Kinetic equation of concurrent nucleation and chemical aging of an ensemble of aqueous organic aerosols

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Abstract

Using the formalism of the classical nucleation theory, we derive a novel kinetic equation for the size and composition distribution of an ensemble of aqueous organic aerosols, evolving via nucleation and concomitant chemical aging. This distribution can be drastically affected by the enthalpy of heterogeneous chemical reactions and the depletion of organic trace gases absorbed by aerosols. A partial differential equation of second order for the temporal evolution of this distribution is obtained from the discrete equation of balance via Taylor series expansions. Once reduced to the canonical form of the multidimensional Fokker-Planck equation, this kinetic equation can be solved via the method of complete separation of variables. The new kinetic equation opens a new direction in the development of the kinetic theory of first-order phase transitions, while its applications to the formation and evolution atmospheric organic aerosols may drastically improve the accuracy of global climate models.

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Liquid organic aerosols (OAs) constitute a significant fraction of atmospheric particulate matter [1-3]. They have a high impact on the Earth climate, air quality, and human health by directly contributing to both the scattering and adsorption of solar radiation [4-6]. Particularly widespread are aqueous aerosols consisting of water and both hydrophobic and hydrophilic compounds [2,3]. Hereafter, such an aerosol particle will be referred to as an aqueous hydrophilic/hydrophobic organic (AHHO) aerosol.

Although the chemical composition of OAs can be extremely complex [2,3], one can anticipate that the hydrophilic parts of organic compounds of an aqueous OA particle will be embedded into its aqueous core, leaving the hydrophobic parts pointed outward [7]. Hydrophobic compounds at the surface of an aerosol hinder its ability to act as a cloud condensation nucleus [8]. However, the hygroscopicity of such aerosols can significantly increase via several mechanisms [9-11], of which the “chemical aging” is the most widespread and least understood. This mechanism consists of heterogeneous chemical reactions between aerosol surface-located hydrophobic molecules and some atmospheric gaseous species which enable aerosols to become cloud condensation nuclei (CCN) [7].

In the atmosphere, the chemical aging of OAs occurs concomitantly [7] with the condensation of water and other vapors, such as oxidized volatile and semi-volatile organic compounds (OVOCs and SVOCs, respectively). Recently, in the framework of classical nucleation theory (CNT) we developed a thermodynamic model [12-16] for the formation and evolution of aqueous organic aerosols via concurrent nucleation/condensation and chemical aging.

That model allows one to determine the threshold parameters necessary for the Köhler activation of such aerosols [12-16]. We have also shown that the size and composition distribution of an ensemble of aqueous organic aerosols, evolving via nucleation/condensation and concomitant chemical aging, may be affected by the release of the enthalpy of heterogeneous reactions and by the depletion of atmospheric trace gases [17], OVOCs, and SVOCs (hence decrease of their saturation ratios) due to
their uptake by aerosols. To properly account of these effects in global climate models, it is necessary to develop an analytical kinetic model for the temporal evolution of an ensemble of atmospheric aqueous organic aerosols occurring via both condensation and concomitant chemical aging.

As a foundation for such a theory, we hereafter present a kinetic equation for the size and composition distribution function of an ensemble of AHHO aerosols evolving via concurrent nucleation and chemical aging. We develop our model by using the formalism of the CNT and treating a particle of a new phase (liquid aerosol) in the framework of capillarity approximation [18,19].

Consider an air parcel containing a ternary mixture of 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; other air components are neglected. An aerosol itself is modeled as a spherical particle of a liquid multicomponent solution. Initially, it contains components 1, 2, and 3 due to their condensation from the surrounding air. Being 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 there. However, owing to chemical reactions with atmospheric species, molecules of component 3 can be transformed into hydrophilic entities.

Such a “hydrophobic-to-hydrophilic” conversion (i.e., chemical aging of organic aerosols) may proceed via diverse pathways each involving a variety of sequential heterogeneous reactions. However, it is most likely initiated [7] by atmospheric OH radicals abstracting H-atoms from the hydrophobic moieties of surfactant molecules on the aerosol surface.

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 steps of the most
probable sequence of reactions, involved in the chemical mechanism of aerosol aging, are [7]:

\[
\begin{align*}
\text{OH} \ (g) + \text{HR}/\text{aerosol} &\rightleftharpoons \text{H}_2\text{O} \ (g) + \text{R}^\cdot/\text{aerosol} . \quad (1) \\
\text{O}_2 \ (g) + \text{R}^\cdot/\text{aerosol} &\rightleftharpoons \text{RO}_2^\cdot/\text{aerosol} . \quad (2) \\
\text{RO}_2^\cdot/\text{aerosol} + \text{NO} \ (g) &\rightleftharpoons \text{RO}^\cdot/\text{aerosol} + \text{NO}_2 (g) . \quad (3)
\end{align*}
\]

