Enthalpy effect on the kinetics of concurrent nucleation and chemical aging of aqueous organic aerosols: The stage of thermal relaxation

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Abstract

The size and composition distribution of an ensemble of aqueous organic droplets, evolving via nucleation and concomitant chemical aging, may be affected by the latent heat of condensation and enthalpy of heterogeneous chemical reactions, so the temperature of the droplet may deviate from the air temperature and thus become an independent variable of its state (additional to its size and composition variables). Using the formalism of the classical nucleation theory, we derive a partial differential equation for the temporal evolution of the distribution of an ensemble of such droplets with respect to all their variables of state via Taylor series expansions of the corresponding multidimensional discrete equation of balance, describing the material and heat exchange between droplets and air. The resulting kinetic equation goes beyond the framework of the Fokker-Planck approximation with respect to the temperature variable. A hierarchy of time scales of nonisothermal nucleation and concomitant chemical aging of aqueous organic aerosols is established and an analytical description of their thermal relaxation stage is developed, allowing one to estimate the characteristic time of the establishment of the equilibrium distribution of aerosol particles with respect to their temperatures. Theoretical results are illustrated with numerical calculations for the concurrent nucleation and chemical aging of model aqueous hydrophilic-hydrophobic organic aerosols in air.

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1 Introduction

Nonisothermal effects can markedly influence first-order phase transitions, particularly condensation. First, the heating of the nascent liquid droplets by the latent heat of condensation causes a reduction of the nucleation rate by increasing the ability of droplets to emit molecules and by decreasing the metastability of the vapor phase (due to the increase in the system temperature). Second, the fluctuations of the droplet temperature exist even in the absence of matter exchange between the nuclei and the medium; they also influence the emissivity of droplets. Third, droplets as particles of condensed matter are thermally quasi-isolate from one another, being surrounded by the low-density vapor-gas medium. Consequently, the temperature of a droplet decreases gradually during every event of emission of a molecule (while the molecule passes from the nucleus through its surface layer into the vapor). Therefore, the droplet emissivity must be determined by some intermediate value of its temperature but neither by the initial one (before the emission event) nor by the final one (after the emission event). Clearly, the latent heat of condensation/evaporation can substantially affect the droplet temperature only if the density of the carrier (passive) gas in the system is so small that its molecules are unable to establish thermal equilibrium between droplet and vapor-gas medium in the time interval between two successive elementary events of emission/absorption of a molecule by the droplet.

At present, there exists a complete enough and adequate theoretical description of nonisothermal nucleation and condensation, both unary\(^1\text{--}^{16}\) and binary\(^{17\text{--}20}\) taking into account the above nonisothermal effects (especially thoroughly they are investigated in the theory of unary condensation). However, as recently pointed out\(^{21}\) there exists an additional nonisothermal effect that may be of significant importance in one of the most widespread naturally occurring first-order phase transitions – the formation of ubiquitous secondary organic or organic-coated aerosols in the atmosphere.
via nucleation/condensation involving atmospheric vapors that are either directly emitted into the atmosphere or products of gas-phase chemical reactions between both anthropogenic and biogenic organic gaseous species.22,23

Secondary organic aerosols (SOA) constitute a large fraction of tropospheric aerosols and directly contribute to both scattering and adsorption of solar radiation, having high impact on the Earth climate, air quality, and human health.24–30 The chemical composition of liquid aqueous SOA (only such aerosols are discussed hereafter) can be extremely complex,24–27 but one can anticipate that the hydrophilic parts of organic compounds of an aqueous organic aerosol (OA) particle will be embedded into its aqueous core, leaving the hydrophobic parts pointed outward.31,32 Surface-located hydrophobic (surfactant) molecules of OA can be processed by their heterogeneous chemical reactions with atmospheric gaseous species.33–36 The latter may not be directly involved in condensation phenomena, but stimulate them by processing hydrophobic patches on the aerosol surface and rendering it more hygroscopic, thus enabling aerosols to become cloud condensation nuclei (CCN);31 this is called “chemical aging” of organic aerosols. In the atmosphere, the chemical aging of an OA particle is likely to occur concomitantly21,37,38 with the condensation of water and other vapors, such as volatile and semi-volatile oxidized organic species. These processes depend not only on the composition of the aerosol outer, surface layer, but also on the physicochemical properties of its core.

Most of (if not all) heterogeneous chemical reactions on the aerosol surface can be expected to be accompanied by the release of some enthalpy. The necessity to release such enthalpy of reaction may constitute one of obstacles hindering a chemical reaction in the gas phase because the surrounding medium is not able to sufficiently quickly remove the released enthalpy from the reagents/products. The same reaction in the presence of a third body (aerosol) would occur without such an impediment because a condensed phase particle would be much more efficient in absorbing the reaction enthalpy.

Therefore, one can assume that during the chemical aging of a liquid organic aerosol heterogeneous
reactions on its surface are exothermic. Due to the released enthalpy, the temperature $T$ of a growing aerosol particle may deviate from (become higher than) the ambient (air) temperature $T_a$, i.e., $T > T_a$. As recently shown, under normal atmospheric conditions, the cooling of the droplet after every such enthalpy release occurs on timescales longer than the characteristic timescales of droplet evolution with respect to total number of molecules therein. Consequently, the release of the enthalpy of heterogeneous reactions involved in chemical aging of organic aerosols leads to the increase of the ability of aerosol particles to emit molecules and, hence, causes the decrease of the nucleation rate. So far, however, this effect has been barely studied and, consequently, has not been implemented in current atmospheric models.

Recently, we have developed thermodynamic and kinetic models for the isothermal formation of aqueous organic aerosols evolving via both nucleation/condensation processes and concomitant chemical reactions on the aerosol surface. Taking into account the first three reactions in the most probable chemical aging mechanism (triggered by atmospheric hydroxyl radicals abstracting hydrogen atoms from surfactant molecules on the aerosol surface), we derived an explicit expression for the free energy of formation of a four-component aqueous organic aerosol particle as a function of its four independent variables of state. We also derived a kinetic equation for the size and composition distribution of an ensemble of aqueous organic droplets, evolving via nucleation and concomitant chemical aging. That kinetic equation explicitly takes account of chemical reactions on the surface of droplets and hence differs from the classical kinetic equation of multicomponent nucleation. We showed that the steady-state solution of this equation subject to appropriate boundary conditions can be found by using the method of complete separation of variables which was developed in CNT by Kuni et al. for the kinetics of multidimensional first-order phase transitions without chemical reactions.

In that theory, the temperature of aerosol particles (hereafter referred to as droplets) was
assumed to be constant and equal to the temperature of the surrounding air and, hence, all non-isothermal effects, involved in concurrent nucleation and chemical aging of organic aerosols were neglected. In the present work, we further develop that theory by expanding it to the case where nonisothermal effects are not negligible.

2 Concurrent nucleation and chemical aging of aqueous organic aerosols

We will use the formalism of classical nucleation theory (CNT) and treat aerosol particles (droplets) in the framework of capillarity approximation,\textsuperscript{45–47} modeling them as spherical particles of a liquid multicomponent solution. Consider an ensemble of such aqueous hydrophilic-hydrophobic organic (AHHO) droplets in the air containing three condensable vapors – water and hydrophilic and hydrophobic organics (components 1, 2, and 3, respectively), as well as non-condensable species – nitrogen oxide, hydroxyl radicals, oxygen, and nitrogen dioxide. Initially, an aerosol contains only components 1, 2, and 3 due to their condensation from the air. The hydrophobic component 3 is mostly (but possibly not exclusively, if it also contains a hydrophilic moiety, however weak) located on the aerosol surface, forming hydrophobic patches. However, owing to chemical reactions with atmospheric species, its molecules can be transformed into hydrophilic entities.

2.1 Chemical aging mechanism

According to Ellison et al.\textsuperscript{31}, the chemical aging of organic aerosols is most likely initiated by atmospheric OH radicals abstracting H-atoms from the hydrophobic moieties of surfactant molecules on the aerosol surface. (There exist other pathways of chemical aging,\textsuperscript{31} each involving a variety of sequential heterogeneous reactions, but we will not consider them in this work because, on the one
hand, they are less probable and, on the other hand, they can be investigated in the same fashion which is presented hereafter).

Denote a hydrophobic/surfactant molecule by HR, with the radical “R” being the entire molecule less one of the hydrogen atoms, “H”, in its hydrophobic moiety. The first three most probable reactions, involved in the chemical mechanism of aerosol aging, are:

\[ \text{OH} \ (g) + \text{HR/} \text{aerosol} \rightarrow \text{H}_2\text{O} \ (g) + \text{R}^*/\text{aerosol}. \]  

(1)

\[ \text{O}_2 \ (g) + \text{R}^*/\text{aerosol} \rightarrow \text{RO}_2^*/\text{aerosol}. \]  

(2)

\[ \text{RO}_2^*/\text{aerosol} + \text{NO} \ (g) \rightarrow \text{RO}^*/\text{aerosol} + \text{NO}_2 \ (g). \]  

(3)

In reaction (1), an OH radical abstracts an H atom from the hydrophobic moiety of a surfactant molecule, thus producing a surface-bound radical R*. The latter is almost immediately oxidized by O2 molecules in reaction (2), thus producing a surface-bound radical RO2*. The further evolution of radicals RO2* may vary, but always results in the formation of water soluble and/or volatile species and/or hydrophilic radicals. Reaction (3) represents one such a pathway (see ref.31 for the discussion of various reactive channels of radicals RO2* and RO*).

