rho} + f_5(\rho)\left(1 - \frac{m_0\eta}{\rho}\right), \tag{44}$$

$$f_4 = \frac{\rho^2}{m_0}\frac{1}{B}\left(\frac{f_1'(\rho)}{f_1(\rho)} - \frac{k_1}{k_2}\frac{f_2'(\rho)}{f_2(\rho)}\right), \qquad f_5 = \rho^2 f_3'(\rho).$$

$$\frac{\rho^2}{m_0}\frac{1}{k_2}\frac{f_2'(\rho)}{f_2(\rho)} + \rho^2 f_3'(\rho) = 0$$

Here m_0 is the normalizing factor such that the ratio $m_0\eta/\rho$ is near to 1 for the gas and near to zero for the liquid. Thus, the pressure of the gas is determined mainly by the first term of Eq. (44), the pressure of the liquid is determined mainly by the second term of this equation. Let us give a concrete expression to functions $f_i(\rho)$.

Suppose that the gas pressure is determined by the first term of the van der Waals equation and assume that a liquid is described in a way similar to the Tumlirz constitutive equation, i.e.

$$p = \frac{RT\rho}{1-b\rho}\frac{m_0\eta}{\rho} + \left(\frac{\lambda\rho^2}{1-b\rho} - a\rho^2\right)\left(1 - \frac{m_0\eta}{\rho}\right),\tag{45}$$

where λ, r and a are parameters of the constitutive equations. Since the term $-a\rho^2$ in van der Waals equation stays for a liquid, we relate it to the liquid part of the pressure.

Then, we obtain:

$$f_1(\rho) = C_1\left(\frac{\rho}{1-b\rho}\right)^{m_0 BR}(1-b\rho)^{m_0 k_1 \lambda/b}e^{m_0 k_1 a\rho},$$

$$f_2(\rho) = C_2(1-b\rho)^{m_0 k_2 \lambda/b}e^{m_0 k_2 a\rho}, \qquad f_3(\rho) = -\frac{\lambda}{b}\ln(1-b\rho) - a\rho + C_3,\tag{46}$$

where C_1, C_3 and $C_2 < 0$ are dimensional integral constants that do not appear in the final equations.

Using the condition of equality of the pressure in the liquid and gas at the boiling point we find the dependence of boiling point T_b on the mass densities of the liquid and gas:

$$f_4(\rho_g)T_b\left(\frac{m_0\eta}{\rho}\right)_g + f_5(\rho_g)\left[1 - \left(\frac{m_0\eta}{\rho}\right)_g\right]$$

$$= f_4(\rho_l)T_b\left(\frac{m_0\eta}{\rho}\right)_l + f_5(\rho_l)\left[1 - \left(\frac{m_0\eta}{\rho}\right)_l\right],$$

where ρ_g and ρ_l are the mass densities of the liquid and gas, respectively.

Expressing, for example, $\left(\dfrac{m_0\eta}{\rho}\right)_g$ in terms of the pressure with the help of the constitutive equation (45) we can obtain the dependence of the boiling temperature on pressure.

Let us determine the specific heats under constant volume for a gas and a liquid. According to the definition the specific heat under constant volume is determined as a partial derivative of the mass density of the internal energy $u_* = u(T, \rho, \eta/\rho)$ with respect to the temperature. By using Eq. (42) we obtain

$$c_v = \frac{\partial}{\partial T}\left(\frac{\eta u}{\rho}\right) = \frac{\partial g(Y)}{\partial T} + \frac{\partial h(X)}{\partial T}.\tag{47}$$

From Eqs. (43), (42) follows that the function $g(Y)$ and $h(X)$ are found as roots of quadratic equations. Since $g(Y)$ has to be positive and $h(X)$ negative we get:

$$g = \frac{T}{B}\frac{\eta}{\rho} + \sqrt{\left(\frac{T}{B}\frac{\eta}{\rho}\right)^2 + A_1},$$

$$h = \frac{B - k_1 T}{Bk_2}\frac{\eta}{\rho} - \sqrt{\frac{(B-k_1 T)^2}{k_2^2 B^2}\left(\frac{\eta}{\rho}\right)^2 + A_2}.$$

The condition $\dfrac{B - k_1 T}{k_2 B} > 0$ is assumed.