On the first step of this pathway, an OH radical abstracts an H atom from the hydrophobic moiety of a surfactant molecule, thus producing a surface-bound radical R^\cdot (reaction (1)). The latter is rapidly oxidized by O_2 molecules at the second step of the sequence, thus producing a new surface-bound radical RO_2^\cdot (reaction (2)). The rate constants of reactions (1) and (2) are of the same order [7], but the concentration of oxygen molecules in the atmosphere is much higher (by \sim 12 orders of magnitude) than that of OH radicals. Hence, every radical R^\cdot produced by reaction (1) is almost immediately oxidized by reaction (2). The further evolution of radicals RO_2^\cdot may vary, but always results in the formation of water soluble and/or volatile species and/or hydrophilic radicals [7]. Reaction (3) represents one such a pathway (see ref.7 for the discussion of various reactive channels of radicals RO_2^\cdot and RO^\cdot).

As a result of sequential reactions (1)-(3), a surface located hydrophobic molecule HR is converted into a radical RO^\cdot. 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^\cdot will be able to diffuse into the aerosol interior. According to recent numerical evaluations [14], the characteristic time of the entire sequence of reactions (1)-(3) is significantly shorter than the characteristic time of the evolution of the total number of molecules in the aerosol. Therefore, the number of intermediate radicals R^\cdot and RO_2^\cdot in the aerosol can be assumed negligible compared to the number of “final” radicals RO^\cdot, so that the entire sequence (1)-(3) produces only one additional component in the aerosol, namely, radical RO^\cdot; it will be referred to as component 4.
Denote the numbers of molecules of components 1 (water), 2 (hydrophilic organic), and 3 (hydrophobic organic) in the aerosol will be denoted by $\nu_1, \nu_2,$ and $\nu_3,$ respectively, and the number of radicals $\text{RO}^\bullet$ (component 4) in the aerosol 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”.

Choosing $\nu_1, \nu_2, \nu_3,$ and $\nu_4$ as the independent variables of state of a single aerosol, consider an ensemble of AHHO aerosols and denote their distribution function with respect to $\nu_1, \nu_2, \nu_3, \nu_4$ at time $t$ by $g(\nu_1, \nu_2, \nu_3, \nu_4, t)$. Hereafter, for the sake of convenience, any function $f$ of variables $\nu_1, \nu_2, \nu_3, \nu_4$ may be denoted either $f(\nu_1, \nu_2, \nu_3, \nu_4)$ or $f(\nu, \tilde{\nu})$, where $\nu$ would represent all four variables $\nu_1, \ldots, \nu_4$, whereas the “complementary” variable $\tilde{\nu}_i$ represents only three of them, the “excluded” variable being $\nu_i$. Thus, e.g., $g(\nu), t) = g(\nu_i, \tilde{\nu}_i, t) = g(\nu_1, \nu_2, \nu_3, \nu_4, t)$.

Let us construct a discrete balance equation governing the temporal evolution of $g(\nu_1, \nu_2, \nu_3, \nu_4, t)$. As usual in CNT,\textsuperscript{18–20} assume that the metastability of vapor mixture in the air is created instantaneously, its temperature $T$ and the number densities of non-condensable gas molecules are also constant, and every aerosol attains its internal thermodynamical equilibrium before each successive interaction with air, so that its temperature is equal to the air temperature $T$.

The material exchange between an aerosol and air occurs via three types of elementary interactions: 1) absorption of a molecule of component $i$ ($i = 1, 2, 3$) from the air into the aerosol; 2) emission of a molecule of component $i$ ($i = 1, 2, 3$) from the aerosol into the air; 3) sequence (1)-(3) of forward and backward chemical reactions on the aerosol surface whereby a radical $\text{RO}^\bullet$ is either produced or destroyed. Therefore, the temporal evolution of the distribution function $g(\nu, t)$ can be described by the discrete balance equation \textsuperscript{[20]}

$$\frac{\partial g(\nu, t)}{\partial t} = - \sum_{i=1}^{3} [J_i(\nu_i + 1, \tilde{\nu}_i, t) - J_i(\nu, t)] - [J_4(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1, t) - J_4(\nu, t)], \quad (4)$$
where the fluxes $J_i(\nu, t)$ ($i = 1, .., 4$) are defined as

$$J_i(\nu, t) = W_i^+(\nu_i - 1, \nu_i)g(\nu_i - 1, \nu_i, t) - W_i^-(\{\nu\})g(\{\nu\}, t) \quad (i = 1, 2, 3),$$

$$J_4(\{\nu\}, t) = W_4^+(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1)g(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1) - W_4^-(\{\nu\})g(\{\nu\}, t),$$

with $W_i^+ = W_i^+(\{\nu\})$ ($i = 1, 2, 3$) and $W_i^- = W_i^-(\{\nu\})$ ($i = 1, 2, 3$) being the numbers of molecules of component $i$ that the aerosol absorbs from and emits into the air ("absorption" and "emission" rates, respectively), and $W_4^+ = W_4^+(\{\nu\})$ and $W_4^- = W_4^-(\{\nu\})$ the aggregate rates of forward and backward reactions, respectively, of the sequence (1)-(3) (the evolution of aerosols is assumed to occur through the absorption from and emission into the vapor of single molecules of components 1, 2, and 3, or through a single sequences (1)-(3) of forward and backward reactions whereby a radical RO$^\ast$ is either formed or destroyed).