Reactions (1)-(3) convert a surface hydrophobic molecule HR into a radical RO*. The latter may still contain hydrophobic parts, but there now appears at least one highly hydrophilic site on its formerly hydrophobic moiety. Consequently, radicals RO* will be able to diffuse into the aerosol interior. According to numerical evaluations,21 the characteristic time of sequence (1)-(3) is much shorter than the characteristic time of the evolution of the total number of molecules in a droplet. Thus, the number of intermediate radicals R* (product of reaction (1)) and RO2* (product of reaction (2)) in the droplet can be assumed negligible compared to the number of final radicals RO*, (product of reaction (3)), so that sequence (1)-(3) produces only one additional aerosol component, namely, radical RO* (component 4).
Denote the numbers of molecules of components 1 (water), 2 (hydrophilic organic), and 3 (hydrophobic organic) in a droplet by $\nu_1, \nu_2,$ and $\nu_3,$ respectively, and the number of radicals $\text{RO}^\bullet$ (component 4) in the droplet by $\nu_4.$ For the sake of simplicity and uniformity, the radicals $\text{RO}^\bullet$ will be also referred to as “molecules of component 4”.

The exothermicity of the gas-phase analogs of reactions (1) and (3) is well-known. For example, in the case where the hydrophobic molecule $\text{HR}$ is that of hexanoic acid, reaction (1) is accompanied by the release of $\sim 20 \text{ kcal/mol}$. Reaction (3) is exothermic with the enthalpy release of $12 \text{ kcal/mol}$. The exothermicity of reaction (2) can be conjectured to be similar to that of reactions (1) and (3).

Denote the aggregate enthalpy released in a single sequence of reactions (1)-(3) by $\Delta H$. All three reactions have very high reaction rates (either due to a high forward reaction rates and low backward reaction rates or high concentration of reagents). Thus, for rough evaluations one can assume that the aerosol receives the heat $\Delta H$ from the entire sequence of reactions (1)-(3) virtually instantaneously.

Since the droplet temperature $T$ may now vary (deviate up from the air temperature $T_0,$ $T > T_0$) due to different nonisothermal effects, it is necessary to introduce a corresponding independent variable of state of a droplet. Every droplet will thus have five independent variables of state: the numbers of molecules of components 1,2,3,4, therein and a temperature related variable. We will choose it to be the droplet thermal energy $E$; it is linear in the temperature, and will be measured from its value at the temperature $T_0$ of the vapor-gas medium. Expressing all the quantities of dimensions of energy in units of $k_B T_0 \ (k_B$ is Boltzmann’s constant), we have

$$E = c\nu(T/T_0 - 1), \quad (4)$$

where $\nu = \sum_{i=1}^{4} \nu_i, \quad c = \sum_{i=1}^{4} \chi_i c_i, \quad \chi_i = \nu_i/\nu \ (i = 1,..,4),$ and $c_i \ (i = 1,..,4)$ is the molecular heat capacity of component $i$ in a droplet (hereafter all heat capacities are expressed in units of $k_B$).
2.2 Free energy of formation of an aqueous organic aerosol via concurrent nucleation and chemical aging

Having chosen $\nu_1, \nu_2, \nu_3, \nu_4,$ and $E$ as the independent variables of state of a single droplet, consider a nascent AHHO droplet in the air, composed of a ternary mixture of condensable vapors – water and low-volatility hydrophilic and hydrophobic organics (components 1, 2, and 3, respectively), as well as non-condensable gases – nitrogen oxide (component 5), hydroxyl radicals (component 6), oxygen (component 7), and nitrogen dioxide (component 8). As noticed by Kuni et al.\textsuperscript{16} and Kurasov,\textsuperscript{20} in the framework of capillarity approximation the free energy of nonisothermal formation $F(\nu_1, .., \nu_4, E)$ of such a droplet can be represented as (recall that all quantities having the dimensions of energy are expressed in units of $k_B T_0$)

$$F(\nu_1, .., \nu_4, E) = F(\nu_1, .., \nu_4) + E^2/2c\nu,$$  \hspace{1cm} (5)

where $F(\nu_1, .., \nu_4)$ is the free energy of \textit{isothermal} formation of a droplet $\nu_1, .., \nu_4$ (i.e., a droplet in internal thermodynamic equilibrium at the same temperature as the surrounding air temperature $T_0$). The term $E^2/2c\nu$ on the RHS of eq.(5) represents the contribution to $F(\nu_1, .., \nu_4, E)$ due to the deviation of the droplet temperature $T$ from the air temperature $T_0$ (i.e., it represents the work of heating/cooling the droplet from temperature $T_0$ to temperature $T$).

An analytic expression for the “isothermal” free energy $F(\nu_1, .., \nu_4)$ was obtained in ref. (see also ref.); it can be written as

$$F \equiv F(\nu_1, \nu_2, \nu_3, \nu_4) = -\sum_{i=1}^{4} \nu_i \ln \frac{\zeta_i}{\chi_i f_i(\chi_1, \chi_2, \chi_3)} + \sigma(\chi_1, \chi_2, \chi_3) A(\nu_1, \nu_2, \nu_3, \nu_4)/k_B T,$$  \hspace{1cm} (6)

where $\zeta_i = P_i/P_{i e} \ (i = 1, 2, 3)$ is the saturation ratio of the condensable component $i$ in air, with $P_i$ being its partial pressure and $P_{i e}$ its equilibrium vapor pressure; $f_i(\chi_1, \chi_2, \chi_3)$ is the activity coefficient of component $i$ in the four-component solution of composition $\chi_1, \chi_2,$ and $\chi_3$ (mole fractions $\chi_i \ (i =$
are related by \( \chi_1 + \chi_2 + \chi_3 + \chi_4 = 1 \); \( \sigma(\chi_1, \chi_2, \chi_3) \) and \( A(\nu_1, \nu_2, \nu_3, \nu_4) \) are the surface tension and surface area of the droplet of radius \( R \). The quantity \( \zeta_4 \) can be loosely (for the sake of convenience) called “the saturation ratio” of component 4; it is defined as \( \zeta_4 = (\zeta_5 \zeta_6 \zeta_7 K_{eq})/(\zeta_1 \zeta_8) \), where \( K_{eq} \) is the aggregate equilibrium constant of sequence (1)-(3), and \( \zeta_j = P_j/P_{j0} \) \( (j = 5, 6, 7, 8) \), with \( P_j \) the partial pressure of component \( j \) in the air and \( P_{j0} \) its standard partial pressure for which the standard Gibbs free energy change (at temperature \( T_0 \)) of reactions (1)-(3) is assumed to be known.

The function \( \tilde{F} = \tilde{F}(\nu_1, \nu_2, \nu_3, \nu_4, E) \) determines a free-energy surface in a 6-dimensional space. Under conditions when a multicomponent first-order phase transition occurs via homogeneous nucleation (as assumed hereinafter), it has a shape of a hyperbolic paraboloid (“saddle-like” shape in three dimensions). Hereafter, the extremum of this surface will be referred to as the “saddle point” and all quantities at this point will be marked with the subscript “c”. An aerosol particle whereof the variables \( (\nu_1, \nu_2, \nu_3, \nu_4, E) \) coincide with the respective coordinates of the saddle point is referred to as a “nucleus”. The nucleus characteristics \( \nu_{1c}, \nu_{2c}, \nu_{3c}, \nu_{4c}, E_c \) are thus determined as the solution of five simultaneous equations

\[
\tilde{F}_{i}'(\{\nu\}, E) \bigg|_{c} = 0 \quad (i = 1, ..., 4), \quad \tilde{F}_{E}'(\{\nu\}, E) \bigg|_{c} = 0, \quad (7)
\]

where \( \tilde{F}_{i}'(\{\nu\}, E) = \frac{\partial \tilde{F}(\{\nu\}, E)}{\partial \nu_i} \bigg|_{\nu_i=\text{const}, E=\text{const}} \), \( \tilde{F}_{E}'(\{\nu\}, E) = \frac{\partial \tilde{F}(\{\nu\}, E)}{\partial E} \bigg|_{\{\nu\}=\text{const}} \), and we introduced the notations \( \{\nu\} \) for the set of variables \( \nu_1, \nu_2, \nu_3, \nu_4 \) (such that \( \{\nu\} \equiv (\nu_1, \nu_2, \nu_3, \nu_4) \)) and defined \( \tilde{\nu}_i \) as a composite variable obtained by excluding \( \nu_i \) from \( \{\nu\} \), so that \( \{\nu\} = (\tilde{\nu}_i, \nu_i) = (\nu_1, \nu_2, \nu_3, \nu_4) \). As clear from eqs.(5) and (6), \( E_c = 0 \). Note that eqs.(5) and (6) involve only approximations intrinsic to the capillarity approximation.\(^{45,46}\)