Then,

$$c_v = \frac{1}{B}\left(1 - \frac{k_1}{k_2}\right)\frac{\eta}{\rho} + \frac{1}{B}\left(\frac{T}{\sqrt{(T\eta/\rho)^2 + A_1 B^2}} + \frac{k_1}{k_2}\frac{B - k_1 T}{k_2 B}\frac{1}{\sqrt{\left(\frac{B-k_1 T}{k_2 B}\frac{\eta}{\rho}\right)^2 + A_2}}\right)\left(\frac{\eta}{\rho}\right)^2.\tag{48}$$

Note that the specific heat is proportional to η/ρ. It was assumed that $n_g > n_l$, at the same time $c_v^g < c_v^l$. It means that the coefficient on η/ρ has to decrease significantly with the temperature increasing. This in turn may complicate the model parameters' determination.

Taking into account that the large values of $\eta/\rho = n_g$ correspond to the gaseous state we obtain the approximate formula for the specific heat of the gas:

$$c_v^g = \frac{n_g}{B}\left(1 + \frac{n_g T}{\sqrt{n_g^2 T^2 + A_1 B^2}}\right). \tag{49}$$

The expression for the specific heat of the liquid can be obtained by putting $\eta/\rho = n_l$ in Eq. (48).

To rewrite the combined equation of structural transitions and heat conduction (17) in terms of the control variables, we have to express $\eta T \dfrac{\delta S}{\delta t} + \eta \dfrac{\delta \psi}{\delta t}$ in terms of T, ρ and η/ρ. From the Eq. (42) one can find:

$$\frac{\delta \psi}{\delta t} = \frac{1}{k_2}\left(\frac{1}{X}\frac{\delta X}{\delta t} - \frac{f_2'(\rho)}{f_2(\rho)}\frac{\delta \rho}{\delta t}\right),$$
$$\frac{\delta S}{\delta t} = \frac{1}{B}\left(\frac{1}{Y}\frac{\delta Y}{\delta t} - \frac{k_1}{k_2}\frac{1}{X}\frac{\delta X}{\delta t} + \left(\frac{k_1}{k_2}\frac{f_2'(\rho)}{f_2(\rho)} - \frac{f_1'(\rho)}{f_1(\rho)}\right)\frac{\delta \rho}{\delta t}\right).$$

By help of Eq. (46) the combined equation of structural transitions and heat conduction has the form:

$$\rho\frac{\delta g}{\delta t} + \rho\frac{\delta h}{\delta t} + \left(\frac{\lambda\rho - RT}{1 - b\rho} - a\rho\right)\frac{m_0 \eta}{\rho}\frac{\delta \rho}{\delta t} = \nabla \cdot \mathbf{h} + \eta q.$$

It is seen that the input of the density change term in the equation of structural transitions and the heat conduction in the case of the liquid phase is very small.

Taking into account Eq. (47) for the specific heat, we can rewrite the combined equation of structural transitions and heat conduction as follows:

$$\rho c_v\frac{\delta T}{\delta t} + \rho\frac{\partial(g+h)}{\delta(\eta/\rho)}\frac{\delta(\eta/\rho)}{\delta t} + \left(\frac{\lambda\rho - RT}{1 - b\rho} - a\rho\right)\frac{m_0 \eta}{\rho}\frac{\delta \rho}{\delta t} = \nabla \cdot \mathbf{h} + \eta q. \tag{50}$$

6.1 The material parameter identification

Now we determine the material parameters of the model for a water vapor phase transition in a homogeneous system.[2]

Since the bulk modulus is defined as $K = \rho\dfrac{\partial p}{\partial \rho}$ we can get the equation:

$$K_w = \frac{R\rho_0 T_0}{(1 - b\rho_0)^2}m_0 n_l + \left(\frac{\lambda\rho_0^2(2 - b\rho_0)}{(1 - b\rho_0)^2} - 2a\rho_0^2\right)(1 - m_0 n_l) \tag{51}$$

where $K_w = 2.2 \times 10^9$ Pa and $\rho_0 = 997.8$ kg m^{-3} are bulk modulus and mass density of water at room temperature $T_0 = 295$ K.

From the expression for the thermal expansion $\alpha = \dfrac{1}{K}\dfrac{\partial p}{\partial T}$ it follows that

$$\frac{RT_0\rho_0}{1 - b\rho_0}m_0 n_l = \alpha_w K_w, \tag{52}$$

where $\alpha_w = 3 \times 10^{-4}$ is the coefficient of water thermal expansion at room temperature.