In CNT, the absorption rate $W_i^+$ ($i = 1, 2, 3$) is provided by the gas-kinetic theory, whereas the emission rate $W_i^-$ is determined through $W_i^+$ by using the principle of detailed balance [18,19]. It requires that for the equilibrium distribution function $g_n(\{\nu\})$ every equilibrium flux $J_n^i \equiv J_n^i(\{\nu\})$ ($i = 1, .., 4$) be equal to 0. Applying this principle to $J_4^i$, one can obtain [20] an interesting relationship between the aggregate rates of forward and backward sequence of heterogeneous chemical reactions (1)-(3),

$$W_4^-(\{\nu\}) \simeq W_4^+(\{\nu\})[1 - (F'_2(\{\nu\}) - F'_4(\{\nu\}))],$$

where $F(\{\nu\})$ denotes the free energy of formation of an AHHO aerosol (expressed in thermal units $k_B T$, with $k_B$ being Boltzmann’s constant), and $F'_i(\nu) = \partial F(\nu)/\partial \nu_i$ ($i = 1, .., 4$). Clearly, this relationship can be also used to obtain a relationship between the corresponding reaction rate constants.

During nucleation, aerosols overcome a free-energy barrier (5D surface determined by the function $F = F(\{\nu\})$) to become growing droplets. At this stage, aerosols evolve in the near-critical region of the space of variables $\nu_1, .., \nu_4$, i.e., in the vicinity of the “saddle point” of the free-energy surface [13].
with the coordinates \( \nu_{1c}, \nu_{2c}, \nu_{3c}, \nu_{4c} \) (subscript “c” marks quantities for the saddle point). Assuming that in this vicinity \( \nu_i \gg 1 \) \((i = 1, \ldots, 4)\), expanding eqs.(4)-(6) in Taylor series in the deviations of aerosol characteristics from \( \nu_1, \nu_2, \nu_3, \) and \( \nu_4 \) and retaining only leading terms therein, and with the same accuracy approximating \( W_i^+ \approx W_i^{+c} \) \((i = 1, \ldots, 4)\), one can [20] reduce eq.(4) to

\[
\frac{\partial g(\{\nu\}, t)}{\partial t} = \sum_{i=1}^{4} W_{ic}^+ \frac{\partial}{\partial \nu_i} \left( F_i'(\{\nu\}) + \frac{\partial}{\partial \nu_i} g(\{\nu\}, t) \right) + W_{4c}^+ \left[ \frac{\partial}{\partial \nu_2} \left( F_2'(\{\nu\}) + \frac{\partial}{\partial \nu_2} \left( F_4'(\nu_i) + \frac{\partial}{\partial \nu_4} \left( F_2'(\nu_i) + \frac{\partial}{\partial \nu_2} \right) \right) \right] \right] g(\{\nu\}, t).
\]

This is the kinetic equation of concurrent multicomponent nucleation and chemical aging of an ensemble of model organic aerosols. Note that the second term on the RHS of eq.(8) arises because any sequence of reactions (1)-(3) is results in the change of not only \( \nu_4 \), but also \( \nu_2 \); the latter also changes independently via the direct exchange of component 2 between aerosol and air.

By definition of the near-critical region [18,21], \( F(\{\nu\}) \) can be approximated there as a bilinear form

\[
F(\{\nu\}) = F_c + \frac{1}{2} \sum_{i=1}^{4} F''_{ijc} (\nu_i - \nu_{ic})(\nu_j - \nu_{jc}) = F_c + \Delta \nu^T A \Delta \nu,
\]

where \( F''_{ij} = \partial^2 F/\partial \nu_i \partial \nu_j \) \((i = 1, \ldots, 4)\) and the matrix notation was introduced with a real symmetric 4 \( \times \) 4-matrix \( A = [a_{ij}] \equiv \frac{1}{2} F''_{ijc} \) \((i, j = 1, \ldots, 4)\) and a real column-vector of length 4 \( \Delta \nu = [\Delta \nu_i] \equiv [\nu_i - \nu_{ic}] \) \((i = 1, \ldots, 4)\); superscript “T” marks the transpose of a matrix/vector. In this approximation, the first derivatives \( F_i'(\{\nu\}) \) \((i = 1, \ldots, 4)\) are linear superpositions of deviations \( \Delta \nu_i \) \((i = 1, \ldots, 4)\). Thus, the accuracy of eq.(8) combined with eq.(9) corresponds to the Fokker-Planck approximation [22], widely used in the kinetics of the first-order phase transitions [18,19,21].

