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The microphysical effects in nonisothermal nucleation

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Abstract

The role of microphysical effects in the ability of a small new phase nucleus to emit molecules into the vapor is revealed on a thermodynamic basis. It is shown that dependence of the surface tension of a nucleus on its temperature and the dependence of the vaporisation heat on the nuclear surface curvature are insignificant in nonisothermal nucleation. The meaning of the quantities used in the one-dimensional theory of isothermal nucleation has been clarified from the point of the two-dimensional nonisothermal theory. Statistical and kinetic treatment of the microphysical effects in the emitting rate of a nucleus has been performed. An association of the microphysical effects with deviation of the kinetic equation of nonisothermal nucleation from the Fokker–Planck form has been examined. © 1998 Elsevier Science B.V. All rights reserved.

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0. Introduction

The state of a condensed phase nucleus is characterised in the theory of nonisothermal nucleation [1–6] by two variables, the number of nuclear molecules and the temperature of the nucleus or the nuclear energy associated with this temperature. Thus, the theory of nonisothermal nucleation is basically two dimensional. This makes an essential difference of nonisothermal nucleation theory from more simple one-dimensional theory of isothermal nucleation where the state of a nucleus is characterised by one variable only, the number of nuclear molecules.

A relation of the theory of nonisothermal nucleation to its thermodynamic, statistical, and kinetic grounds is quite nontrivial. Earlier this relation had been considered in Ref. [1], mostly from thermodynamic point of view, in Refs. [2–5] through statistical

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and kinetic approach, and recently in Ref. [6], where the role of temperature in classical nucleation theory was examined. Nevertheless, this relation is still not completely clear even from the thermodynamic point. This missing relation in the theory will be established in the present paper. Simultaneously, the meaning of the quantities used in the one-dimensional nucleation theory will be clarified from the point of more general two-dimensional nonisothermal theory.

The sizes of nuclei involved in fluctuation formation, i.e. overcoming the activation barrier of nucleation, are not too large: these nuclei contain only several tens of molecules. Only such size of nuclei allow rather high nucleation rates under conditions of barrier nucleation.

The heat of vaporisation, given to or taken off the new phase nucleus with absorption or emission of a vapour molecule is, as a rule, large. If the sizes of nuclei involved in fluctuation formation are not large, then the mean-squares fluctuation of nuclear energy is also not large. In this case, the ratio of the vaporisation heat to the mean-squares energy fluctuation appears comparable with unity. This fact shows the existence and importance of the microphysical effects (or effects associated with rather large latent heat and small size of the nucleus) which complicate significantly the theory of nonisothermal nucleation. The microphysical effects reveal themselves not only through the ability of nuclei to emit vapour molecules, but also through the deviation of the kinetic equation of nonisothermal nucleation from the Fokker–Planck form.

Thermodynamic, statistical and kinetic treatment of the microphysical effects in nonisothermal nucleation will be the main goal of the present paper. This complex treatment has not been performed earlier.

The small size of nuclei, that are of interest for nucleation, complicates the theory because of existence of the microphysical effects but allows us, at the same time, to bring a simplification into the theory. As was shown in Ref. [2], the time of the internal thermal relaxation for such nuclei is much smaller than the time between two events of absorption or emission of a vapour molecule by the nucleus, and much smaller than the time between the events of collisions of vapour and carrier gas molecules with the nucleus. Therefore, the nucleus is in a state of internal thermodynamic equilibrium before the events of interaction with the vapour–gas environment, and can be considered as a closed system with the number of molecules and the energy fixed. This important fact which simplifies the theory will be taken into account and used below.

1. The work of nuclear formation

Let T be the temperature of the vapour–gas environment, ν and T_e the number of molecules and the temperature of the new phase nucleus, respectively. These two quantities, ν and T_e , characterise the state of internal thermodynamic equilibrium of a nucleus with a small compressibility of the condensing substance.

As well as T_e , we will use another quantity,

$$E = cv(T_e - T)/T, \quad (1.1)$$

where cv stands for the heat capacity of the nucleus in units of the Boltzmann constant k (c is the heat capacity per molecule of the nucleus). Evidently, the quantity E plays the role of the nuclear energy expressed in units kT and counted off the value corresponding to $T_e = T$.

For nuclei involved in fluctuation formation, the characteristic values of the energy E are limited [3] within the mean-squares energy fluctuation, $(cv)^{1/2}$ (calculated from the equilibrium distribution of nuclei in energy). Therefore we have

$$|E| \leq (cv)^{1/2}. \quad (1.2)$$

As we said in the Introduction, the number ν of molecules in a nucleus involved in fluctuation formation consists of several tens. Thus the number satisfies inequality $\nu \gg 1$. This yields

$$(cv)^{1/2} \gg 1. \quad (1.3)$$

Then according to Eqs. (1.1)–(1.3) we have

$$T_e/T \approx 1. \quad (1.4)$$

Let q be the vaporisation heat (latent heat) per molecule of the condensing substance. We assume that $\beta \equiv q/kT$ is the dimensionless molecular vaporisation heat in units kT . The large value of the vaporisation heat means

$$\beta \gg 1. \quad (1.5)$$

Experiment shows that the quantity q depends on the temperature weaker than the reciprocal power of temperature (with the temperature counted off absolute zero). In view of Eq. (1.4), this fact will allow us to linearise the exponential in the Clausius–Clapeyron equation in small temperature deviations under the condition of constant q (not the condition of constant dimensionless quantity β).

In spite of Eq. (1.3), with rather small number of molecules in a nucleus involved in fluctuation formation, we have due to Eq. (1.5):

$$\beta/(cv)^{1/2} \sim 1. \quad (1.6)$$

This relationship guarantees, as we will see below, an existence and importance of microphysical effects in nonisothermal nucleation.