To determine the parameters we have to choose the normalizing factor m_0 and the coefficient b that is related to the molecule size. Following [15], we suppose that $b = 0.007$ m^3 kg^{-1}. Let us choose the normalizing factor as the atomic mass of water multiplied by 10^{26}. Thus, $m_0 = 3$ kg. Note that the parameter m_0

---

[2] The experimental data are taken from [47].

appears in the equations only in combination with η/ρ. Then, solving Eqs. (51) and (52) together with the conditions that the boiling temperature $T_b = 373$ K corresponds to the normal pressure $p_b = 0.1$ MPa for both phases, allows us to determine the parameters of the constitutive equation:

$$a = 826.776 \, \mathrm{N m^6 \, kg^{-2}}, \quad \lambda = 270.105 \, \mathrm{N m^6 \, kg^{-2}},$$
$$n_l = 0.00144 \, \mathrm{kg^{-1}}, \quad n_g = 0.3318 \, \mathrm{kg^{-1}}.$$

It is easy to check that at the critical point ($\rho_{cr} = 322 \, \mathrm{kg m^{-3}}$ $T_{cr} = 647.096$ K, $p_{cr} = 22.064 \times 10^6 \, \mathrm{N m^{-2}}$) the ratio $\eta/\rho = 0.1375 \, \mathrm{kg^{-1}}$ is much closer to the ratio η/ρ for the gas state than for the water state.

The parameters A_1 and B can be found from Eq. (49) for different temperatures. Thus, since $c_v^g = 1.508 \, \mathrm{kJ \, kg^{-1} \, K^{-1}}$ at 400 K and $c_v^g = 1.689 \, \mathrm{kJ \, kg^{-1} \, K^{-1}}$ at 800 K, then

$$A_1 = 1.52 \times 10^{11} \, \mathrm{m^4 c^{-4}}, \quad B = 0.00037 \, \mathrm{K J^{-1}}.$$

The specific heat of vaporization (or the specific enthalpy of vaporization) corresponds to the amount of energy that must be supplied to the system to convert a unit mass of water into the vapor phase at a constant temperature and a given pressure. Thus [36],

$$
\begin{aligned}
H &= \left. \frac{\eta u}{\rho} \right|_{n_l}^{n_g} + p_b \left(\frac{1}{\rho_g} - \frac{1}{\rho_l} \right) \\
&= (g+h)|_{n_l}^{n_g} + \frac{\lambda}{b} \ln \frac{(1 - b\rho_l)}{(1 - b\rho_g)} - a(\rho_g - \rho_l) + p_b \left(\frac{1}{\rho_g} - \frac{1}{\rho_l} \right),
\end{aligned}
\tag{53}
$$

where $H = 2.260 \times 10^6 \, \mathrm{J \, kg^{-1}}$ is the specific heat of vaporization, $\rho_l = 958.6 \, \mathrm{kg \, m^{-3}}$, $\rho_g = 0.59 \, \mathrm{kg \, m^{-3}}$ are the water and vapor densities at the boiling temperature. Note that the same expression for the specific heat can be received after integration of Eq. (50).

Since the expression $\dfrac{B - k_1 T}{k_2 B}$ has to be positive over the entire temperature range, let us take

$$k_1 = B/T_f, \quad k_2 < 0,$$

where $T_f = 273.15$ K is the freezing point of water.

Then, from the Eq. (53) and the condition that the specific heat of water $c_v^l = 4.15 \, \mathrm{kJ \, kg^{-1} \, K^{-1}}$ at room temperature, one can find the last parameters of the model:

$$A_2 = 2.658 \times 10^{12} \, \mathrm{m^4 c^{-4}}, \quad k_2 = -1.197 \times 10^{-9} \, \mathrm{J^{-1}}.$$

Now it is easy to check that approximate expression Eq. (49) for the specific heat of gas is valid.

As a result the all parameters of the model are determined.

The dependencies of the specific heat of the different phases on temperature are presented in Fig. 6. It is seen that the specific heat of water decreases and the specific heat of gas increases with increasing temperature. It is in agreement with experimental data but the water-specific heat decreases faster that it should.