Equation (8) must be solved subject to appropriate boundary conditions. In the framework of CNT, the latter are formulated by using the equilibrium distribution \( g_e(\{\nu\}) \) [18,21]. In the near-
critical region, $g_e(\nu)$ can be written (in virtue of eq.(9)) as [21]

$$g_e(\nu) = \left(\frac{1}{v_c}\right) \exp\left[-F_c - \frac{1}{2} \sum_{i=1}^{4} F''_{ijc} \Delta \nu_i \Delta \nu_j\right], \quad (10)$$

where $v_c$ is the volume per molecule in the saddle point aerosol (nucleus). As clear, the variables $\nu_1, \ldots, \nu_4$ are not separated in the equilibrium distribution (nor in the kinetic equation (8)). Hence, they are not convenient to formulate simple enough boundary conditions to the kinetic equation (8).

The problem can be overcome by using an elegant method of complete separation of variables developed by Kuni and co-workers [23,21]. Its most general presentation can be found in Ref.[24].

First, it is necessary to introduce such new variables (instead of $\nu_1, \ldots, \nu_4$) that would transform the bilinear form in eq.(9) into a quadratic one, without cross terms. Let us denote a set of such variables by $\{x\} = (x_1, \ldots, x_4)$ and the corresponding column-vector by $x = [x_i]$ ($i = 1, \ldots, 4$).

According to the spectral theorem [25], matrix $A$ is orthogonally diagonalizable because it is real and symmetric. Hence, there exists a real orthogonal $4 \times 4$-matrix $P \equiv [p_{ij}]$ ($i, j = 1, \ldots, 4$), such that

$$P^T A P = D, \quad (11)$$

where the columns of the matrix $P$ are 4 linearly independent orthonormal eigenvectors of $A$, and the diagonal elements of the diagonal matrix $D$ are the corresponding eigenvalues $\lambda_1, \ldots, \lambda_4$ of $A$.

Under conditions when a multicomponent first-order phase transition occurs via nucleation, the corresponding free energy surface has a shape of a hyperbolic paraboloid (“saddle” shape in three dimensions). Therefore, one of the eigenvalues of matrix $A$ is negative while all others are positive, so that $\det(A) < 0$. Denoting the negative eigenvalue by $\lambda_1$, one can thus define the variables

$$x_i = |\lambda_i|^{1/2} \sum_{j=1}^{4} p_{ji} \Delta \nu_j \quad (i = 1, \ldots, 4), \quad (12)$$

in which the bilinear form (9) transforms into

$$F(\{x\}) = F_c - \sum_{i=1}^{4} \epsilon_i x_i^2 \quad (\epsilon_1 = 1, \epsilon_2 = \epsilon_3 = \epsilon_4 = -1). \quad (13)$$
The transformation of variables (12) allows one to re-write the kinetic equation of nucleation and chemical aging, eq.(8), in the canonical form of Fokker-Planck equation

$$\frac{\partial g(\{x\}, t)}{\partial t} = \sum_{i,j=1}^{4} b_{ij} \frac{\partial}{\partial x_i} \left( \frac{\partial}{\partial x_j} - \epsilon_j^2 x_j^2 \right) g(\{x\}, t), \quad (14)$$

where $b_{ij}$ ($i, j = 1, \ldots, 4$) are the elements of a $4 \times 4$ matrix $B$ of diffusion coefficients in variables $\{x\}$,

$$b_{ij} = |\lambda_i \lambda_j|^{1/2} \left[ \sum_{k=1}^{4} W_{ki}^+ p_{kpkj} - W_{ki}^- (p_{2i} p_{2j} - p_{2i} p_{4j} - p_{4i} p_{2j}) \right]. \quad (15)$$

Clearly, the matrix $B$ is real and symmetric, but its positiveness is not obvious. The physically reasonable boundary conditions to equation (14) can be now rigorously formulated:

$$g(\{x\}, t) / \text{ge}(\{x\}) = \begin{cases} 1 & (x_0 \to -\infty \text{ and } \sum_{i=1}^{4} \epsilon_i x_i^2 > 0), \\ 0 & (x_0 \to \infty \text{ and } \sum_{i=1}^{4} \epsilon_i x_i^2 > 0), \end{cases} \quad (16)$$

and $g(\{x\}, t) \to 0$ as $\sum_{i=1}^{4} \epsilon_i x_i^2 \to -\infty$.

Solving the kinetic equation (14) subject to conditions (16) still remains a formidable task because the variables $x_1, \ldots, x_4$ do not separate in eq.(14) - the diffusion matrix $B$ is not diagonal. Such a difficulty can be overcome by introducing new variables $\xi_1, \ldots, \xi_4$ via the Lorentz transformation, whereof the Jacobian equals 1 and which leaves the quadratic form $\sum_i \epsilon_i x_i^2$ invariant, so that

$$\xi_i = \sum_j L_{ij} x_j, \quad F = F_c - \sum_{i=1}^{4} \epsilon_i \xi_i^2, \quad g(\{x\}, t) = g(\{\xi\}, t), \quad (17)$$

where $L_{ij}$ are the Lorentz transformation coefficients. This allows one to find the solution of the kinetic equation and thoroughly investigate its properties. The most general formulation of the method is presented in Ref.[24], while its applications to various particular problems of the kinetics of first-order phase transitions without chemical reactions were reported in Ref.[23].