The work of nuclear formation serves as a starting quantity for thermodynamic consideration. We will express this work in units kT . Two-dimensional work $F(\nu, E)$ of formation of the nucleus which is kept in the state of internal thermodynamic equilibrium with the number ν of molecules and with energy E can be written on a strict thermodynamic basis as

$$F(\nu, E) = F(\nu) + E^2/2cv, \quad (1.7)$$

where $F(v)$ is the one-dimensional work of formation of the nucleus which is kept in the state of internal thermodynamic equilibrium with the number v of molecules and with the same temperature T as the temperature of environment, $E^2/2cv$ stands for the work of heating (or cooling) of the nucleus when its temperature T_e deviates from the environment temperature T .

According to thermodynamics of isothermal nucleation we have

$$F(v) = -b(v-1) + av^{2/3}. \quad (1.8)$$

Here b is the vapour chemical potential expressed in units kT and counted from the value corresponding to the equilibrium of the vapour and the condensing substance with the flat interface between them. The quantity a stands for the dimensionless surface tension of the nucleus,

$$a = (4\pi\sigma/kT)(3v/4\pi)^{2/3}, \quad (1.9)$$

where σ is the surface tension of the nucleus, v the molecular volume for the condensing substance (the quantity a is defined in such a way to obtain that $av^{2/3}$ is the surface energy of the nucleus in units kT). The fact that v is counted from 1 in Eq. (1.8) indicates that the homogeneous formation of the nucleus from v molecules of vapour proceeds by attachment of $v-1$ vapour molecules to one of its molecules serving as a centre of condensation [7]. For the sake of simplicity we dropped the microscopic corrections to the dependence of the surface tension of the nucleus on the curvature of its surface and on the compressibility of its substance. These corrections had been considered in Ref. [8].

The activation barrier of nonisothermal nucleation determined by two-dimensional work $F(v, E)$ has, according to Eqs. (1.7) and (1.8), the saddle form with the line of “waterfall” defined by equality $E=0$ ($T_e=T$) and the line of “watershed” defined by equality $v=(2a/3b)^3$. In this case variable E can be called stable and variable v can be called unstable.

2. The role of corrections arising from the surface tension dependence on temperature

Let us clarify the role of corrections to the work of nuclear formation, which arise from the dependence of the nuclear surface tension on temperature. This also allows us to refine the meaning of quantities a and β introduced in Section 1.

Let us consider an elementary event of absorption of a vapour molecule by a nucleus (we consider absorption, not the reverse process of emission of a molecule, just for the sake of definiteness). Let δF be the work performed on the nucleus in this elementary event.

We will find δF with taking into account the curving of the nuclear surface as a first step and the heating of the nucleus by the vaporisation heat as a second step. In this case, the vaporisation heat will be different from that for the flat surface of

the condensing substance. Let us denote this heat as β_v , with index v indicating the dependence of the vaporisation heat on the nuclear curvature. The nuclear energy E will increase by the amount β_v in the event of absorption of a vapour molecule. According to Eqs. (1.7) and (1.8), we have in the linear order in variations of the nuclear number of molecules and energy in the event of absorption

$$\delta F = -b + 2a(T)/3v^{1/3} + (E/cv)\beta_v, \quad (2.1)$$

where $a(T)$ is the dimensionless surface tension of the nucleus at $T_e = T$.

Let us now find δF with taking into account the heating of the nucleus by the vaporisation heat as a first step and the curving of the nuclear surface as a second step. The vaporisation heat coincides now with that for the flat surface of the condensing substance. Let us denote this heat as β_∞ , with index ∞ indicating that β_∞ is the limiting value for β_v as $v \rightarrow \infty$. Now the nuclear energy increases by amount β_∞ during the event of absorption of a vapour molecule. However, the surface tension deviates already from the surface tension under the condition of equality of the nuclear temperature T_e and the environment temperature T . Therefore, according to Eqs. (1.7) and (1.8), we have in the linear order in variations of the nuclear number of molecules and energy in the event of absorption

$$\delta F = -b + 2a(T_e)/3v^{1/3} + (E/cv)\beta_\infty, \quad (2.2)$$

where $a(T_e)$ is the dimensionless surface tension of the nucleus at temperature T_e .

According to principles of thermodynamics, the work performed on a nucleus in a process does not depend on the specific way of realisation of the process. Therefore, two expressions for δF , Eqs. (2.1) and (2.2), should coincide. Setting these two expressions to be equal and assuming rather smooth dependence of the surface tension on temperature,

$$a(T_e) = a(T) + [\partial a(T)/\partial T]TE/cv \quad (2.3)$$

(we have used the definition (1.1)), we come to

$$\beta_v = \beta_\infty + (2/3v^{1/3})\partial a(T)/\partial \ln T. \quad (2.4)$$

Energy E and heat capacity c dropped out of Eq. (2.4).

According to Eq. (1.9), the dimensionless nuclear surface tension a depends on nuclear temperature by means of σ and v . The factor $1/kT$ in Eq. (1.9) appeared as a result of the procedure which we used to make the quantities dimensionless. Therefore this factor does not depend on the nuclear temperature.

Using Eqs. (2.4) and (1.9) yields

$$\beta_v = \beta_\infty + \frac{2a}{3v^{1/3}} \left(\frac{\partial \ln \sigma}{\partial \ln T} + \frac{2}{3} \frac{\partial \ln v}{\partial \ln T} \right), \quad (2.5)$$

where all the quantities on the right-hand side are related to the temperature of environment. The relationship (2.5) represents Sresnevskii's formula. Most detailed derivation

including direct thermodynamic finding of β_v and generalisation of this formula to take into account the microscopic corrections and possible effect of the central electric field in the case of heterogeneous nucleation was performed in Ref. [9].