During nucleation, aerosol particles overcome a free-energy barrier (6D surface determined by the function \( F = \tilde{F}(\{\nu\}, E) \)) to become irreversibly growing droplets. The crucial role in this process
is played by the evolution of aerosol particles in the saddle-point region of the space of variables $\nu_1, \ldots, \nu_4, E$. At this stage droplets are assumed to be large enough to be treated in the capillarity approximation, conventionally used in the framework of CNT. In the isothermal CNT, the saddle-point region itself is defined as the vicinity of the saddle point in which the bilinear approximation for $F(\{\nu\})$ is acceptable, \cite{46,48,53}

$$F(\{\nu\}) = F_c + \frac{1}{2} \sum_{i,j=1}^{4} F''_{ijc}(\nu_i - \nu_{ic})(\nu_j - \nu_{jc}), \quad (8)$$

where $F \equiv F(\{\nu\})$, $F''_{ij} = \partial^2 F/\partial \nu_i \partial \nu_j$ ($i, j = 1, \ldots, 4$). In this approximation, the first derivatives $F'_i \equiv F'_i(\{\nu\}) = \partial F/\partial \nu_i$ ($i = 1, \ldots, 4$) are linear superpositions of deviations $(\nu_i - \nu_{ic})$ ($i = 1, \ldots, 4$).

### 2.3 Temporal evolution of an ensemble of aqueous organic droplets with variable temperature

Consider an ensemble of AHHO droplets (evolving via both nucleation and concomitant chemical aging) and denote their distribution function with respect to $\nu_1, \nu_2, \nu_3, \nu_4, E$ at time $t$ by $g(\nu_1, \nu_2, \nu_3, \nu_4, E, t)$. According to the definition of $\{\nu\}$ and $\tilde{\nu}_i$ any function $f$ of variables $\nu_1, \nu_2, \nu_3, \nu_4$ may be denoted as either $f(\nu_1, \nu_2, \nu_3, \nu_4)$ or $f(\{\nu\})$ or $f(\tilde{\nu}_i, \nu_i)$; e.g., $g(\{\nu\}, E, t) \equiv g(\tilde{\nu}, \nu, E, t) \equiv g(\nu_1, \nu_2, \nu_3, \nu_4, E, t)$.

A differential equation, governing the temporal evolution of an ensemble of such aqueous organic droplets (with the distribution function $g(\{\nu\}, E, t)$) and taking into account the relevant nonisothermal effects, can be derived by combining the procedure used to derive the kinetic equation of the isothermal process \cite{41,42} with the procedure of Kuni and Grinin \cite{5,6,7,8,54} for the derivation of the kinetic equation of nonisothermal unary nucleation. First, it is necessary to construct a discrete five-dimensional balance equation of nonisothermal ternary nucleation and concomitant chemical aging taking into account all types of elementary interactions of nascent droplets with the vapor-gas medium (air).
2.3.1 Discrete equation of balance for the distribution function

As usual in the simplest version of CNT, let us assume that the metastability of the vapor mixture is created instantaneously and does not change during the whole nucleation-chemical aging process process. The temperature $T_0$ of the vapor-gas medium (air) and the number density of passive gas molecules are also fixed. At the nucleation stage, the droplets are so small that the timescale of their internal relaxation processes are very small in comparison with the timescale between successive elementary interactions between droplet and air and even smaller compared to the timescale between two successive sequences of chemical reactions (1)-(3); elementary interactions between droplets and air are assumed to take place under a free-molecular regime. This allows one to assume that a liquid droplet attains its internal thermodynamical equilibrium before each successive interaction with the vapor-gas medium and before each sequence of reactions (1)-(3).

Let $\varepsilon$ be the thermal energy of molecules striking a nucleus and let $\varepsilon'$ be the thermal energy of molecules reflected or emitted by a nucleus. Since the times of internal relaxation processes of nucleus are small, the number $W_i^-(i = 1, 2, 3)$ of molecules of component $i$ which a droplet emits per unit time as well as the distribution $w'$ of the emitted or reflected molecules with respect to their energy $\varepsilon'$ are determined (assuming the complete thermal adaptation of reflected molecules) by the droplet energy: $W_i^- \equiv W_i^-\{(\nu), E\} (i = 1, 2, 3)$, $w' \equiv w'(\{(\nu), E|\varepsilon'\})$. Here the variables $\nu_i$ ($i = 1, .., 4$), and $E$ correspond to the state of the nucleus before the interaction (because the temperature fluctuation effect and the effect of nucleus thermal quasi-isolation compensate each other$^6$). On the other hand, the distribution $w \equiv w(\varepsilon)$ of molecules striking a droplet with respect to their energy $\varepsilon$, and the number $W_i^+ \equiv W_i^+\{(\nu)\} (i = 1, 2, 3)$ of molecules of component $i$ that the droplet absorbs from air per unit time are independent of the droplet temperature; they are both determined by the temperature $T_0$ of the vapor-gas medium.
The material and thermal exchange between droplet and air occurs via the following elementary interactions:

(a123) absorption of a molecule of component 1 or 2 or 3 from the air into the droplet \( \{ \nu \} \) with the rate \( W_i^+ \) \( (i = 1, 2, 3) \) accompanied by the release of the latent heat of condensation \( \beta_i \) \( (i = 1, 2, 3) \) to the droplet (recall that all quantities having the dimension of energy are expressed in units of \( k_B T_0 \));

(e123) emission of a molecule of component 1 or 2 or 3 from the aerosol \( \{ \nu \} \) into the air with the rate \( W_i^- \) \( (i = 1, 2, 3) \), accompanied by the removal of the latent heat of evaporation/condensation \( \beta_i \) \( (i = 1, 2, 3) \) from the droplet;

(f4) production of a “molecule” of component 4 \( (\text{radical RO}^\bullet) \) via the forward sequence of heterogeneous chemical reactions (1)-(3) on the surface of aerosol \( \{ \nu \} \), with the rate \( W_4^+ = W_4^+ \{ \nu \}, E \), accompanied by the release of the aggregate enthalpy of reactions (1)-(3) \( \beta_4 \equiv \Delta H/k_B T_0 \) from the droplet;

(b4) destruction of a “molecule” of component 4 \( (\text{radical RO}^\bullet) \) via the backward sequence of chemical reactions (1)-(3) on the surface of droplet \( \{ \nu \} \), with the rate \( W_4^- = W_4^- \{ \nu \}, E \), accompanied by the removal of the aggregate enthalpy of reactions (1)-(3) \( \beta_4 \) from the droplet;

(r123g) reflection of a molecule of the vapor-gas medium (components 1, 2, 3, and passive gas).

Thus, one can write the initial discrete equation of balance, governing the evolution of the distribution \( g(\{ \nu \}, E, t) \), as

\[
\frac{\partial g(\{ \nu \}, E, t)}{\partial t} = \sum_{i=1}^{3} D_i' + D_4 + D_E, \tag{9}
\]

where

\[
D_i' = \int_0^\infty d\varepsilon \left[ W_i^+(\nu_i, \nu_i - 1)w(\varepsilon)g(\nu_i, \nu_i - 1, E - \beta_i - \varepsilon) - W_i^+(\{ \nu \})w(\varepsilon)g(\{ \nu \}, E, t) \right] \\
+ \int_0^\infty d\varepsilon' \left[ W_i^-(\nu_i, \nu_i + 1, E + \beta_i + \varepsilon')w'(\nu_i, \nu_i + 1, E + \beta_i + \varepsilon', \nu_i + 1, E + \beta_i + \varepsilon'|\varepsilon') \times \\
g(\nu_i + 1, E + \beta_i + \varepsilon', t) - W_i^- \{ \nu \}, E \}w'(\{ \nu \}, E|\varepsilon')g(\{ \nu \}, E, t) \right] \quad (i = 1, 2, 3), \tag{10}
\]
\[ D_4 = W_4^+(\nu_1, \nu_2, \nu_3 + 1, \nu_4 - 1, E - \beta_4)g(\nu_1, \nu_2, \nu_3 + 1, \nu_4 - 1, E - \beta_4, t) - W_4^+(\nu, E)g(\nu, E, t) \]

\[ + W_4^-(\nu_1, \nu_2, \nu_3 - 1, \nu_4 + 1, E + \beta_4)g(\nu_1, \nu_2, \nu_3 - 1, \nu_4 + 1, E + \beta_4, t) - W_4^-((\nu), E)g((\nu), E, t), \]

\[ D_E = \int_0^\infty d\varepsilon' \int_0^\infty \varepsilon' W_{\text{ref}}^{\text{ret}}((\nu)) [w(\varepsilon)w'(\nu, E-\varepsilon+\varepsilon')g((\nu), E-\varepsilon+\varepsilon')-w(\varepsilon)w'(\nu, E|\varepsilon')g((\nu), E)], \]