As a numerical illustration of the foregoing, we considered the concurrent nucleation and chemical aging of model AHHO aerosols in the air containing a ternary vapor mixture of water, 2–methylglyceric acid $[C_4H_8O_4]$, and 3–methyl-4–hydroxy-benzoic acid $[C_8H_8O_3]$, as well as nitrogen oxide, hydroxyl...
radicals, oxygen, and nitrogen dioxide. According to Couvidat et al. [17], 2-methylglyceric acid can be classified as a hydrophilic compound, whereas 3-methyl-4-hydroxy-benzoic acid can be characterized as a hydrophobic one. The atmospheric conditions were assumed to be as in Refs.[13-16].

Hydrophobic molecules of 3-methyl-4-hydroxy-benzoic acid are mostly located at the aerosol surface, with the methyl groups -CH$_3$ exposed to the air. The abstraction of an H-atom from the methyl group of a 3-methyl-4-hydroxy-benzoic acid molecule can be considered as the first step in its hydrophobic-to-hydrophilic conversion, so that the radicals R$^\bullet$ and RO$^\bullet$ in eqs.(1)-(3) are can be identified as -CH$_2$-C$_6$H$_3$-OH-COOH and -OCH$_2$-C$_6$H$_3$-OH-COOH, respectively. Thus, one can consider the 4-component solution in the aerosol as a liquid mixture of functional groups whereof all relevant parameters for activity coefficients are given in the updated tables of UNIFAC method [13].

The free energy of formation of an AHHO aerosol as a function of four variables $F = F(\nu_1, \ldots, \nu_4)$ was obtained in Ref.[13]. Its second derivatives at the saddle point (under the same conditions as in Refs.[13-16]) provide the matrix $A$ in eq.(9). This matrix $A$, the corresponding orthogonal matrix
P which diagonalizes A, and the resulting diagonal matrix \( D = P^T A P \) are

\[
A = \begin{bmatrix}
0.00508819 & -0.0102213 & 0.000425629 & -0.00779759 \\
-0.0102213 & 0.029559 & -0.00841285 & -0.00106402 \\
0.000425629 & -0.00841285 & 0.04116663 & -0.0144458 \\
-0.00779759 & -0.00106402 & -0.0144458 & 0.0108751
\end{bmatrix},
\]

\[
P = \begin{bmatrix}
-0.151706 & 0.283741 & 0.60688 & 0.726755 \\
0.393328 & -0.859266 & 0.155576 & 0.287666 \\
-0.846176 & -0.367706 & -0.311695 & 0.227209 \\
0.325981 & 0.214351 & -0.71438 & 0.580906
\end{bmatrix},
\]

\[
D = \begin{bmatrix}
0.0507183 & 0 & 0 & 0 \\
0 & 0.0295995 & 0 & 0 \\
0 & 0 & 0.0114281 & 0 \\
0 & 0 & 0 & -0.00505728
\end{bmatrix}
\]

As required, the diagonal elements \( \lambda_1, .., \lambda_4 \) of the matrix D and the corresponding columns \( \overline{P}_i, .., \overline{P}_4 \) of the orthogonal matrix P represent the eigenvalues and eigenvectors of the original matrix A, so that \( A \overline{P}_i = \lambda_i \overline{P}_i \) (i = 1, ..., 4). (Numerical orthogonal diagonalization was performed with Mathematica 11.3; the off-diagonal elements of D are equal to zero with the accuracy of \( 10^{-16} \) or better).

In summary, we have derived the kinetic equation for the distribution function of an ensemble of aqueous organic aerosols evolving via concurrent nucleation and chemical aging. The proposed equation takes account of heterogeneous chemical reactions on the surface of aerosols and hence differs from the classical kinetic equation of multicomponent nucleation. The principle of detailed balance allows one to obtain a relationship between aggregate forward and backward rates (and hence rate constants) of the sequence of reaction whereby the chemical aging occurs. This relationship can
be experimentally verified in appropriate experiments or it can serve as a means for the indirect experimental determination of the rates or rate constants of some of the chemical reactions involved. We have also reduced the new kinetic equation to the canonical form of a 4-dimensional Fokker-Planck equation, whereof the diffusion coefficients depend on the aggregate rate of the forward sequence of chemical reactions, and formulated rigorous boundary conditions to this equation. As outlined, this kinetic equation can be solved by using the method of complete separation of variables developed in CNT for the kinetics of multidimensional first-order phase transitions without chemical reactions.