The results of numerical calculations presented in Ref. [9] show that for water and many other liquids under typical conditions for their nucleation from vapour, at $T = 300\text{ K}$ and $v^{1/3} \approx 3 - 5$, the relative deviation of the heat β_v from the value β_∞ is, according to Eq. (2.5), within 10%.

Using Eqs. (1.2) and (2.3) and taking into account Eq. (1.9), we find for the relative deviation $\Delta a/a$ of the surface tension $a(T_e)$ from the surface tension $a(T)$

$$\frac{|\Delta a|}{a} \leq \frac{1}{(cv)^{1/2}} \left| \frac{\partial \ln \sigma}{\partial \ln T} + \frac{2}{3} \frac{\partial \ln v}{\partial \ln T} \right|. \quad (2.6)$$

According to Ref. [9], the second factor on the right-hand side of Eq. (2.6) (taken in the absolute value) is less than unity for water at $T = 300\text{ K}$ and only slightly exceeds unity for many other liquids. Then, according to Eqs. (2.6) and (1.3), the quantity $|\Delta a|/a$ is much less than unity.

So we see that the dependence of the surface tension on the nuclear temperature and the associated dependence of the vaporisation heat on the surface curvature of the nucleus give only minor corrections to the work of nuclear formation in nonisothermal nucleation. We see also that these corrections duplicate each other. So we can omit the dependence of the surface tension on temperature, but take into account the dependence of the vaporisation heat on surface curvature.

We will neglect these corrections below and refer the nuclear surface tension a to the temperature of environment. The vaporisation heat β will be referred to its limiting value β_∞ at the flat interface of the condensing substance.

3. Two-dimensional equilibrium distribution of nuclei

Let us find two-dimensional equilibrium distribution of nuclei in variables v and E . We will denote this distribution as $n(v, E)$. The equilibrium distribution of nuclei is important in nucleation theory because it is used in the boundary conditions for the kinetic equation governing the development of nucleation. We will need the equilibrium distribution for thermodynamic derivation of the emitting rate from a nucleus to the vapour.

The equilibrium distribution $n(v, E)$ has the form of a Gibbs distribution,

$$n(v, E) = A \exp[-F(v, E)], \quad (3.1)$$

where A is the pre-exponential factor. With very strong dependence of the exponential on v and E in Eq. (3.1), this factor can be considered practically as a constant.

As we see from Eqs. (1.7) and (3.1) with account of Eq. (1.1), at every v , the average energy and average temperature of nuclei, calculated from their equilibrium distributions, equal zero and the environment temperature T , respectively. Therefore,

we can give the following interpretation for the quantity $F(v)$ in Eq. (1.7). This quantity represents the work of formation of a nucleus which is kept in the state of internal thermodynamic equilibrium with the number v of molecules and with the temperature T_e which equals the average temperature of nuclei calculated from their equilibrium distribution. This is the meaning of the one-dimensional work $F(v)$ in the two-dimensional nonisothermal theory. As also follows from Eqs. (1.7) and (3.1), the mean-squares fluctuation of the energy of nuclei in their equilibrium distribution equals, as mentioned in Section 1, $(cv)^{1/2}$.

One-dimensional equilibrium distribution $n(v)$ of nuclei in variable v is related to two-dimensional equilibrium distribution $n(v, E)$ by the apparent equality,

$$n(v) = \int_{-\infty}^{\infty} n(v, E) dE. \quad (3.2)$$

According to Eqs. (1.7), (3.1) and (3.2) we have

$$n(v) = A(2\pi cv)^{1/2} \exp[-F(v)]. \quad (3.3)$$

Using Eqs. (1.7) and (3.3), we can write Eq. (3.1) as

$$n(v, E) = (2\pi cv)^{-1/2} n(v) \exp(-E^2/2cv). \quad (3.4)$$

The fact that the main contribution to the integral in Eq. (3.2) is given by the region $|E| \leq (cv)^{1/2}$ confirms the estimate (1.2).

The exponential in Eq. (3.3) depends on v much stronger than the pre-exponential factor does. So Eq. (3.3) can be reduced, with the logarithmic accuracy which is sufficient for experiment, to the form

$$n(v) = \text{const} \times \exp[-F(v)], \quad (3.5)$$

which again has a form of Gibbs distribution. Then the formula (3.4) can be written as

$$n(v, E) = \text{const} \times n(v) \exp(-E^2/2cv). \quad (3.6)$$

(the constants in Eqs. (3.5) and (3.6) are different).

The formula (3.5) is well known in the one-dimensional theory of nucleation. This formula is correct at such very small v and even at $v = 1, 2, 3 \dots$ where the thermodynamic expression (1.8) for quantity $F(v)$ is no longer valid, but, however, the physical meaning of this quantity as a work of the isothermal formation of a nucleus from v vapour molecules is preserved.

Let us show how the pre-exponential factor in Eq. (3.5) can be found. Let n_v be the number of vapour molecules per unit volume of the vapour–gas environment. We will refer the distribution of nuclei to this unit volume. Let us take into account the boundary condition $n(v)|_{v=1} = n_v$ (at $v = 1$ the nuclei are just single vapour molecules). We should recognise also equality $F(v)|_{v=1} = 0$ (vapour molecules are initially present and do not require a work of formation performed on them). We see now that the

pre-exponential factor in Eq. (3.5) equals n_v . Then formula (3.5) can be reduced to the form

$$n(v) = n_v \exp[-F(v)]. \quad (3.7)$$

The formula (3.7) determines the distribution $n(v)$ and together with Eq. (3.4) determines the distribution $n(v, E)$, including the pre-exponential factors in these distributions. These factors play an important role in the boundary conditions for the kinetic equation of nucleation, but, however, they will not have a significance for our subsequent analysis.