\[ W_{\text{ref}}((\nu)) = \sum_{i=1}^3 \frac{1-\alpha_{ci}}{\alpha_{ci}} \alpha_{ti} W_i^+(\nu) + \alpha_g W_g(\nu), \]

\[ \alpha_{ci} \text{ and } \alpha_{ti} (i = 1, 2, 3) \text{ are the condensation (sticking) coefficient and coefficient of thermal adaptation in a reflection event, respectively, of molecules of component } i; \ \alpha_{tg} \text{ is the coefficient of thermal adaptation in a reflection event of a passive gas molecule; } W_g((\nu)) \text{ is the number of molecules of the passive gas impinging on a droplet per unit time. Clearly, } W_{\text{ref}} \text{ would determine the total number of molecules reflected by the droplet per unit time if } \alpha_{ti} (i = 1, 2, 3) \text{ and } \alpha_g \text{ were all equal to 1. Note again that these equations assume the evolution of aerosols to occur through the absorption from and emission into the vapor of single molecules of components 1, 2, and 3 (i.e., multimer absorption and emission are neglected), as well as through the single sequences (1)-(3) of forward and backward reactions whereby a radical } RO^\bullet \text{ is either formed or destroyed.} \]

The terms \( D_1', D_2', \text{ and } D_3' \) on the RHS of eq.(9) represent the contributions to \( \partial g((\nu), E, t)/\partial t \) from the material exchange events of type (a123) and (b123), whereas the term \( D_4 \) represents the contributions to \( \partial g((\nu), E, t)/\partial t \) from the elementary events of type (f4) and (b4); the term \( D_E \) represents the contribution to \( \partial g((\nu), E, t)/\partial t \) from elementary events of type (r), i.e., from the the kinetic/internal energy exchange between droplets and all molecules reflected from droplets without being absorbed by them. Furthermore, on the RHS of the each of eq.(8) the first integral represents the contributions to \( \partial g((\nu), t)/\partial t \) from the absorption events (a123), whereas the second integral is due to the emission of molecules from aerosols into the air. On the RHS of eq.(11), the first two terms represent the contributions to \( \partial g((\nu), t)/\partial t \) from the forward sequences (1)-(3) of chemical reactions
on aerosols (whereby radicals RO$^\bullet$ are produced), whereas the third and fourth terms therein are due to the backward sequences (1)-(3) (whereby radicals RO$^\bullet$ are destroyed). As clear from eq.(11) and in consistency with the sequence of chemical reactions (1)-(3), the change of the aerosol distribution due to the variable $\nu_4$ is always accompanied by its change due to the variable $\nu_3$, while the latter can also change independently due to the direct material exchange between aerosols and air.

Expanding eqs.(10)-(12) in Taylor series in the deviations of nucleus characteristics from $\nu_1, \nu_2, \nu_3, \nu_4,$ and $E$, after simple transformations one can reduce eq.(9) to

$$
\frac{\partial g(\{\nu\}, E, t)}{\partial t} = \sum_{i=1}^{4} D_i + \frac{\partial}{\partial E} I_E,
$$

where

$$D_i = W_i^+(\bar{\nu}_i, \nu_i - 1)g(\bar{\nu}_i, \nu_i - 1, E - \beta_i) - W_i^+(\{\nu\})g(\{\nu\}, E, t)
+ W_i^-(\bar{\nu}_i, \nu_i + 1, E + \beta_i)g(\bar{\nu}_i, \nu_i + 1, E + \beta_i, t) - W_i^-(\{\nu\}, E)g(\{\nu\}, E, t) \quad (i = 1, 2, 3),
$$

$$I_E = -\sum_{i=1}^{3} \frac{\beta_i^2}{k_i} W_i^+ \left( \frac{E}{c_v} + \frac{\partial}{\partial E} \right) g(\nu_1, \nu_2, E),$$

$$\frac{1}{k_i} = \frac{\bar{c}_i}{\alpha_{ci}\beta_i^2} \left[ \alpha_{ci} + \alpha_{ci}(1 - \alpha_{ci}) + \alpha_{tg}p_i \right] \quad (i = 1, 2, 3),
$$

$$p_i = \left( \frac{m_i}{m_g} \right)^{1/2} \frac{n_g c_g}{2n_i \bar{c}_i} \quad (i = 1, 2, 3),$$

$\bar{c}_i, m_i,$ and $n_i$ ($i = 1, 2, 3$) are the effective (in the sense of energy transfer to the nucleus) heat capacity, mass, and number density of molecules, respectively, of component $i$ of the vapor mixture; $c_g, m_g,$ and $n_g$ are the analogous values of the passive gas.

The terms $D_1, D_2,$ and $D_3$ in eq.(14) describe the simultaneous transfer of both the substance and the latent heat of condensation to droplets by the molecules of condensable components of the air ($1, 2,$ and $3$, respectively). These terms have the structure characteristic of the Zeldovich–Frenkel nucleation equation, but modified to take into account that in every adsorption or emission of a
molecule of component $i$ ($i = 1, 2, 3$) by a droplet not only does the corresponding $\nu_i$ change by $\pm 1$, but also the variable $E$ changes by $\pm \beta_i$. Having a similar structure, the term $D_4$ in eq.(14) takes into account that in every sequence of reactions (1)-(3) the change of the variable $\nu_4$ by $\pm 1$ is accompanied by changes in $\nu_2$ and $E$ by $\mp 1$ and $\pm \beta_4$, respectively.

The term $-\partial I_E/\partial E$ in eq.(14) describes the transfer of the kinetic and internal energies to the droplets by all the molecules of the vapor-gas medium. Its Fokker-Planck form corresponds to the fulfillment of the condition

$$1/(c\nu)^{1/2} \ll 1,$$

meaning the smallness of the energy transfer by a molecule of the vapor-gas medium in comparison with the rms fluctuation of the droplet energy (recall that, according to the thermodynamic theory of fluctuations, $(c\nu)^{1/2} = (\sum_{i=1}^{4} c_i \nu_i)^{1/2}$ represents the rms fluctuation of the droplet energy in the absence of material exchange between droplet and vapor mixture).

### 2.3.2 Kinetic equation of nonisothermal concurrent nucleation and chemical aging

Let us introduce the variable $\xi$ instead of variable $E$ as

$$\xi = \frac{E}{(2c\nu)^{1/2}},$$

and present the distribution $g(\nu, E)$ in the form

$$g(\nu, E, t) = [2\pi c\nu]^{-1/2} e^{-\xi^2} P(\nu, \xi, t),$$

where the function $P(\nu, \xi, t)$ of $\nu, \xi, t$ will be referred to as “the distribution of droplets with respect to $\nu$ and $\xi$ at time $t$”, although, strictly speaking, such a distribution is represented by the product $\pi^{-1/2} e^{-\xi^2} P(\nu, \xi, t)$.

Usually $\beta_i \gg 1$ ($i = 1, \ldots, 4$), so the parameter

$$\alpha_i = \frac{\beta_i}{(2c\nu)^{1/2}} \quad (i = 1, \ldots, 4)$$

will not be small despite inequality (19). For the three condensable air components \( \alpha_j \ (j = 1, 2, 3) \) represents the relative latent heat of condensation/vaporization of component \( j \) per molecule, i.e. the latent heat of component \( j \) per molecule expressed in units of \((2c\nu)^{1/2}\), rms fluctuation of a droplet energy (in the absence of material exchange between droplet and vapor mixture) multiplied by \( \sqrt{2} \); likewise, for component 4 (product of the sequence of reactions (1)-(3)), \( \alpha_4 \) represents the relative aggregate enthalpy released in a single sequence of reactions (1)-(3), i.e. the aggregate enthalpy of reactions (1)-(3) expressed in units of \((2c\nu)^{1/2}\). Although \( \alpha_i \ (i = 1, \ldots, 4) \) is always smaller than 1, in order of magnitude \( \alpha_i \sim 1 \) (all \( \alpha_i \ (i = 1, \ldots, 4) \) are assumed to be constant and equal to their values for the nucleus\(^5,16\)).