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Supplementary Material for:
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1 Derivation of equation (4)

Denote the numbers of molecules of components 1 (water), 2 (hydrophilic organic), and 3 (hydrophobic organic) in an AHHO aerosol by \( \nu_1, \nu_2, \) and \( \nu_3, \) respectively, and the number of radicals \( \text{RO}^\bullet \) (component 4) in the aerosol by \( \nu_4; \) for the sake of simplicity and uniformity, radicals \( \text{RO}^\bullet \) will be sometimes referred to as “molecules of component 4”. Since components 2 and 4 are mostly hydrophilic, they are assumed to be distributed more or less uniformly within the aerosol, while molecules of component 3 will be located mostly on the aerosol surface (although their dissolution within the aerosol core can not be excluded).

Choosing \( \nu_1, \nu_2, \nu_3, \) and \( \nu_4 \) as the independent variables of state of a single aerosol, consider an ensemble of AHHO aerosols in the air and denote their distribution function with respect to \( \nu_1, \nu_2, \nu_3, \) and \( \nu_4 \) at time \( t \) by \( g(\nu_1, \nu_2, \nu_3, \nu_4, t) \). Let us construct a discrete balance equation governing the temporal evolution of \( g(\nu_1, \nu_2, \nu_3, \nu_4, t) \). Depending on the convenience, any function \( f \) of variables \( \nu_1, \nu_2, \nu_3, \nu_4 \) can be denoted either \( f(\nu_1, \nu_2, \nu_3, \nu_4) \) or \( f(\{\nu\}) \) or \( f(\nu_i, \tilde{\nu}_i) \), where \( \{\nu\} \) would denote either the aerosol itself or, as a function argument, all four independent variables of state of the aerosol, \( \nu_1, \nu_2, \nu_3, \nu_4 \), whereas the “complementary” variable \( \tilde{\nu}_i \) would represents only three of them.

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the “excluded” variable being \( \nu_i \) (the total number of molecules in the aerosol will be denoted by \( \nu = \nu_1 + .. + \nu_4 \)). In this notation, e.g., \( g(\{\nu\}, t) = g(\nu_i, \tilde{\nu}_i, t) = g(\nu_1, \nu_2, \nu_3, \nu_4, t) \)

As usual in CNT, let us first assume that the metastability of vapor mixture in the air is created instantaneously and does not change during the whole nucleation process; this assumption can be subsequently removed and the kinetic theory properly modified for application to more complicated (and more realistic) environmental conditions. The temperature \( T \) of the air parcel and the number densities of non-condensible gas molecules are also fixed. Aerosols during the nucleation stage are so small that the characteristic times of their internal relaxation processes are very small in comparison with the time between two of its successive interactions with the air, and the interactions themselves take place under a free-molecular regime. Thus, one can assume that the aerosol attains its internal thermodynamical equilibrium before each successive interaction with air, so that the aerosol temperature can be also assumed to be equal to \( T \).

The material exchange between an aerosol 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 aerosol \( \{\nu\} \) with the rate \( W_i^+ = W_i^+(\{\nu\}) \);

(e123) emission of a molecule of component 1 or 2 or 3 from the aerosol \( \{\nu\} \) into the air with the rate \( W_i^- = W_i^-(\{\nu\}) \);

(f4) production of a “molecule” of component 4 (radical \( RO^* \)) via the forward sequence of heterogeneous chemical reactions (1)-(3) on the surface of aerosol \( \{\nu\} \), with the aggregate rate \( W_4^+ = W_4^+(\{\nu\}) \);

(b4) destruction of a “molecule” of component 4 (radical \( RO^* \)) via the backward sequence of heterogeneous chemical reactions (1)-(3) on the surface of aerosol \( \{\nu\} \), with the aggregate rate \( W_4^- = W_4^-(\{\nu\}) \);
Therefore, the temporal evolution of the distribution function \( g(\nu_1, \nu_2, \nu_3, \nu_4, t) \) can be described by the discrete balance equation

\[
\frac{\partial g(\nu_1, \nu_2, \nu_3, \nu_4, t)}{\partial t} = D_1 + D_2 + D_3 + D_4, \tag{S1}
\]

where

\[
D_1 = W_1^+(\nu_1 - 1, \nu_2, \nu_3, \nu_4)g(\nu_1 - 1, \nu_2, \nu_3, \nu_4, t) - W_1^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \]
\[
+ W_1^-(\nu_1 + 1, \nu_2, \nu_3, \nu_4)g(\nu_1 + 1, \nu_2, \nu_3, \nu_4, t) - W_1^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \tag{S2}
\]

\[
D_2 = W_2^+(\nu_1, \nu_2 - 1, \nu_3, \nu_4)g(\nu_1, \nu_2 - 1, \nu_3, \nu_4, t) - W_2^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \]
\[
+ W_2^-(\nu_1, \nu_2 + 1, \nu_3, \nu_4)g(\nu_1, \nu_2 + 1, \nu_3, \nu_4, t) - W_2^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \tag{S3}
\]

\[
D_3 = W_3^+(\nu_1, \nu_2, \nu_3 - 1)g(\nu_1, \nu_2, \nu_3 - 1, \nu_4, t) - W_3^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \]
\[
+ W_3^-(\nu_1, \nu_2, \nu_3 + 1, \nu_4)g(\nu_1, \nu_2, \nu_3 + 1, \nu_4, t) - W_3^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \tag{S4}
\]

\[
D_4 = W_4^+(\nu_1, \nu_2 + 1, \nu_3, \nu_4 - 1)g(\nu_1, \nu_2 + 1, \nu_3, \nu_4 - 1, t) - W_4^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \]
\[
+ W_4^-(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1)g(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1, t) - W_4^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t). \tag{S5}
\]

Note 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 \( RO^* \) is either formed or destroyed.