4. The thermodynamic derivation of the nuclear emitting rate

The emitting rate of nuclei is important in nucleation theory because it appears as a coefficient function in the kinetic equation of nucleation.

From the conditions of detailed balance which fulfil for the equilibrium distribution of nuclei we have

$$W^+(v-1)n(v-1, E-\beta) = W^-(v, E)n(v, E). \quad (4.1)$$

Here $W^+(v)$ and $W^-(v, E)$ are the numbers of vapour molecules absorbed and correspondingly emitted per unit time by the nucleus with the number of v of molecules and the energy E . We neglect the dependence of $W^+(v)$ on E because it is small. Thus, the quantity $W^+(v)$ is the same for nonisothermal and isothermal nucleation. This quantity can be easily found with the help of kinetic theory of gases, and therefore we can assume it known. Note that the argument v in $W^+(v)$ stands for the number of nuclear molecules before the event of absorption of a vapour molecule, and the arguments v and E in $W^-(v, E)$ stand for the number of nuclear molecules and the nuclear energy, respectively, before the event of emission of a vapour molecule.

After absorption of a vapour molecule by a nucleus, the number of molecules and the energy of the nucleus increase correspondingly by unity and by β . After emission of a vapour molecule by the nucleus, the number of molecules in the nucleus and the nuclear energy decrease correspondingly by unity and by β (assigning $\beta \gg 1$ we neglect the thermal dispersion in energies of adsorbed and emitted molecules [2]). Therefore, condition (4.1) expresses the equality of rates of direct and reverse transitions $v-1, E-\beta \Leftrightarrow v, E$ which is reasonable for the two-dimensional equilibrium distribution.

The quantity $W^-(v, E)$ is related to a single nucleus and (as well as the quantity $W^+(v)$) does not depend on actual distribution of nuclei, which can be non-equilibrium. So, we will use formula (4.1) for a thermodynamic derivation of the emitting rate $W^-(v, E)$ through known equilibrium distribution of nuclei (and known absorption rate $W^+(v)$).

Let us introduce the quantity $W^-(v)$,

$$W^-(v) = W^+(v-1) \exp(-b + 2a/3v^{1/3}). \quad (4.2)$$

As follows from Eqs. (1.8), (3.5) and (4.2) with account of equality $F(v) - F(v-1) = \partial F(v)/\partial v$ (which fulfils with a great accuracy at $v \gg 1$),

$$W^+(v-1)n(v-1) = W^-(v)n(v). \quad (4.3)$$

This is the equation of the detailed balance in the theory of isothermal nucleation which deals with one-dimensional distribution of nuclei. This equation shows that quantity $W^-(v)$ has meaning of the number of vapour molecules emitted under isothermal conditions per unit time by the nucleus containing the number v of molecules.

Using Eqs. (3.6), (4.1) and (4.3) and recognising that the variation of the quantity cv with changing the number v by unity is negligible at $v \gg 1$, we obtain

$$W^-(v, E) = W^-(v) \exp(\beta E/cv) \exp(-\beta^2/2cv). \quad (4.4)$$

Substituting Eqs. (4.2) in (4.4) yields

$$W^-(v, E) = W^+(v-1) \exp(-b + 2a/3v^{1/3}) \exp(\beta E/cv) \exp(-\beta^2/2cv). \quad (4.5)$$

Formula (4.5) gives the expression for the nuclear emitting rate $W^-(v, E)$ in non-isothermal nucleation. This expression agrees with the formula used in Ref. [1].

The quantity $\beta^2/2cv$ in Eq. (4.5) takes account of the correction dropped in Eqs. (2.1) and (2.2). This correction is square in the nuclear energy change in the course of absorption of a vapour molecule by the nucleus. This quantity is associated with the microphysical effects (which we are interested in) in nonisothermal nucleation. Being of order of unity according to Eq. (1.6), the quantity $\beta^2/2cv$ is essential in Eq. (4.5). It is of order of the classical nucleation theory terms, $-b$ and $2a/3v^{1/3}$, and exceeds significantly the errors of the theory (mentioned in Section 2) due to neglecting the nuclear surface tension dependence on nuclear temperature and the vaporisation heat dependence on nuclear curvature. So we can say that it lies within the limits of validity of the theory.

At small compressibility of the substance in the nucleus, the emitting rates $W^-(v)$ and $W^-(v, E)$ do not depend on the vapour chemical potential b and are determined by the chemical potential of the nucleus. This can be easily seen from Eqs. (4.2) and (4.5) with taking into account the Gibbs–Kelvin relation and recognising that the absorption rate $W^+(v-1)$ depends on b proportionally to $\exp(b)$.

The emitting rate $W^-(v, E)$ does not depend on the temperature of the vapour–gas environment and is determined by the temperature of nucleus. This can be easily seen from Eq. (4.5) by taking into account the definition (1.1), the definition of the chemical potential b and recognising that the saturated vapour density depends on temperature T according to the Clausius–Clapeyron equation, i.e. the saturated vapour density is proportional to $\exp(-q/kT)$ if the vaporisation heat q is constant.

The equilibrium distributions (3.5), (3.6) and the detailed balance equations (4.3), (4.1) are physically realised only in the sub-threshold region of the variable v which occupies at least a half-width of the potential hump of the activation energy of nucleation in the v -axis before the “watershed” line $v = (2a/3b)^3$. Since emitting rates

$W^-(v)$ and $W^-(v, E)$ do not depend on the vapour chemical potential b , then the limitation in their determination by the sub-threshold region of variable v do not affect the quantities given by formulae (4.2) and (4.5). Indeed, in order to determine $W^-(v)$ and $W^-(v, E)$ at every large v , we can consider an imaginary vapour with such a small value of the chemical potential b that v appears in the sub-threshold region.