Equation (14) can be transformed into a differential equation for the distribution \( P(\{\nu\}, \xi, t) \) in a standard way\(^5,8\) by expanding the terms \( D_i \ (i = 1, \ldots, 4) \) therein in Taylor series in the deviations of \( \nu_i \pm 1 \) from \( \nu_i \) and \( E \pm \beta_i \) from \( E \ (i = 1, \ldots, 4) \) and (as usual in CNT) assuming that with respect to the variables \( \nu_i \ (i = 1, \ldots, 4) \) the resulting differential equation has the form of the Fokker-Planck equation (with linear force coefficients) (see ref.53 for more details):
\[
\frac{\partial P}{\partial t} = \sum_{i=1}^{4} \frac{\partial}{\partial \nu_i} \left( \hat{L}_i - W_i^+ \sum_{m=1}^{\infty} \frac{\alpha^m_i}{m!} \frac{\partial^m}{\partial \xi^m} \right) P \quad (a)
\]

\[
+ \left( \frac{\partial}{\partial \nu_3} \hat{L}_{43} - \frac{\partial}{\partial \nu_4} \hat{L}_{44} \right) P \quad (b)
\]

\[
- \frac{\partial}{\partial \nu_4} W_4^+ \sum_{m=1}^{\infty} \frac{\alpha^m_i}{m!} \frac{\partial^m}{\partial \xi^m} P \quad (c)
\]

\[
+ \sum_{i=1}^{4} \sum_{m=1}^{\infty} \frac{(-1)^m \alpha^m_i}{m!} \hat{L}_i \left( \frac{\partial}{\partial \xi} - 2 \xi \right)^m P \quad (d)
\]

\[
+ \sum_{m=1}^{\infty} \frac{(-1)^m \alpha^m_i}{m!} \hat{L}_{43} \left( \frac{\partial}{\partial \xi} - 2 \xi \right)^m P \quad (e)
\]

\[
- \sum_{i=1}^{4} W_i^+ \sum_{m \neq m'}^{\infty} \frac{(-1)^m \alpha^{m+m'}_i}{m!m'} \left( \frac{\partial}{\partial \xi} - 2 \xi \right)^{m'} \frac{\partial^m}{\partial \xi^m} P \quad (f)
\]

\[
+ \left[ \sum_{i=1}^{3} \frac{k_i + 1}{k_i} W_i^+ \frac{\alpha^2_i}{m!m'} \left( \frac{\partial}{\partial \xi} - 2 \xi \right) \frac{\partial}{\partial \xi} \right] P \quad (g1)
\]

\[
- \sum_{i=1}^{4} \sum_{m=2}^{\infty} W_i^+ \frac{(-1)^m \alpha^{2m}_i}{m!m!} \left( \frac{\partial}{\partial \xi} - 2 \xi \right)^m \frac{\partial^m}{\partial \xi^m} P \quad (g2)
\]

(for the sake of simplicity of notation, the independent arguments \(\nu_1, .., \nu_4, \xi,\) and \(t\) of \(W_i^+\) \((i = 1, .., 4)\) and \(P\) are omitted), where we introduced the operators

\[
\hat{L}_{43} \equiv -W_4^+(F'_3 + \frac{\partial}{\partial \nu_3}), \quad \hat{L}_i \equiv -W_i^+(F'_i + \frac{\partial}{\partial \nu_i}) \quad (i = 1, .., 4),
\]

with \(F'_i \equiv \partial F/\partial \nu_i\), and \(F\) the free energy of formation of a droplet with characteristics \(\nu_1, \nu_2, \nu_3, \nu_4,\) and \(E = 0:\) \(F \equiv F(\{\nu\}, E = 0)).\)

Hereafter, we will be interested only in the saddle point region \(|\nu_i - \nu_{ic}| \lesssim \Delta \nu_{ic}\), because the evolution of droplets there plays the determining role for the nucleation kinetics.5–12,43,44,46,48–52

The half-width of this region \(\Delta \nu_{ic} \quad (i = 1, .., 4)\) represents a characteristic scale of change of \(\nu_i\)-dependent functions and, consequently, we have the operator estimate \(\partial/\partial \nu_i \sim 1/\Delta \nu_{ic}\). On the other hand, \(|F'_i| \lesssim 1/\Delta \nu_{ic} \quad (i = 1, .., 4)\) in this region, according to eq.(8). Therefore, in this region, the
second term on the RHS of eq.(27) is dominant, which substantiates the following operator estimates:

\[ \frac{1}{W_i} \hat{L}_i \sim \frac{\partial}{\partial \nu_i} \sim \frac{1}{\Delta \nu_{ic}} \quad (i = 1, \ldots, 4) \quad (25) \]

The terms \( \partial L_i P / \partial \nu_i \quad (i = 1, \ldots, 4) \), in the RHS of eq.(27) have the second order of smallness in \( 1/\Delta \nu_{ic} \), but they are retained in the framework of CNT because they are necessary for the self-consistent description of the kinetics of nucleation.

According to eq.(21), the characteristic values of \( \xi \) lie in the interval \( |\xi| \lesssim 1 \), where we have the estimates

\[ \frac{\partial}{\partial \xi} \sim \xi \sim 1 \quad (26) \]

Therefore, \( \alpha_i \quad (i = 1, \ldots, 4) \) are the expansion parameters in the series in \( m \) and \( l \). Retaining all the terms of those series means that we extend the theory to values \( \alpha_i \sim 1 \quad (i = 1, \ldots, 4) \) and hence go beyond the framework of the Fokker-Planck approximation.

Let us establish a relative importance of the terms on the RHS of eq.(23), taking into account the estimates (25),(26), and \( |F'_i| \lesssim 1/\Delta \nu_{ic} \quad (i = 1, \ldots, 4) \). Since the terms (a)-(e) on the RHS of eq.(23) contain the operators \( L_i, \partial / \partial \nu_i \quad (i = 1, \ldots, 4), L_3^{(4)}, L_4^{(4)} \), we conclude that their ratios to the last, seventh, term do not exceed \( 1/\Delta \nu_{ic} \quad (i = 1, \ldots, 4) \) (which are much smaller than 1) in order of magnitudes.

Comparing the first member of the last term (g) on the RHS of eq.(23) with the second member therein, we conclude that the first member is the main one in this term, because of the inequalities \( (k_i + 1)/k_i > 1 \quad (i = 1, \ldots, 4) \) and factorials \( m!m! \). One can also see that the ratio of the term (f) to the last term (g) does not exceed the parameter

\[ \delta_f^g \equiv \frac{\sum_{i=1}^4 W_i^+ \alpha_i^3}{2 \left( \sum_{i=1}^3 W_i^+ \alpha_i^3 (k_i + 1)/k_i + W_4^+ \alpha_4^3 \right)} \]

Assuming it to be much smaller than unity, \( \delta_f^g \ll 1 \), one can conclude that on the RHS of eq.(23) the last term is the predominant one.
Equation (23) governs the time evolution of the five-dimensional distribution $P$. The hierarchy of terms established above corresponds to the hierarchy of time scales in the development of this distribution.

Denote the principal operator of the governing equation (23), i.e., the operator of the dominant term on its RHS, by $\hat{\Lambda}$:

$$\hat{\Lambda} = \left( \sum_{i=1}^{3} \frac{k_i + 1}{k_i} W_i \alpha_i^2 + W_4 \alpha_4^2 \right) \left( \frac{\partial}{\partial \xi} - 2\xi \right) \frac{\partial}{\partial \xi} - \sum_{i=1}^{4} \sum_{m=2}^{\infty} W_i^{+} \frac{(-1)^m \alpha_i^{2m}}{m!m!} \left( \frac{\partial}{\partial \xi} - 2\xi \right)^m \frac{\partial^m}{\partial \xi^m}. \quad (27)$$

One can see that the eigenfunctions of this operator are the Hermite polynomials $H_j \equiv H_j(\xi)$ ($H_0 = 1, H_1 = 2\xi, H_2 = 4\xi^2 - 2, ...$), satisfying the recursion relations

$$\frac{\partial}{\partial \xi} H_j = 2jH_{j-1}, \quad \left( \frac{\partial}{\partial \xi} - 2\xi \right) H_j = -H_{j+1}, \quad (j = 1, 2, ...), \quad (28)$$

so that

$$\hat{\Lambda} H_j = \Lambda_j H_j \quad (j = 0, 1, ...), \quad (29)$$

where $\Lambda_j$ ($j = 0, 1, 2, ...$) is the eigenvalue, corresponding to the eigenvector $H_j$. As clear from eqs. (27) and (28),

$$\Lambda_j = -j\lambda_j, \quad \lambda_j = 2 \left( \sum_{i=1}^{3} \frac{k_i + 1}{k_i} W_i \alpha_i^2 + W_4 \alpha_4^2 \right) + (j - 1)! \sum_{i=1}^{4} \sum_{m=2}^{\infty} W_i^{+} \frac{(2\alpha_i^2)^m}{m!m!(j - m)!} \quad (30)$$

(for $j = 0$ and $j = 1$ the sum over $m$ on the RHS of the latter equality is absent; $0! = 1$ is adopted).

Since $0 < \lambda_0 < \lambda_1 < \lambda_2 < ...$, one can conclude that all the eigenvalues $\Lambda_j$ with $j = 1, 2, ...$ are negative, whereas the eigenvalue $\Lambda_0$ is equal to zero: $\Lambda_0 = 0, \quad \Lambda_j < 0 \quad (j = 1, 2, ...)$.