The terms \( D_1, D_2, \) and \( D_3 \) on the RHS of eq.(S1) represent the contributions to \( \partial g(\{\nu\}, t)/\partial t \) from the material exchange events of type (a123) and (b123), whereas the term \( D_4 \) represents the contributions to \( \partial g(\{\nu\}, t)/\partial t \) from the elementary events of type (f4) and (b4). Furthermore, on the RHS of the each of eqs.(S2)-(S4) the first two terms represent the contributions to \( \partial g(\{\nu\}, t)/\partial t \)
from the absorption events (a123) of air molecules by aerosols, whereas the third and forth terms therein are due to the emission of molecules from aerosols into the air. On the RHS of eq.(S5), 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 $RO^*$ are produced), whereas the third and fourth terms therein are due to the backward sequences (1)-(3) (whereby radicals $RO^*$ are destroyed). As clear from eq.(S5) 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 $\nu_2$, while the latter can also change independently due to the direct material exchange between aerosols and air.

In the space of variables $\nu_1, .., \nu_4$, let us introduce the flux of aerosols along the axis $\nu_i$ ($i = 1, 2, 3$) at time moment $t$ as

$$J_i(\{\nu\}, t) = W_i^+(\nu_i - 1, \bar{\nu}_i)g(\nu_i - 1, \bar{\nu}_i, t) - W_i^-((\nu))g((\nu), t) \quad (i = 1, 2, 3), \quad (S6)$$

and the flux of aerosols along the axis $\nu_4$ as

$$J_4(\{\nu\}, t) = W_4^+(\nu_1, \nu_2 + 1, \nu_3, \nu_4 - 1)g(\nu_1, \nu_2 + 1, \nu_3, \nu_4 - 1) - W_4^-((\nu))g((\nu), t). \quad (S7)$$

Taking these definitions into account, one can rewrite equations (S1)-(S5) as

$$\frac{\partial g(\{\nu\}, t)}{\partial t} = -\sum_{i=1}^{3} [J_i(\nu_i + 1, \bar{\nu}_i, t) - J_i((\nu), t)] - [J_4(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1, t) - J_4((\nu), t)], \quad (S8)$$

which is equation (4) in the main text.

### 2 Derivation of equation (7)

In CNT, the expressions for the absorption rates $W_i^+(\nu_1, \nu_2, \nu_3, \nu_4)$ ($i = 1, 2, 3$) are provided by the gas-kinetic theory, as

$$W_i^+(\{\nu\}) = \frac{1}{4} \alpha_i n_i v_{10} S(\{\nu\}) \quad (i = 1, 2, 3), \quad (S9)$$
where $\alpha_i$, $n_i$, $v_{Ti}$ $(i = 1, 2, 3)$ are the sticking coefficient, number density, and mean thermal velocity, respectively, of molecules of component $i$, and $S(\{\nu\})$ is the surface area of the aerosol. The emission rates $W_i^-(\{\nu\})$ $(i = 1, 2, 3)$ are determined through the corresponding $W_i^+(\{\nu\})$ on the basis of the principle of detailed balance [18,19]. According to the requirement of this principle, for the equilibrium distribution function $g_e(\{\nu\})$ not only the entire RHS of eq.(S8) is equal to 0, but every equilibrium flux $J_e^i \equiv J_e^i(\{\nu\})$ must be equal to 0.

Applying this principle to the flux $J_e^i$ $(i = 1, 2, 3)$ and taking into account that $g_e(\{\nu\}) = N_f \exp[-F(\{\nu\})]$, where $N_f$ is the normalization factor and $F(\{\nu\})$ is the free energy of formation of an aerosol $\{\nu\}$ in thermal units $k_B T$, we have

$$W_i^-(\{\nu\}) = W_i^+(\nu_i - 1, \tilde{\nu}_i) \exp[-(F(\nu_i - 1, \tilde{\nu}_i) - F(\{\nu\}))]. \quad (S10)$$

In the near-critical region (i.e., vicinity of the “saddle point” of the 5D free-energy surface determined by the function $F = F(\{\nu\})$), aerosols are large enough, $\nu_i \gg 1$ $(i = 1, \ldots, 4)$, one can use conventional for CNT approximations

$$W_i^+(\nu_i - 1, \tilde{\nu}_i) \approx W_i^+(\{\nu\}), \quad F(\nu_i - 1, \tilde{\nu}_i) \approx F(\{\nu\}) - F'_i(\{\nu\}). \quad (S11)$$