Figure 7 shows the dependence of the specific heat on the ratio η/ρ at the boiling temperature. It is seen that the specific heat increases and then decreases drastically at the beginning of the structural transformation. Then, around the value $\eta/\rho = (\eta/\rho)_{cr}$ the specific heat starts to grow slowly as it should do in the gas state.

It should be noted that in the classical approaches it is assumed that total heat supply goes to specific heat changes, as a result the specific heat has a maximum around the phase transition point. We suppose that the energy supply at the boiling point does not only lead to specific heat changes but also lead to a structural modification that is why the specific heat decreases during the phase transition.

In this section the model of the liquid–gas phase transition, based on the assumption that the particle is either a single molecule or a cluster of several molecules was constructed. A mathematical feature of this concept is that the number of particles per unit mass increases dramatically during the transition from liquid to gas (see Fig. 5). Several problems appeared in the process of practical implementation of the model. The expression for the internal energy is quite complex, and attempts to simplify it lead to incorrect description of some properties of either liquid or gas. Chemical potential in the cases of both liquid and gas phases does not approach a constant and therefore significantly affects the structural changes and heat conduction equation not only at the phase transition temperature, but far from it as well. It is at least counterintuitive. Attempts to
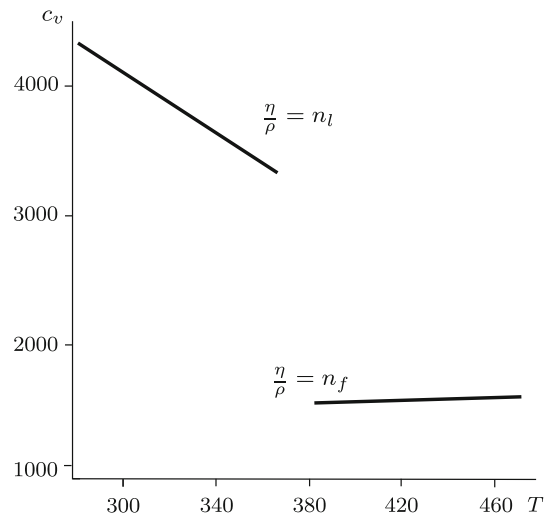
Fig. 6 Dependence of specific heat on temperature
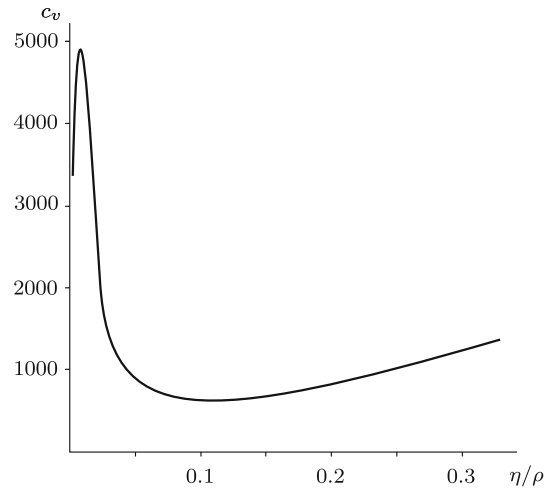
Fig. 7 Dependence of specific heat on the ratio η/ρ. $T = T_b$

develop a model that does not have these disadvantages were not successful. Difficulties arose also at the step of the identification of the model parameters. A very slight change in the thermodynamic characteristics of the material caused significant changes in the model parameters. Detailed analysis revealed that these problems are related to the poor agreement between the following two factors: the heat capacity of the gas is less than that of the liquid and the number of particles in the gas is greater than the number of particles in the liquid.

7 Description of the liquid–gas phase transition in view of structure transformations: variant 2

Below we present a model of the liquid–gas phase transition that is based on the assumption that the particles are molecules and the bonds that hold them in clusters. The mathematical feature of this concept is that the number of particles per unit mass decreases sharply in the transition process from liquid to gas. Thus, reducing the number of particles corresponds to the reduction in the specific heat in this model. Therefore, this model should be free from the shortcomings of the previous one. Next, we will see that this is indeed true. Let us start with the assumption that the chemical potential approaches constant values for both liquid and gas states —ψ_l and ψ_g correspondingly. Next, we will see that, in the framework of this model, the natural consequence of the mentioned assumption is the constancy of the relation η/ρ.