The importance of the formulated conclusion for the theory of nucleation is seen from the fact that usually the possibility of extension of the expressions for the coefficient functions in kinetic equation over the sub-threshold region of nuclear sizes is motivated [10] only by absence of mathematical peculiarities in these functions.

5. The critical nucleus

Let us consider the thermodynamic approach to determination of the nuclear emitting rate with the help of conception of the critical nucleus. This allows us to clarify the meaning of isothermal emitting rate from the point of two-dimensional nonisothermal theory. The conception about the critical nucleus in nonisothermal nucleation had not been introduced previously.

As follows from Eq. (4.2) at $v = v_c$, where

$$v_c = (2a/3b)^3, \quad (5.1)$$

we have

$$W^-(v_c) = W^+(v_c - 1). \quad (5.2)$$

It means that the value $v = v_c$ is related to the critical nucleus in isothermal nucleation. According to Eq. (5.2), such nucleus emits per unit time the same number of molecules as it absorbs, i.e. this nucleus stays in the state of material equilibrium with the vapour.

This equilibrium is not stable. Indeed, we have from Eq. (4.2): $W^-(v) > W^+(v - 1)$ at $v < v_c$ (the nucleus shrinks) and $W^-(v) < W^+(v - 1)$ at $v > v_c$ (the nucleus grows).

As follows from Eq. (4.5), at $v = v_c$ and $E = E_c$ where v_c is still defined by Eq. (5.1) and E_c is determined as

$$E_c = \beta/2, \quad (5.3)$$

we have

$$W^-(v_c, E_c) = W^+(v_c - 1). \quad (5.4)$$

Thus, the nucleus corresponding to values $v = v_c$ and $E = E_c$ is critical in nonisothermal nucleation. According to Eq. (5.4), such nucleus, even with taking into account the vapourisation heat, emits and absorbs per unit time the same number of vapour molecules. Alternating sequence of the events of emission and absorption initiates direct and reverse transitions $v_c, E_c \Leftrightarrow v_c - 1, E_c - \beta$, i.e. the transitions $v_c, \beta/2 \Leftrightarrow v_c - 1, -\beta/2$, where we have taken into account of Eq. (5.3). In view of Eqs. (5.3) and (5.1) the

temperature of the critical nucleus is higher than the temperature T of the vapour–gas environment by quantity δT_e given by equality

$$\delta T_e = \beta T / 2cv_c . \tag{5.5}$$

The material equilibrium of the critical nucleus with the vapour is, evidently, still unstable. By contrast, the thermal equilibrium of the critical nuclei with the vapour–gas environment is stable. Indeed, we see from Eq. (4.5) that $W^-(v, E) < W^+(v - 1)$ (the nucleus grows and increases its energy) at $E < E_c$ and $W^-(v, E) > W^+(v - 1)$ (the nucleus decreases and lowers its energy) at $E > E_c$. Let us remind that it is just the equality $v = v_c$ which determines the “watershed” line on the saddle surface of the nucleation activation barrier.

According to Eqs. (4.2), (4.5) and (5.3), we can write

$$W^-(v) = W^-(v, E_c) . \tag{5.6}$$

Formula (5.6) reveals the meaning of the nuclear isothermal emitting rate $W^-(v)$ from the point of the nonisothermal theory. From this point, the quantity $W^-(v)$ is related to the nucleus which contains the number v of molecules and has the temperature exceeding the temperature T of the vapour–gas environment by the quantity δT . The quantity δT is determined, according to Eqs. (5.3) and (1.1), as

$$\delta T = \beta T / 2cv . \tag{5.7}$$

In view of conditions (1.3) and (1.6), the formulae (5.5) and (5.7) provide a fulfilment of inequalities $\delta T_e / T \ll 1$, $\delta T / T \ll 1$ which are consistent with Eq. (1.4).

Because quantity $W^-(v)$ is independent of the vapour chemical potential b (as was shown in Section 4), we can rewrite Eq. (5.2), with taking into account Eq. (5.1), as

$$W^-(v) = W^+(v - 1)|_{b=b_c} \tag{5.8}$$

where

$$b_c = 2a / 2v^{1/3} . \tag{5.9}$$

The nuclear absorption rate on the right-hand side of Eq. (5.8) is related to an imaginary vapour–gas environment with the vapour chemical potential b_c determined by the Gibbs–Kelvin relation, Eq. (5.9), and with the temperature that equals the temperature T of the actual vapour–gas environment.

Because the quantity $W^-(v, E)$ is independent of the vapour chemical potential b and of the temperature T of the vapour–gas environment (as was shown in Section 4), we can rewrite Eq. (5.4), with taking into account Eqs. (5.1), (5.3), as

$$W^-(v, E) = W^+(v - 1)|_{b=b_c, T = T_c - \delta T} . \tag{5.10}$$

The nuclear absorption rate on the right-hand side of Eq. (5.10) is related to an imaginary vapour–gas environment with the vapour chemical potential b_c and the temperature which is less than temperature T_e by the quantity δT determined by Eq. (5.7).

The formulae (5.8) and (5.10) give a useful physical interpretation for the nuclear emitting rates $W^-(v)$ and $W^-(v, E)$.

6. The statistical derivation of the nuclear emitting rate

Let us consider the statistical ground for formula (4.5) describing the nuclear emitting rate. Because formula (3.6) follows from Eq. (4.5) in view of detailed balance equations (4.1), so we can also give a statistical foundation for thermodynamic formula (3.6) which describes the equilibrium two-dimensional distribution of nuclei.

As we said previously, the nucleus is in the state of internal thermodynamic equilibrium before the events of interaction with the vapour–gas environment. Thus the nucleus can be considered as a closed system with the fixed number v of molecules and the fixed energy E . Being in this state, the nucleus emits a molecule into the vapour.