The Hermite polynomials form a complete system of eigenfunctions (an orthogonal basis) satisfying the orthogonality and normalization relations

$$(H_j, H_k) = \delta_{jk}2^j j! \quad (j, k = 0, 1, 2, ...), \quad (31)$$

where $\delta_{jk}$ is the Kronecker delta and the scalar product $(\Phi, \Psi)$ of function $\Phi$ and $\Psi$ of $\xi$ is defined as

$$(\Phi, \Psi) = \pi^{-1/2} \int_{-\infty}^{\infty} d\xi \ e^{-\xi^2} \Phi(\xi) \Psi(\xi). \quad (32)$$
As follows from eqs.(21),(32), and \( H_0 = 1 \), the four-dimensional distribution \( f \equiv f(\nu_1, \ldots, \nu_4) \) of droplets with respect to variables \( \nu_1, \ldots, \nu_4 \) is given by the equation \( f = (H_0, P) \), i.e. the four-dimensional distribution \( f \) is the projection of the five-dimensional distribution \( P \) on \( H_0 \). Taking this into account, let us take the projection of governing equation (23) on \( H_0 \). According to eqs.(28) and (31), non-zero contributions to this projection arise only from the first member of the first term, (a), of the order of \( 1/(\Delta \nu_{ic})^2 \) \((i = 1, \ldots, 4)\). One can thus obtain

\[
\frac{\partial f}{\partial t} = - \sum_{i=1}^{4} \frac{\partial J_i}{\partial \nu_i},
\tag{33}
\]

where

\[
J_i = \left( H_0, \left( \hat{L}_i - W_i^+ \sum_{m=1}^{\infty} \frac{\alpha_i^m}{m!} \frac{\partial^m}{\partial \xi^m} \right) P \right) \quad (i = 1, 2),
\tag{34}
\]

\[
J_3 = \left( H_0, \left[ \left( \hat{L}_3 - W_3^+ \sum_{m=1}^{\infty} \frac{\alpha_3^m}{m!} \frac{\partial^m}{\partial \xi^m} \right) P \right) \right),
\tag{35}
\]

\[
J_4 = \left( H_0, \left[ \left( \hat{L}_4 - W_4^+ \sum_{m=1}^{\infty} \frac{\alpha_4^m}{m!} \frac{\partial^m}{\partial \xi^m} \right) + (-\hat{L}_{43}) \right) P \right),
\tag{36}
\]

is the (averaged over \( \xi \)) flux of nuclei along the \( \nu_i \)-axis.

2.3.3 The stage of thermal relaxation

Retaining on the RHS of governing equation (21) only the leading term (g) (containing two members), and taking into account definition (21), we obtain

\[
\frac{\partial P}{\partial t} \equiv \dot{\Lambda} P \tag{37}
\]

The solution of this equation is given, according to relation (29), by

\[
P = f + \sum_{j=1}^{\infty} e^{-j\lambda_j t} f_j H_j,
\tag{38}
\]

where \( f \) and \( f_j \) are independent of \( \xi \) and \( t \) and can be presented, by virtue of eq.(32), as

\[
f = (H_0, P) = (H_0, P|_{t=0}), f_j = (2^j j!)^{-1} (H_j, P|_{t=0})
\tag{39}
\]

20
\( P |_{t=0} \) is the three dimensional distribution \( P \) at \( t = 0 \). From \( f = (H_0, P) \) and eq.(43) it follows that \( f \) still represents the four-dimensional distribution of droplets with respect to \( \nu_1, ..., \nu_4 \) and it does not change as long as \( P \) is governed by eq.(41). Therefore, eq.(42) describes the stage of thermal relaxation of droplets; this stage is characterized by the spectrum of relaxation times \( 1/j\lambda_j \) \( (j = 1, 2, ...) \), which decrease with increasing \( j \).

As follows from eqs.(21), (32) and \( f = (H_0, P) \), if \( \Phi \) is some function of the variable \( \xi \), its average value \( \Phi \) with respect to the variable \( \xi \) is determined as \( \bar{\Phi} = \langle \Phi, P \rangle / f \). Therefore, average values with respect to \( \xi \) will also change together with \( P \) in the process of thermal relaxation.

According to eq.(38), at the end of the thermal relaxation

\[
P \simeq f \quad (t \gtrsim t_\xi),
\]

\[
t_\xi = 1/\lambda_1 = \frac{1}{2} \left( \sum_{i=1}^{3} \frac{k_i + 1}{k_i} W_i^+ \alpha_i^2 + W_4^+ \alpha_4^2 \right)^{-1},
\]

where \( t_\xi \) is the principal thermal relaxation time. Since \( f \) does not depend on \( \xi \), by virtue of eqs.(21),(40), we can conclude that the distribution of droplets with respect to temperature approaches a quasiequilibrium Gaussian distribution by the end of the thermal relaxation stage, whereof the duration is given by \( t_\xi \). The inverse quantity \( 1/t_\xi \) determines the “speed” of thermal relaxation, and it contains the contributions from the latent heat of condensation and the enthalpy of chemical reactions, as well as from the exchange of kinetic (thermal) energy between droplets and molecules of vapor-gas medium.

Denote by \( t_{\nu} \) the characteristic time of change of the size (four-dimensional) distribution \( f \). In order to obtain an estimate for \( t_{\nu} \) at the end of the stage of thermal relaxation, let us replace \( P \) by \( f \) in eqs.(34)-(36) (which is an accurate enough approximation by virtue of eq.(40)) and then substitute \( J_i \) \( (i = 1, .., 4) \) in eq.(33). Using estimates (25), one can obtain for \( t_{\nu} \):

\[
t_{\nu} \sim \left( \sum_{i=1}^{4} W_i^+ \frac{1}{(\Delta_i^\nu)^2} + W_4^+ \frac{1}{(\Delta_4^\nu)^2} - 2W_4^+ \frac{1}{(\Delta_3^\nu \Delta_4^\nu)^2} \right)^{-1},
\]
where the parameters
\[
\frac{1}{\Delta \nu_i} \equiv \left| \sum_{\alpha=1}^{4} p_{i\alpha} \sqrt{|\lambda_{\alpha}|} \right| \quad (i = 1, \ldots, 4),
\] (43)
must fulfill the strong inequalities
\[
\frac{1}{\Delta \nu_i} \ll 1 \quad (i = 1, \ldots, 4),
\] (44)
for the kinetic equation to have the Fokker-Planck form with respect to variables \(\nu_1, \ldots, \nu_4\).

Thus, we have
\[
\frac{t_{\xi}}{t_{\nu}} \sim \frac{1}{2} \frac{\sum_{i=1}^{4} W_i^+ \frac{1}{(\Delta \nu_i)^2} + W_4^+ \frac{1}{(\Delta \nu_4)^2} - 2W_4^+ \frac{1}{\Delta \nu_4}}{\sum_{i=1}^{3} \frac{k_{i+1}}{k_i} W_i^+ \alpha_i^2 + W_4^+ \alpha_4^2} \ll 1.
\] (45)
This strong inequality expresses the hierarchy of time scales which has allowed us to identify the thermal relaxation stage. During this stage the distribution of nuclei with respect to the variable \(\xi\) approaches the quasi-equilibrium distribution, while the distribution with respect to \(\nu_1, \nu_2, \nu_3,\) and \(\nu_4\) practically does not change.

The quasiequilibrium distribution is an eigenfunction of the principal operator of governing equation (23) with zero eigenvalue. Therefore, as follows from eq.(38), the operators of the first four terms on the RHS of eq.(23) also become important at the end of the stage of thermal relaxation.

3 Numerical evaluations

For a numerical illustration of our model, we carried out calculations for the concurrent nucleation and chemical aging of AHHO aerosols in the air containing the vapors of three condensable components – water, 2–methylglyceric acid (C\(_4\)H\(_8\)O\(_4\), as a representative of hydrophilic organics in air), and 3–methyl–4–hydroxy–benzoic acid (C\(_8\)H\(_8\)O\(_3\), as a representative of hydrophobic organics in air), as well as non-condensable nitrogen oxide, hydroxyl radicals, oxygen, and nitrogen dioxide (components 1,2,3,5,6,7, and 8, respectively). The non-condensable air components thus played also the role of the carrier (passive) gas in the system.
Besides the air temperature \( T = 293.15 \text{ K} \), the atmospheric conditions were specified by the saturation ratios of vapors of water \( \zeta_1 \), 2-methylglyceric acid \( \zeta_2 \), and 3-methyl-4-hydroxy-benzoic acid \( \zeta_3 \), and by the analogous parameters of noncondensable species assumed to be fixed, \( \zeta_5 = \zeta_6 = \zeta_7 = \zeta_8 = 1.001 \). The saturation ratio of water vapor was varied.