The source term in this model can be written analogous to Eq. (41) with the opposite sign.

$$\chi = \frac{\eta q + \nabla \cdot \mathbf{h}}{\varepsilon H} e^{-\frac{(T-T_b)^2}{\varepsilon_1 T_b^2}} \left[\left(n_l - \frac{\eta}{\rho} \right) e^{-\frac{\text{sign}(q+\nabla\cdot\mathbf{h})}{\varepsilon_2}} + \left(\frac{\eta}{\rho} - n_g \right) e^{\frac{\text{sign}(q+\nabla\cdot\mathbf{h})}{\varepsilon_2}} \right].$$

Let us assign the internal energy as

$$\eta u = \rho C_1 f_1(\rho)^{\varphi_1(\psi/\psi_0)} e^{BS} + \rho C_2 \varphi_2(\psi/\psi_0) + \rho f_2(\rho)(1 - \varphi_3(\psi/\psi_0)), \tag{54}$$

where ψ_0 is a normalizing parameter, C_1, C_2 and B are dimensional constants.

By using the Cauchy Green relations $(19)_{2,3}$ we find

$$\frac{\eta}{\rho} T = BC_1 f_1(\rho)^{\varphi_1} e^{BS},$$

$$\frac{\eta}{\rho} \psi_0 = C_1 \ln(f_1(\rho)) f_1(\rho)^{\varphi_1} e^{BS} \varphi_1' + C_2 \varphi_2' - f_2(\rho) \varphi_3'. \tag{55}$$

Here $\varphi_i' = \dfrac{\partial \varphi_i(\psi/\psi_0)}{\partial(\psi/\psi_0)}$.

Then, we can rewrite Eq. (54) as follows:

$$\frac{\eta u}{\rho} = \frac{(C_2 \varphi_2' - f_2(\rho)\varphi_3')T}{B\psi_0 - \ln(f_1(\rho))\varphi_1' T} + C_2 \varphi_2 + f_2(\rho)(1 - \varphi_3).$$

As a result the specific heat is as follows:

$$c_v = \frac{(C_2 \varphi_2' - f_2(\rho)\varphi_3')B\psi_0}{\left(B\psi_0 - \ln(f_1(\rho))\varphi_1' T\right)^2}. \tag{56}$$

In order that the specific heats of the liquid and gas states will not depend on the density let us choose the functions $\varphi_1(\psi/\psi_0)$ and $\varphi_3(\psi/\psi_0)$ in such a way that:

$$\varphi_1'(\psi_g/\psi_0) = 0, \qquad \varphi_1'(\psi_l/\psi_0) = 0,$$
$$\varphi_3'(\psi_g/\psi_0) = 0, \qquad \varphi_3'(\psi_l/\psi_0) = 0.$$

The following functions have the listed properties:

$$\varphi_1(\psi/\psi_0) = -2\left(\frac{\psi}{\psi_0}\right)^3 + 3\frac{\psi_l + \psi_g}{\psi_0}\left(\frac{\psi}{\psi_0}\right)^2 - 6\frac{\psi_l \psi_f}{\psi_0^2}\frac{\psi}{\psi_0} + C_3,$$

$$\varphi_3(\psi/\psi_0) = A_1\left(-2\left(\frac{\psi}{\psi_0}\right)^3 + 3\frac{\psi_l + \psi_g}{\psi_0}\left(\frac{\psi}{\psi_0}\right)^2 - 6\frac{\psi_l \psi_f}{\psi_0^2}\frac{\psi}{\psi_0}\right) + A_2$$

where C_3, A_1 and A_2 are dimensionless constants.

Then, the specific heat of liquid and gas in a distance from the boiling point have the form:

$$c_v^l = \frac{C_2 \varphi_2'(\psi_l/\psi_0)}{B\psi_0}, \qquad c_v^g = \frac{C_2 \varphi_2'(\psi_g/\psi_0)}{B\psi_0}. \tag{57}$$

From Eqs. (55), (56) follows

$$\frac{\eta}{\rho}\psi_0 = c_v(B\psi_0 - \ln(f_1(\rho))\varphi_1' T). \tag{58}$$

It should be noted that in the cases of sufficiently low and hight temperatures, when the chemical potential does not depend on the temperature and being equal to ψ_l or ψ_g, the function η/ρ is also a constant for both states:

$$\left(\frac{\eta}{\rho}\right)_g = n_2 = c_v^g B, \qquad \left(\frac{\eta}{\rho}\right)_l = n_1 = c_v^l B.$$

It is seen that since $c_v^l > c_v^g$ the ratio η/ρ should be greater for the liquid phase than for the gas phase.