The rate $W^-(v, E)$ of emission of a vapour molecule by the nucleus is, evidently, proportional to the part of nuclear molecules having the kinetic energy of translation motion higher than the vaporisation heat. So we can write

$$W^-(v, E) \propto \int_{\beta}^{\infty} f(\varepsilon) d\varepsilon. \quad (6.1)$$

Here, we use symbol \propto to mark the proportionality of quantities, ε is the kinetic energy of translation motion of a nuclear molecule (as well as the nuclear energy E and the vaporisation heat β , ε is expressed in units kT of the thermal energy of the vapour–gas environment), $f(\varepsilon)$ is the distribution function for the nuclear molecules in their kinetic energy ε . The dependence of $f(\varepsilon)$ on variables v and E of the state of internal nuclear equilibrium is not indicated. In view of meaning of function $f(\varepsilon)$, we can write the normalisation condition:

$$\int_0^{\infty} f(\varepsilon) d\varepsilon = 1. \quad (6.2)$$

The state of nuclear internal thermodynamic equilibrium preceding the event of emission of a vapour molecule is described by the microcanonical distribution function. In order to find function $f(\varepsilon)$, we can follow Ref. [11] and apply the method used to prove the Gibbs theorem for the canonical distribution function [12].

Considering the nucleus before the event of emission as a closed system in the microcanonical ensemble, we will assume that an individual nuclear molecule represents a small subsystem. Correspondingly, the large subsystem of the whole closed system is the population of other $v - 1$ nuclear molecules.

According to the Gibbs theorem for the canonical distribution function, for the probability function $\omega(\varepsilon)$ of finding the nuclear molecule in one of its microstates, we have

the following relation:

$$\omega(\varepsilon) = \exp[\bar{S}(E - \varepsilon) - S(E)]. \quad (6.3)$$

Here $\bar{S}(E - \varepsilon)$ and $S(E)$ are the entropies of the large subsystem and the whole system expressed in units of the Boltzmann constant k and determined as functions of the corresponding energies $E - \varepsilon$ and E . For the sake of simplicity, the dependence of the entropies on the number of molecules (and on the volumes) of the large subsystem and the whole system is not indicated.

Let us find the dependence of entropy $\bar{S}(E - \varepsilon)$ on ε with the help of first three terms in expansion of $\bar{S}(E - \varepsilon)$ in the Taylor series in powers of ε . Using thermodynamic relation $\partial\bar{S}/\partial E = T/T_e$ and relation $\partial^2\bar{S}/\partial E^2 = -T^2/cvT_e^2$ (which follows from $\partial\bar{S}/\partial E = T/T_e$ in view of Eq. (1.1)), we have

$$\bar{S}(E - \varepsilon) = \bar{S}(E) - \varepsilon T/T_e - \varepsilon^2 T^2/2cvT_e^2. \quad (6.4)$$

Recognising that the number of molecular microstates contained within the element $d\varepsilon$ of the kinetic energy ε of a nuclear molecule is proportional to $\varepsilon^{1/2} d\varepsilon$ and using Eqs. (6.3), (6.4) and (6.2), we find

$$f(\varepsilon) = f_0(\varepsilon) \exp(-\varepsilon^2 T^2/2cvT_e^2), \quad (6.5)$$

where

$$f_0(\varepsilon) = (2/\pi^{1/2})(T/T_e)^{3/2} \varepsilon^{1/2} \exp(-\varepsilon T/T_e) \quad (6.6)$$

(here we have recognised that the main contribution to the normalisation relation (6.2) is given, according to Eqs. (1.3) and (1.4), by factor $f_0(\varepsilon)$).

Apparently, function $f_0(\varepsilon)$ represents the Maxwell distribution function. The deviation of $f(\varepsilon)$ from $f_0(\varepsilon)$ caused by small size of the nuclei is the manifestation of the microphysical effects.

Let us substitute Eqs. (6.5) and (6.6) into Eq. (6.1). According to Eqs. (1.3)–(1.6) we can replace ε and T_e in the exponential in Eq. (6.5) by β and T , and also replace the pre-exponential factor $\varepsilon^{1/2}$ in Eq. (6.6) by $\beta^{1/2}$. Carrying out integration over ε in Eq. (6.1), we obtain

$$W^-(v, E) \propto \exp(-\beta T/T_e) \exp(-\beta^2/2cv), \quad (6.7)$$

where we have taken into account, in accordance with Eqs. (1.4) and (1.5), only the factors giving the main contribution to the dependence of $W^-(v, E)$ on β and T_e .

Recognising $\beta T/T_e = q/kT_e$, let us linearise the exponent in the first exponential in Eq. (6.7) in deviation of temperature T_e from temperature T under condition of constant vaporisation heat q . Using Eq. (1.1), we can rewrite Eq. (6.7) in the form

$$W^-(v, E) \propto \exp(\beta E/cv) \exp(-\beta^2/2cv). \quad (6.8)$$

Taking into account the dependence of $W^-(v, E)$ on the nuclear chemical potential which is determined by factor $W^-(v)$ in Eq. (4.4) (this factor is not explicitly included

in proportionality relations (6.1) and (6.8)), we see that formula (6.8) can be reduced to formula (4.5). This makes a statistical foundation for formula (4.5).

7. The kinetic treatment of the event of emission of a vapour molecule by the nucleus

Let us investigate the event of emission of a vapour molecule by the nucleus as a subject by itself. Certainly, it will require invoking some kinetic conceptions. As a result we will give some additional confirmation to relations (6.7) and (6.8) for the nuclear emitting rate $W^-(\nu, E)$.

The nucleus in the course of emission of a vapour molecule does not already represent the closed system. Correspondingly, the distribution of the nuclear molecules in energy ε is different in the course of emission from that given by formulae (6.5) and (6.6) for the equilibrium distribution before the event of vapour molecule emission.