According to Couvidat et al.,\(^{55}\) the molecules of 2-methylglyceric acid can be considered to be hydrophilic, whereas 3-methyl-4-hydroxy-benzoic acid molecules are hydrophobic. The latter will be mostly located at the aerosol surface, with the methyl groups -CH\(_3\) exposed to the air. Thus, one can consider the abstraction of the H-atom from the methyl group of a 3-methyl-4-hydroxy-benzoic acid molecule as reaction (1), and identify the radical \( \text{R}^\bullet \) in eqs.(1)-(3) and component 4 as the radicals

\[-\text{CH}_2\text{C}_6\text{H}_3\text{OH-COOH}, \text{ and } -\text{OCH}_2\text{C}_6\text{H}_3\text{OH-COOH},\]

respectively. Thus, the solution in droplets can be treated as a mixture of functional groups with all relevant parameters available in the tables of UNIFAC method for activity coefficients.\(^{56-58}\)

The effect of the droplet surface tension on condensation/nucleation phenomena has been well investigated.\(^{46}\) Aiming mainly at the qualitative sensitivity studies of the thermal relaxation process with respect to the aggregate equilibrium constant \( K_{eq} \), one can conjecture that the effect of radicals \( \text{R}_4 \) (resulting from the hydrophobic-to-hydrophilic conversion of 3-methyl-4-hydroxy-benzoic acid) on the surface tension will be roughly similar to the effect of a hydrophilic component on the surface tension of its aqueous solutions. Taking this into consideration, we have modeled the surface tension \( \sigma^{\alpha\beta}(\chi_1, \chi_2, \chi_3) \) of the four-component solution “water/2-methylglyceric acid/3-methyl-4-hydroxy-benzoic acid/radical \( \text{R}_4 \)” with the surface tension of a model ternary solution “water/hydrophilic solute (which would represent 2-methylglyceric acid and radicals \( \text{R}_4 \) combined) /hydrophobic solute (which would represent 3-methyl-4-hydroxy-benzoic acid)”. As such, we chose the solution of water, \( n \)-penty acetate (surrogate hydrophobic solute), and methanol.
(surrogate hydrophilic solute). An analytical expression for its surface tension $\tilde{\sigma}$ as a function of its composition was obtained by Santos et al.\textsuperscript{59} (see refs.38 and 39 for more details).

The rate constants of forward reactions in sequence (1)-(3) can be roughly estimated to equal their gas-phase analogs, but there are no data on the rate constants of corresponding backward reactions. Thus, in the function $F = F(\nu_1, \ldots, \nu_4)$ the aggregate equilibrium constant $K_{eq}$ of sequence (1)-(3) has to be considered as an adjustable parameter.

The heat capacities of air $c_g \approx 4.01$ and pure water vapor $c_1 \approx 4.54$ were determined by linearly extrapolating data in \textit{CRC Handbook of Chemistry and Physics}\textsuperscript{60} and with the help of formulas given in \textit{Thermophysical Properties of Matter}.\textsuperscript{61} The heat capacity $c_2$ of 2–methylglyceric acid vapor was roughly approximated by that of the gaseous propylbenzene,\textsuperscript{62} thus setting $c_2 \approx 17.34$, whereas the heat capacity $c_3$ of 3–methyl–4–hydroxy-benzoic acid vapor was assumed to be roughly equal to $c_3 = \frac{m_2}{m_3} \times c_2 \approx 22.08$. To estimate the heat capacity $c\nu$ of a four component nucleus, we assumed that it can be expected to be similar to the heat capacity of a droplet of an aqueous binary solution of some heavy organic compound with the total number of molecules equal to $\nu_c$ and the mole fraction of the organic compound equal to $\chi_2c + \chi_3c + \chi_4c$. We used the data for the the binary solution of water–glycerol\textsuperscript{63} at 293.15 K and appropriate glycerol mole fraction $\chi_2c + \chi_3c + \chi_4c$.

The equilibrium vapor pressure and latent heat of condensation/evaporation of pure water were obtained by linearly interpolating data in \textit{CRC Handbook of Chemistry and Physics},\textsuperscript{60} with $n_{1\infty} = 5.78 \times 10^{17}$ cm$^{-3}$ and $\beta_1 = 18.14$. The equilibrium vapor pressures and latent heats of condensation/evaporation of pure 2–methylglyceric acid and 3–methyl–4–hydroxy-benzoic acid were evaluated by averaging their values (two for each quantity, one from ref.48 and one from the web-site [http://www.chemspider.com]), so that $n_{2\infty} = 7.0 \times 10^{12}$ cm$^{-3}$, $\beta_2 = 23.23$ and $n_{3\infty} = 5.4 \times 10^{12}$ cm$^{-3}$, $\beta_3 = 22.70$.

Although the exothermicity of the gas-phase analogs of reactions (1)-(3) is well-known, we were
unable to find data on the enthalpy of reactions (1)-(3) in the case where the hydrophobic molecule HR is that of 3-methyl-4-hydroxy-benzoic acid. Taking into account data provided in ref.31 on the enthalpy of similar reactions and aiming at only rough, qualitative numerical estimates, we thus assumed the aggregate enthalpy $\Delta H$ of the sequence of reactions (1)-(3) to be about 40 kcal/mol, or $\beta_4 = 72.15$.

Since there exist virtually no theoretical nor experimental data on the thermal accommodation and sticking coefficients, the calculations were carried out assuming $\alpha_{ci} = 1$, $\alpha_{ti} = \alpha_g = 1$ ($i = 1, 2, 3$). To illustrate the typical dependence of theoretical predictions on the parameters of the air wherein an ensemble of model AHNO aerosols is evolving via nucleation and chemical aging, we evaluated the thermal relaxation time $t_\xi$ and the characteristic time of change of the (four-dimensional) size distribution of such aerosols $t_\nu$ for various vapor saturation ratios of water ($\zeta_1$), hydrophilic organic ($\zeta_2$), and hydrophobic organic ($\zeta_3$), considering also several values of the aggregate equilibrium constant $K_{\text{eq}}$. Some of the results of calculations are presented in Figures 1 and 2 and Table 1.

Figure 1a presents the typical dependence of the thermal relaxation time $t_\xi$ on $K_{\text{eq}}$, with the latter changing in the range from $K_{\text{eq}} = 1$ (weak chemical aging) to $K_{\text{eq}} = 5$ (intensive hydrophobic-to-hydrophilic conversion), for five saturation ratios of water vapor in the air: the solid curve is for $\zeta_1 = 0.15$, the long-dashed curve for $\zeta_1 = 0.14$, dash-dotted line for $\zeta_1 = 0.13$, short-dashed curve for $\zeta_1 = 0.12$, and dotted curve for $\zeta_1 = 0.11$. In Figure 2b, the typical dependence of $t_\xi$ is plotted as a function of $\zeta_1$ in the range from $\zeta_1 = 0.11$ to $\zeta_2 = 0.15$ at five values of $K_{\text{eq}}$: the solid curve is for $K_{\text{eq}} = 0.15$, the long-dashed curve for $K_{\text{eq}} = 0.14$, dash-dotted line for $K_{\text{eq}} = 0.13$, short-dashed curve for $K_{\text{eq}} = 0.12$, and dotted curve for $K_{\text{eq}} = 0.11$. All results in Figure 1 are for $T_0 = 293.15$ K, $\zeta_2 = 0.01$, and $\zeta_3 = 0.3$ (the parameters of noncondensable species are specified above).

Figure 2 presents the typical dependence of the thermal relaxation time $t_\xi$ on the saturation ratio
ζ_2 of the hydrophilic organic vapor at a fixed saturation ratio ζ_3 = 0 of the hydrophobic organic vapor (Figure 2a) and on the saturation ratio ζ_3 of the hydrophobic organic vapor at a fixed saturation ratio ζ_2 = 0.01 of the hydrophilic organic vapor (Figure 2b). All results in both Figure 2 are for T_0 = 293.15 K, K_{eq} = 3, and ζ_1 = 0.13 (the parameters of noncondensable species are specified above).

As clear from Figures 1 and 2, the thermal relaxation time t_ξ monotonically decreases with increasing saturation ratio ζ_i (i = 1, 2, 3) of each condensable component of the air. It is also monotonically decreases with increasing equilibrium constant K_{eq} = 3 of the sequence of reactions (1)-(3). Thus, one can conclude that the quasi-equilibrium distribution of an ensemble of AHHO droplets with respect to their temperatures is reached faster in more metastable vapor mixtures (with higher saturation ratios of vapors of water and hydrophilic and hydrophobic organics) and when the equilibrium of the sequence of chemical aging reactions (1)-(3) is shifted more towards products. These results indicate that the chemical aging of aqueous organic aerosols significantly enhances the hierarchy of time scales in the evolution of the droplet distribution function. Since the mechanism of chemical aging of aqueous organic aerosols (i.e., the sequence of reactions (1)-(3)) strongly favors the products over reagents, our results indicate that the above presented procedure for finding the distribution function of the ensemble of droplets at the stage of thermal relaxation is well substantiated at virtually any combination of saturation ratios of air components, both condensable and inert.