In view of Eqs. (54), (55) from the Cauchy Green relation for pressure (19)$_1$ we find

$$p = \rho^2 \left(\ln \left(f_1(\rho) \right) \right)' \frac{C_2 \varphi_2' - f_2(\rho) \varphi_3'}{B\psi_0 - \ln \left(f_1(\rho) \right) \varphi_1' T} \varphi_1 T + \rho^2 f_2'(\rho) \left(1 - \varphi_3 \right).$$

Let us choose functions $f_1(\rho)$ and $f_2(\rho)$ so that the pressure equation will be similar to Eq. (45). We can take:

$$f_1(\rho) = \frac{C_4 \rho}{1 - b\rho}, \qquad f_2(\rho) = -\frac{\lambda \ln(1 - b\rho)}{b} - a\rho,$$

where C_4 is a dimensional integral constant.

Since the function $\varphi_1(\psi_g/\psi_0)$ equals to constants at $\psi = \psi_g$ and $\psi = \psi_l$ we can denote:

$$F_g = \frac{c_v^g}{R} \varphi_1(\psi_g/\psi_0), \qquad F_l = \frac{c_v^l}{R} \varphi_1(\psi_l/\psi_0).$$

We may then choose the constants A_i so that:

$$\varphi_3(\psi_g/\psi_0) = F_g, \qquad \varphi_3(\psi_l/\psi_0) = F_l$$

As a result, the pressure for the liquid state is determined by the equation:

$$p|_{\psi = \psi_l} = \frac{RT\rho}{1 - b\rho} F_l + \left(\frac{\lambda \rho^2}{1 - b\rho} - a\rho^2 \right) \left(1 - F_l \right). \tag{59}$$

The expression for the gaseous state is analogous.

From the Eq. (59) we can find the bulk modulus $K = \rho \dfrac{\partial p}{\partial \rho}$ and the coefficient of thermal expansion $\alpha = \dfrac{1}{K} \dfrac{\partial p}{\partial T}$ for the liquid state. Then, similar to the Variant 1, we put $b = 0.007 \, \mathrm{m^3 \, kg^{-1}}$ and find the parameters for the water vapor phase transition:

$$a = 826.776 \, \mathrm{Nm^6 \, kg^{-2}}, \ \lambda = 270.105 \, \mathrm{Nm^6 \, kg^{-2}}, \tag{60}$$
$$F_l = 0.0004, \qquad F_g = 0.9955.$$

Assume that function $\varphi_2(\psi/\psi_0)$ has a form:

$$\varphi_2(\psi/\psi_0) = (\psi/\psi_0)^{1/2}.$$

Then, from Eq. (57) for the specific heats it follows:

$$\frac{\psi_l}{\psi_g} = \left(\frac{c_v^g}{c_v^l} \right)^2, \qquad B\psi_0 = \frac{C_2}{2c_v^g} \left(\frac{\psi_g}{\psi_0} \right)^{-1/2},$$
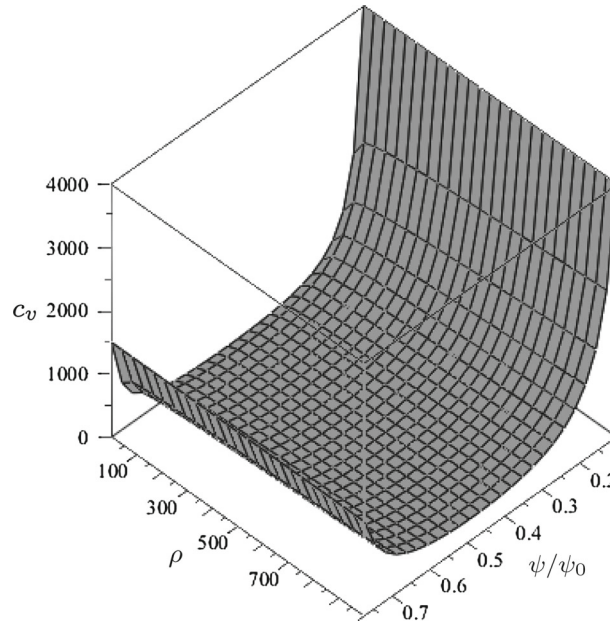
and thus, from Eq. (60)$_{(3,4)}$ one can find

$$\frac{\psi_g}{\psi_0} = 0.7750, \quad C_3 = 0.0233.$$

To determine C_2 write down the expression for the specific enthalpy of vaporization.