Let $f(\varepsilon, t)$ be the distribution of nuclear molecules in energy ε at the moment t . The argument t underlines the difference between distribution $f(\varepsilon, t)$ and the equilibrium distribution $f(\varepsilon)$. We will assume (and justify this assumption later) that the distribution $f(\varepsilon, t)$ varies in time according to the Fokker–Planck equation,

$$\partial f(\varepsilon, t) / \partial t = -\partial J(\varepsilon, t) / \partial \varepsilon. \quad (7.1)$$

Here $J(\varepsilon, t)$ is the flux of nuclear molecules along the axis of energy ε . We have for this flux

$$J(\varepsilon, t) = -Df(\varepsilon) \partial [f(\varepsilon, t) / f(\varepsilon)] / \partial \varepsilon, \quad (7.2)$$

where D is the diffusion coefficient for nuclear molecules in the ε -axis. We have taken into account in Eq. (7.2) that the flux $J(\varepsilon, t)$ equals zero for the equilibrium distribution of nuclear molecules. The value of coefficient D is not essential for the following consideration.

Two boundary condition to Eq. (7.1) may be imposed as

$$f(\varepsilon, t) / f(\varepsilon) |_{\varepsilon=\beta} = 0, \quad (7.3)$$

$$f(\varepsilon, t) / f(\varepsilon) |_{\varepsilon=0} = 1. \quad (7.4)$$

Condition (7.3) expresses the reasonable requirement that the number of molecules with energy $\varepsilon = \beta$, which are able to leave the nucleus, is practically equal to zero. Condition (7.4) expresses another reasonable requirement that the distribution of nuclear molecules with energy $\varepsilon = 0$, which is certainly insufficient for leaving the nucleus, practically coincides with the equilibrium distribution. We will see below that the value $\varepsilon = 0$ of energy ε in condition (7.4) can be increased to the value $\varepsilon \leq \beta/p$ where $p = 1.5-2$.

Strictly speaking, the Fokker–Planck equation (7.1) is applicable if the following inequality takes place:

$$\delta\varepsilon/\Delta\varepsilon \ll 1, \tag{7.5}$$

where $\delta\varepsilon$ is the characteristic change in the energy ε of nuclear molecule in the collisions with other nuclear molecules, $\Delta\varepsilon$ the mean-squares fluctuation of energy of nuclear molecules under the equilibrium distribution. Evidently, we can estimate $\delta\varepsilon$ as $\delta\varepsilon \leq T_e/T$. Recognising due to Eqs. (1.3) and (1.4) that we can replace in the expression for $\Delta\varepsilon$ the equilibrium distribution $f(\varepsilon)$ by the Maxwell distribution $f_0(\varepsilon)$ given by formula (6.6) (as we did in normalisation relation (6.2)), we have $\Delta\varepsilon = (3/2)^{1/2} T_e/T$. We see, that inequality (7.5) and, together with it, the Fokker–Planck equation (7.1) are only marginally valid. Nevertheless, it justifies using of the Fokker–Planck equation for an approximate treatment of the event of emission of a vapour molecule by the nucleus.

Let us suppose that the emission takes place at the steady distribution of nuclear molecules in energy ε . The assumption requires a fast establishment of the steady distribution which seems reasonable for such condensed system as nucleus.

For a steady state (we indicate this state by index s), the distribution $f_s(\varepsilon)$ does not depend on t , and the flux J_s does not depend on t and, due to Eq. (7.1), on ε . We have in this case from Eqs. (7.2)–(7.4):

$$\frac{f_s(\varepsilon)}{f(\varepsilon)} = J_s \int_{\varepsilon}^{\beta} \frac{d\varepsilon'}{Df(\varepsilon')}, \tag{7.6}$$

$$\frac{1}{J_s} = \int_0^{\beta} \frac{d\varepsilon}{Df(\varepsilon)}. \tag{7.7}$$

For the sake of simplicity, we will consider the diffusion coefficient D to be constant. With taking account of Eqs. (6.5) and (6.6), equalities (7.6) and (7.7) can be written as

$$\frac{f_s(\varepsilon)}{f(\varepsilon)} = \frac{\pi^{1/2} J_s}{2D} \left(\frac{T_e}{T}\right)^{3/2} \int_{\varepsilon}^{\beta} \varphi(\varepsilon') d\varepsilon', \tag{7.8}$$

$$\frac{1}{J_s} = \frac{\pi^{1/2}}{2D} \left(\frac{T_e}{T}\right)^{3/2} \int_0^{\beta} \varphi(\varepsilon) d\varepsilon, \tag{7.9}$$

where

$$\varphi(\varepsilon) = \varepsilon^{-1/2} \exp(\varepsilon T/T_e) \exp(\varepsilon^2 T^2/2cvT_e^2). \tag{7.10}$$

Let us now take into account the limitations (1.3)–(1.6). Now, we can see the following. With decreasing ε from the value $\varepsilon = \beta$ to value $\varepsilon = T_e/2T$ which, according to

Eq. (7.10), determines with a high accuracy the location of the minimum of function $\varphi(\varepsilon)$, the second factor in Eq. (7.10) decreases already significantly as variable ε achieves value β/p where $p \approx 1.5-2$. The last two factors in Eq. (7.10) do not essentially change before ε achieves value β/p . With further decreasing ε from value $\varepsilon = T_e/2T$ to value $\varepsilon = 0$, the right-hand side of Eq. (7.10) grows infinitely due to factor $\varepsilon^{-1/2}$. However, since the singularity introduced by this factor at $\varepsilon = 0$ is integrable, the integral of function $\varphi(\varepsilon)$ over the region $0 \leq \varepsilon \leq T_e/2T$ is small in comparison with the integral of function $\varphi(\varepsilon)$ over the region $T_e/2T \leq \varepsilon \leq \beta$ (the ratio of these integrals does not exceed small quantity $\beta^{1/2} \exp(-\beta T/T_e) \exp(-\beta^2/2cv)$). As a result we have with a high accuracy

$$\int_{\varepsilon}^{\beta} \varphi(\varepsilon') d\varepsilon' = \beta^{-1/2} \exp(\beta T/T_e) \exp(\beta^2/2cv) \quad (0 \leq \varepsilon \leq \beta/p, \quad p \approx 1.5-2). \quad (7.11)$$