Table 1 presents the characteristic time of change of the (four-dimensional) size distribution of AHHO aerosols t_ν and the ratio t_ξ/t_ν for various combinations of ζ_1, ζ_2, ζ_3, and K_{eq}. As evident from this table, the thermal relaxation time remains much smaller (by at least two orders of magnitude) than the characteristic time t_ν of the size evolution of the distribution of droplets. Thus, one can expect that the hierarchy of time scales in the evolution of droplet distribution (identified on the
basis of relative importance of terms on the RHS of eq. (25)), which allowed us to obtain an analytical solution (40) of the kinetic equation (25) at the stage of thermal relaxation, exists for a variety of hydrophilic and hydrophobic organic vapors (participating in nucleation and chemical aging of organic aerosol) and a wide range of atmospheric conditions.

4 Concluding remarks

In the atmosphere, the formation and evolution of secondary aqueous organic aerosols is most likely to occur via concurrent nucleation and chemical aging (heterogeneous chemical reactions on aerosol particles). Most of heterogeneous chemical reactions on the aerosol surface can be expected to be exothermic, accompanied by the release of some enthalpy. Therefore, one can assume that during the chemical aging of a liquid organic aerosol, heterogeneous reactions on its surface are exothermic. Due to the released enthalpy, the aerosol temperature may deviate up from the ambient (air) temperature. This can substantially affect the process of formation and evolution of organic aerosols.

So far, however, this effect has never been studied, whereas other non-isothermal effects (such as the effects of latent heat of condensation/evaporation, temperature fluctuations, thermal quasi-isolateness of a nascent droplet) of both unary and multicomponent vapor-to-liquid phase transitions have been relatively well investigated (especially thoroughly in the theory of unary condensation). In this work, taking account of the deviation of the droplet temperature from the air temperature (due to all these nonisothermal effects) and using the formalism of classical nucleation theory, we have derived a kinetic equation for the distribution of an ensemble of aqueous organic aerosols, evolving via nucleation and concomitant chemical aging.

Our kinetic equation governs the temporal evolution of the five-dimensional distribution function not only in the case where the latent heats of condensation and the enthalpy of chemical reactions
Table: The characteristic time of change of the (four-dimensional) size distribution of AHHO aerosols $t_\nu$ and the ratio $t_\xi/t_\nu$ for various combinations of $\zeta_1, \zeta_2, \zeta_3$, and $K_{eq}$.

| $K_{eq}$ | $\zeta_1$ | $\zeta_2$ | $\zeta_3$ | $t_\nu$ (µs) | $t_\xi/t_\nu$ |
|---------|-----------|-----------|-----------|-------------|---------------|
| 1       | 0.11      | 0.01      | 0.3       | 119.90      | 0.0001        |
|         | 0.13      | 0.01      | 0.3       | 0.73        | 0.02          |
|         | 0.15      | 0.01      | 0.3       | 9.65        | 0.001         |
|         | 0.15      | 0.019     | 0.4       | 0.58        | 0.02          |
|         | 0.15      | 0.019     | 0.5       | 0.38        | 0.02          |
|         | 0.15      | 0.019     | 0.6       | 0.24        | 0.03          |
|         | 0.17      | 0.019     | 0.4       | 0.55        | 0.02          |
|         | 0.19      | 0.019     | 0.4       | 2.66        | 0.003         |
| 3       | 0.11      | 0.01      | 0.3       | 11.55       | 0.0007        |
|         | 0.13      | 0.01      | 0.3       | 8.25        | 0.0009        |
|         | 0.13      | 0.01      | 0.36      | $5 \times 10^4$ | $10^{-6}$ |
|         | 0.13      | 0.01     | 0.42      | 0.17        | 0.04          |
|         | 0.13      | 0.04      | 0.3       | 8.25        | 0.0009        |
|         | 0.13      | 0.07      | 0.3       | 8.25        | 0.0009        |
|         | 0.15      | 0.01      | 0.3       | 9.22        | 0.0008        |
|         | 0.15      | 0.019     | 0.6       | 5.13        | 0.001         |
| 5       | 0.11      | 0.01      | 0.3       | 0.08        | 0.08          |
|         | 0.13      | 0.01      | 0.3       | 0.22        | 0.03          |
|         | 0.15      | 0.01      | 0.3       | 5.48        | 0.001         |
are relatively small, per-molecule quantities being much smaller than the rms equilibrium fluctuation of the droplet energy, but also in the case where they are of the same order of magnitude as the rms fluctuation of the droplet energy. In the former case the kinetic equation reduces to the canonical form of the five-dimensional Fokker-Planck equation, whereas in the latter case it goes beyond the framework of the Fokker-Planck equation with respect to the variable related to the droplet temperature.

We have established that under conditions of the applicability of the capillarity approximation there exists the hierarchy of the time scales in the evolution of the five-dimensional distribution function of droplets. This allows one to identify the stage of thermal relaxation of droplets at which their distribution with respect to their temperatures approaches a quasi-equilibrium Gaussian distribution, while their distribution with respect to the numbers of molecules practically does not change.

As a numerical illustration, we have considered the homogeneous formation (via nucleation and concomitant chemical aging) of model aqueous hydrophilic/hydrophobic organic (AHHO) aerosols consisting of water, 2−methylglyceric acid (as a hydrophilic compound), and 3−methyl-4-hydroxybenzoic acid (as a hydrophobic organic compound), in the air containing the vapors of these compounds, as well as typical atmospheric gaseous species. Calculations were carried out for various values of sticking and thermal adaptation coefficients.

Numerical evaluations have shown that, in the model system considered, the condition of the hierarchy of time scales is well fulfilled. This means, as first predicted in CNT by Grinin and Kuni (1989), that the thermal relaxation of the droplet distribution function occurs much faster than its evolution with respect to numbers of droplet molecules. Our estimates also suggest that the chemical aging of aqueous organic aerosols may markedly enhance their formation via nucleation and that such an enhancement becomes more pronounced with decreasing saturation ratio of water vapor, when
the nucleation rate decreases.

At present, it is not possible to make a comparison between our theoretical predictions and experimental data, because even the most modern experimental methods can not provide data on the time dependence of the distribution of aqueous organic droplets with respect to the temperature. Such a comparison will be eventually necessary when appropriate experimental data become available.

In order to describe the evolution of the system after the stage of thermal relaxation and to obtain an expression for the rate of non-isothermal formation of aqueous organic aerosols via concurrent nucleation and chemical aging, it is necessary to solve the full kinetic equation taking account of all the terms contributing to the temporal evolution of the droplet distribution function. This problem will be the object of our further research. Of course, as long as there are no experimental nor theoretical data on sticking and thermal accommodation coefficients and the aggregate forward reaction rate and equilibrium constants of the sequence of chemical reactions (involved in aerosol aging), theoretical predictions will remain uncertain enough. Nevertheless, we would be able to get approximate magnitudes of these coefficients by theoretical predictions and experimental data for the rates of concurrent nucleation and chemical aging once the experimental ones become available.

However, it is already clear that the enthalpy of heterogeneous chemical reactions can have a significant impact on the formation and evolution of aqueous organic aerosols via nucleation and concomitant chemical aging.\textsuperscript{21,39} Therefore, the proposed approach to developing a non-isothermal theory of this phenomenon can be expected to improve current computer models for the distribution of such aerosol particles with respect to their size and chemical composition; such a distribution constitutes a necessary component of climate models.\textsuperscript{2,3}
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Captions

to Figures 1 and 2 of the manuscript “Enthalpy effect on the kinetics of concurrent nucleation and chemical aging of aqueous organic aerosols: The stage of thermal relaxation” by Y. S. Djikaev and B. I. Djikkaity.

Figure 1. The dependence of the thermal relaxation time $t_\xi$ of an ensemble of atmospheric AHHO aerosols, evolving via nucleation and concomitant chemical aging, on various parameters of the surrounding air: a) the relaxation time $t_\xi$ as a function of the aggregate equilibrium constant $K_{eq}$ at various saturation ratios of the water vapor, $\zeta_1$, as indicated in the figure panel; b) the relaxation time $t_\xi$ as a function of the saturation ratio of the water vapor $\zeta_1$ at various aggregate equilibrium constants $K_{eq}$, as indicated in the figure panel. In both panels (a) and (b) $T_0 = 293.15$ K, $\zeta_2 = 0.01$, and $\zeta_3 = 0.3$ (the parameters of noncondensable species are specified in the text).

Figure 2. The dependence of the thermal relaxation time $t_\xi$ of an ensemble of atmospheric AHHO aerosols, evolving via nucleation and concomitant chemical aging, on the saturation ratios of organic vapors in the the surrounding air: a) the relaxation time $t_\xi$ as a function of the saturation ratio $\zeta_2$ of the hydrophilic organic vapor at a fixed saturation ratio $\zeta_3 = 0$ of the hydrophobic organic vapor; b) the relaxation time $t_\xi$ as a function of the saturation ratio $\zeta_3$ of the hydrophobic organic vapor at a fixed saturation ratio $\zeta_2 = 0.01$ of the hydrophobic organic vapor. In both panels (a) and (b) $T_0 = 293.15$ K, $K_{eq} = 3$, and $\zeta_1 = 0.13$ (the parameters of noncondensable species are specified in the text).
Figure 1:
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