$$\left. \frac{\eta u}{\rho} \right|_{\psi_l}^{\psi_g} + p_b \left(\frac{1}{\rho_g} - \frac{1}{\rho_l} \right) = (c_v^g - c_c^l) T_b + A \left(\left(\frac{\psi_g}{\psi_0} \right)^{1/2} - \left(\frac{\psi_l}{\psi_0} \right)^{1/2} \right)$$
$$+ \frac{\lambda}{b} \ln \frac{1 - b\rho_l}{1 - b\rho_g} - a(\rho_g - \rho_l) + p_b \left(\frac{1}{\rho_g} - \frac{1}{\rho_l} \right).$$

Fig. 8 Dependence of the specific heat on the density and ψ/ψ_0 at $T = T_b$

Set the specific enthalpy of vaporization equal to the specific heat of vaporization $H = 2.260 \times 10^6 \, \mathrm{J\,kg^{-1}}$ analogous to the Variant 1, we find:

$$C_2 = 4.5387 \times 10^6 \, \mathrm{J\,kg^{-1}}, \qquad B\psi_0 = 1718.5827 \, \mathrm{K}.$$

To find the two last constant C_1 and C_4 we have to find the specific entropies for both phases. Note that from the Eq. (55) follows:

$$e^{BS} = \frac{(C_2\varphi_2' - f_2(\rho)\varphi_1')T}{Cf_1(\rho)^{\varphi_1}(B\psi_0 - \ln(f_1(\rho))\,\varphi_1'T)}. \tag{61}$$

Thus, we have

$$S_g = \frac{1}{B} \ln \frac{c_v^g T}{C_1 f_1(\rho_g)^{\varphi_1(\psi_g/\psi_0)}}, \qquad S_l = \frac{1}{B} \ln \frac{c_v^l T}{C_1 f_1(\rho_l)^{\varphi_1(\psi_l/\psi_0)}}.$$

Taking into account Eq. (58) we can write the mass density of the entropies:

$$S_*^g = c_v^g \ln \frac{c_v^g T}{C_1} - R\varphi_1^g \ln \frac{C_4\rho_g}{1 - b\rho_g},$$

$$S_*^l = c_v^l \ln \frac{c_v^l T}{C_1} - R\varphi_1^l \ln \frac{C_4\rho_l}{1 - b\rho_l}.$$

Since $S_*^g = 7.9447 \, \mathrm{kJ\,kg^{-1}\,K^{-1}}$ at 500 K and $S_*^l = 0.3228 \, \mathrm{kJ\,kg^{-1}\,K^{-1}}$ at 295 K, we find that:

$$C_1 = 1.1379 \times 10^6 \, \mathrm{kJ\,kg^{-1}} \qquad C_3 = 1.8195 \times 10^{-8} \, \mathrm{m^3\,kg^{-1}}.$$

Now, we can display the dependence of the specific heat on the density and chemical potential. The specific heat at the boiling point is shown at Fig. 8. It is seen that it is a smooth function that decreases during structural transformations and starts do grow slowly close to gaseous state.

To rewrite the combined equation of structural transitions and head conduction in more usual form one has to find the expression for $\eta T \frac{\delta S}{\delta t} + \eta \frac{\delta \psi}{\delta t}$ in terms of the temperature, density and chemical potential. To do

this we have to find the material derivation of e^{BS} (Eq. 61) and, take into account the expression Eq. (56) for the specific heat. As a result we get:

$$\rho c_v \frac{\delta T}{\delta t} + \frac{c_v}{\rho} \left[\left(\frac{T\varphi_1'}{\phi} - \varphi_1 \right) \frac{T\rho}{1 - b\rho} - \frac{\varphi_1' T}{\phi} \left(\frac{\lambda \rho^2}{1 - b\rho} - a\rho^2 \right) \right] \frac{\delta \rho}{\delta t}$$
$$+ \rho c_v \frac{\phi}{B\psi_0} \left[\frac{\varphi_1'' \ln f_1}{\phi} T^2 + \frac{\varphi_2'' - f_2 \varphi_1''}{\varphi_2' - f_2 \varphi_1'} + \phi \right] \frac{\delta(\psi/\psi_0)}{\delta t} = \nabla \cdot \mathbf{h} + \eta q,$$