Substituting Eq. (7.9) in Eq. (7.11) gives

$$J_s = \frac{2D}{\pi^{1/2}} \left(\frac{T}{T_e} \right)^{3/2} \beta^{1/2} \exp(-\beta T/T_e) \exp(-\beta^2/2cv). \quad (7.12)$$

Relations (7.8) and (7.11) show that the steady distribution $f_s(\varepsilon)$ of the nuclear molecules coincides with the equilibrium distribution $f(\varepsilon)$ not only at the point $\varepsilon = 0$ (as it was demanded by the boundary condition (7.4)), but they practically coincide even at $\varepsilon \leq \beta/p$ where $p \approx 1.5-2$.

Evidently, flux J_s is proportional to the nuclear emitting rate $W^-(v, E)$. In this case we have previous relations (6.7) and (6.8) from Eq. (7.12) under conditions (1.3)–(1.6). The fact that conditions (1.3)–(1.6) are the same for the whole consideration in the paper reveals self-consistence of the consideration.

It is not to be supposed that distribution of nuclear molecules in energy stays steady after the event of emission of a vapour molecule. Indeed, the time interval required in the kinetic theory for averaging of kinetic characteristics is limited from above, as was mentioned in Ref. [2], by the time $1/W^-(v, E)$ which allows no more than one event of emission of a vapour molecule by the nucleus. After the event, the nucleus passes into the state of internal equilibrium for comparatively long period (in a full agreement with the assumptions made in the paper).

8. Deviation of the kinetic equation of nonisothermal nucleation from the Fokker–Planck equation

Let us consider finally the manifestation of the microphysical effects in deviation of the kinetic equation of nonisothermal nucleation from the Fokker–Planck equation.

The kinetic equation of nonisothermal nucleation governing the development of nonisothermal nucleation in time was proposed in Ref. [1] and explicitly derived in

Ref. [3]. As was shown in Ref. [3], the deviation of this equation from the Fokker–Planck equation is associated with the relative weight of two following quantities. The first quantity represents the ratio of the change in the nuclear energy in the elementary event of absorption or emission of a vapour molecule to the half-width $(cv)^{1/2}$ of the potential well of the activation energy of nucleation, i.e. it equals $\beta/(cv)^{1/2}$. The larger this quantity, the larger the rate of development of the stable variable E in time.

The second quantity represents the ratio of the change in the number of nuclear molecules in the elementary event of absorption or emission of a vapour molecule to the half-width Δv of the potential hump for the activation energy of nucleation, i.e. it equals $1/\Delta v$. The larger this quantity, the larger the rate of development of the unstable variable v in time.

If the ratio of the first quantity to the second quantity, i.e. $(\Delta v)\beta/(cv)^{1/2}$, is much larger than unity, then stable variable E varies in time much faster than unstable variable v does. Then we need to take into account all derivatives with respect to E in the kinetic equation of nonisothermal nucleation. This means that we need to go out of the scope of Fokker–Planck approximation with respect to variable E . At the same time, it is sufficient to keep only the first and second derivative with respect to v which is characteristic for Fokker–Planck approximation in this variable [3]. This is the situation which we meet in the case of nonisothermal nucleation because due to Eq. (1.6) and inequality $\Delta v \gg 1$ (which fulfils at moderately high vapour supersaturation ratios) we have

$$(\Delta v)\beta/(cv)^{1/2} \gg 1. \quad (8.1)$$

Though the kinetic equation of nonisothermal nucleation is considerably complicated after adding the higher-order derivatives with respect to E in the situation under discussion, we surely have the hierarchy of the characteristic time scales in this situation. The hierarchy reflects that the stable variable E varies much faster in comparison with the unstable variable v , and it allows us to use an iteration method, derived in Ref. [3], for solving the kinetic equation of nonisothermal nucleation. The fulfilment of inequality (8.1) is provided by the microphysical effects in nonisothermal nucleation.

Finally, we can make the following important conclusion. If we cannot limit ourselves with the Fokker–Planck approximation in the kinetic equation of nonisothermal nucleation, we surely have a hierarchy of the characteristic time scales for development of nonisothermal nucleation. This hierarchy makes possible solving of the kinetic equation of nonisothermal nucleation by the iteration procedure developed in Ref. [3]. Thus, we can say that the sources which cause the deviation of the kinetic equation of nonisothermal nucleation from the Fokker–Planck equation show the way how this kinetic equation can be solved.

The conclusion formulated concerns with not only two-dimensional nonisothermal nucleation, but with kinetics of multi-dimensional phase transitions as well.

As was shown in Ref. [3], the hierarchy of characteristic time scales of nonisothermal nucleation becomes stronger in presence of passive gas-carrier in the vapour–gas

environment. Strengthening the hierarchy, the presence of the gas-carrier, however, does not allow us to reduce the kinetic equation to the Fokker–Planck form.

If the vaporisation heat is not so large (in fact, we cannot exclude this possibility from the consideration), then the two-dimensional kinetic equation of nonisothermal nucleation has the Fokker–Planck form. However, then the hierarchy of time scales of development of nonisothermal nucleation no longer exists at small concentration of the carrier gas in the vapour–gas environment. The general method for solving of multi-dimensional equation of the Fokker–Planck form in kinetics of phase transitions with the help of special technic of separation of variables was proposed in Refs. [13,14].

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