$F'_i(\{\nu\}) = \partial F(\{\nu\})/\partial \nu_i$ $(i = 1, \ldots, 4)$ Expanding the exponential in eq.(S10) in Taylor series and neglecting terms of the order of $1/\nu^2$ and smaller therein, we obtain

$$W_i^-(\{\nu\}) \approx W_i^+(\{\nu\})(1 + F'_i(\{\nu\})) \quad (i = 1, 2, 3). \quad (S12)$$

Note that this approximation is valid only for large enough aerosols $\nu \gg 1$ in the near-critical region.

Applying the principle of detailed balance to the flux $J_e^4$ and using similar considerations, one can obtain one can obtain an interesting approximate relationship between the aggregate rates of forward and backward sequence of heterogeneous chemical reactions (1)-(3):

$$W_4^-(\{\nu\}) \approx W_4^+(\{\nu\})(1 - (F'_2(\{\nu\}) - F'_4(\{\nu\}))), \quad (S13)$$
which is eq.(7) in the main text. Clearly, this relationship between aggregate forward and backward reaction rates of sequence (1)-(3) can be also used to obtain a relationship between the corresponding reaction rate constants; such a relationship would depend on whether the heterogeneous reactions in sequence (1)-(3) are of the first or second order.

3 Derivation of equation (8)

In order to obtain eq.(8) from eq.(4), let us first expand in Taylor series (in deviations of \(\nu_i\pm 1\) from \(\nu_i\)) the fluxes \(J_i\) \((i = 1, .., 4)\) on the RHS of eq.(4):

\[
J_i(\nu_i + 1, \nu_i, t) \simeq J_i(\{\nu\}, t) + \frac{\partial J_i(\{\nu\}, t)}{\partial \nu_i} (i = 1, 2, 3),
\]

\[
J_4(\nu_1, \nu_2 - 1, \nu_3, \nu_4 + 1, t) \simeq J_4(\{\nu\}, t) - \frac{\partial J_4(\{\nu\}, t)}{\partial \nu_2} + \frac{\partial J_4(\{\nu\}, t)}{\partial \nu_4}.
\]

Here, it is taken into account that nucleating aerosols (in the near-critical region) are large enough so that \(\nu_i \gg 1\) \((i = 1, .., 4)\) and the terms with the second and higher order derivatives with respect to \(\nu_i\) \((i = 1, .., 4)\) in the Taylor series expansions can be neglected, as usual in CNT [18,19,21].

Next, with the same degree of accuracy, one can obtain the Taylor series expansions (in deviations of \(\nu_i\pm 1\) from \(\nu_i\)) of the distribution functions \(g(\{\nu\}, t)\) on the RHSs of eqs.(S6),(S7):

\[
g(\nu_i - 1, \nu_i, t) \simeq g(\{\nu\}, t) - \frac{\partial g(\{\nu\}, t)}{\partial \nu_i} (i = 1, 2, 3),
\]

\[
g(\nu_1, \nu_2 + 1, \nu_3, \nu_4 - 1, t) \simeq g(\{\nu\}, t) + \frac{\partial g(\{\nu\}, t)}{\partial \nu_2} - \frac{\partial g(\{\nu\}, t)}{\partial \nu_4}.
\]

Finally, according to the definition of the near-critical region, the width of the region is much smaller than the size of the critical aerosol, i.e., \((\nu_i - \nu_{ic})/\nu_c \ll 1\) in the near-critical region. Therefore, according to eq.(S9), one can assume that with a high degree of accuracy in that region \(W^+_i(\{\nu\}) \approx W^+_{ic}\) (subscript “c” marks quantity for the nucleus (critical aerosol). Taking this into
account, substituting eqs.(S14)-(S17) into the RHS of eq.(S8) and combining together appropriate
terms, one can obtain

\[
\frac{\partial g(\{\nu\}, t)}{\partial t} = \sum_{i=1}^{4} W_{ic}^{+} \frac{\partial}{\partial \nu_{i}} \left( F_{i}'(\{\nu\}) + \frac{\partial}{\partial \nu_{i}} g(\{\nu\}, t) \right) \\
+ W_{4c}^{+} \left[ \frac{\partial}{\partial \nu_{2}} \left( F_{2}'(\{\nu\}) + \frac{\partial}{\partial \nu_{2}} \right) \\
- \frac{\partial}{\partial \nu_{2}} \left( F_{4}'(\{\nu\}) + \frac{\partial}{\partial \nu_{4}} \right) - \frac{\partial}{\partial \nu_{4}} \left( F_{2}'(\{\nu\}) + \frac{\partial}{\partial \nu_{2}} \right) \right] g(\{\nu\}, t), \quad \text{(S18)}
\]

which is the Fokker-Planck equation (8) of the main text.