where

$$\phi = B\psi_0 - \ln (f_1(\rho)) \varphi_1' T.$$

This expression is simplified at some distance from the boiling point. For example, for the gas phase it has the form:

$$\rho c_v^g \frac{\delta T}{\delta t} - \frac{RT}{1 - b\rho} F_g \frac{\delta \rho}{\delta t} = \nabla \cdot \mathbf{h} + \eta q.$$

The carried out investigation has shown that the model based on the concept that the ratio η/ρ increases in the structure transition process well describes the water vapor phase transition. All material parameters can be identified easily and the proposed expression for the internal energy or the thermal equation of state $p = p(T, \rho)$ can be modified to describe some other specific features of the phase transition.

8 Discussion

In conclusion we give a comparison of the proposed method with the most famous descriptions of phase transitions. Chemical thermodynamics description of phase transitions is based on the chemical potentials and the chemical affinity of the phase transformation. Our definition of the chemical potential differs from the classical ones. This definition allows us to consider the density of particle distribution and the mass density as independent variables. Just due to this fact we can use ratio of the density of particle distribution to the mass density as an order parameter. In addition, we proceed from the supposition that phase transitions are dynamical processes and they can be very quickly ones. That is why the system of basic equations of the proposed model includes the equations of motion. As a result the proposed approach allows us to describe essentially non-equilibrium processes. In contrast to this approach in chemical thermodynamics quasi-equilibrium processes are considered since the method of description of evaporation and condensation processes is based on the Clausius-Clapeyron equation (see [14] for example) which describes the sequence transitions from one equilibrium state to another.

We describe the liquid–gas phase transition on the base of the fundamental laws of mechanics. There are different approaches to the description of the thermodynamic processes within the framework of continuum mechanics. In some models the existence of a sharp boundary between phases is of great importance. There are so-called interface tracking methods, which connected phase transition with the interface movement. In the frame of our approach the present of a distinct phase boundary is not essential, and its existence is not assumed a priori and the phase transition can occur simultaneously everywhere. If the phase boundary is present, then its position can be determined as a result of the problem solution. A sign of phase boundary existence will be a dramatic change of ratio η/ρ with respect to spatial coordinates changing.

Since the ratio η/ρ being the characteristic of number of clusters in a given point of the medium can be considered as an order parameter which describes the process of phase transition, the phase-field approach with the field variable corresponding to an order parameter is most similar to our approach. The distinction is that the phase-field approach uses the difference of the mass densities as the order parameter for liquid/gas transitions. Another difference between these two approaches is that in the frame of phase-field method the time evolution of order parameter is usually assumed to be proportional to the derivative of free energy with respect to the order parameter, whereas in accordance with our approach the source term in the balance equation for η/ρ is not the derivative of free energy or some other thermodynamic potentials.

Almost all known models of continuum mechanics describe the situation when the number of particles in the medium does not vary. That means the linear dependence between the density of particle distribution and the density of mass. In this case the density of particle distribution is excluded and all quantities are

considered to be additive functions of mass. We consider the density of particle distribution and the density of mass as independent variables and following to [50] we assume the internal energy and the entropy to be additive functions of number of particles, i.e. that variable which is associated with the order parameter. This circumstance and the fact that the ideas of methods based on the use of order parameters are combined with the methods of continuum mechanics and applied to the description of phase transitions associated rather with the change of aggregative state of matter than with change of its certain physical characteristics distinguish our method from the known approaches. Our approach allows us to describe both phase states with different mechanical and thermodynamic parameters in a framework of a unified model. At the same time our approach allows us to describe the behavior of matter immediately during the phase transition.

Within the framework of the proposed approach we have considered two interpretations of the concept of particle in a liquid. Two mathematical models corresponding to one and another concept have been constructed. The detail analysis shows that the second model based on the viewpoint that the particles are molecules and the bonds which hold the molecules in clusters should be preferred. The reason is that the mathematical implementation of the second model is much easier than that of the first model, and hence, the second model is more consistent with the nature.

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