

Supplementary Information for:  
“Effect of chemical aging of aqueous organic aerosols on the rate of  
their steady-state nucleation”

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## 1 Derivation of equation (8)

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 RO $\bullet$  (component 4) in the aerosol by  $\nu_4$ ; for the sake of simplicity and uniformity, radicals 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 represent 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  $\nu = \nu_1 + \dots + \nu_4$ ). 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-condensable 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  $\text{RO}^\bullet$ ) 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  $\text{RO}^\bullet$ ) 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

$$\frac{\partial g(\nu_1, \nu_2, \nu_3, \nu_4, t)}{\partial t} = D_1 + D_2 + D_3 + D_4, \quad (\text{S1})$$

where

$$D_1 = W_1^+(\nu_1 - 1, \nu_2, \nu_3, \nu_4)g(\nu_1 - 1, \nu_2, \nu_3, \nu_4, t) - W_1^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \\ + W_1^-(\nu_1 + 1, \nu_2, \nu_3, \nu_4)g(\nu_1 + 1, \nu_2, \nu_3, \nu_4, t) - W_1^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \quad (\text{S2})$$

$$D_2 = W_2^+(\nu_1, \nu_2 - 1, \nu_3, \nu_4)g(\nu_1, \nu_2 - 1, \nu_3, \nu_4, t) - W_2^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \\ + W_2^-(\nu_1, \nu_2 + 1, \nu_3, \nu_4)g(\nu_1, \nu_2 + 1, \nu_3, \nu_4, t) - W_2^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \quad (\text{S3})$$

$$D_3 = W_3^+(\nu_1, \nu_2, \nu_3 - 1)g(\nu_1, \nu_2, \nu_3 - 1, \nu_4, t) - W_3^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \\ + W_3^-(\nu_1, \nu_2, \nu_3 + 1, \nu_4)g(\nu_1, \nu_2, \nu_3 + 1, \nu_4, t) - W_3^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \quad (\text{S4})$$

$$D_4 = W_4^+(\nu_1, \nu_2, \nu_3 + 1, \nu_4 - 1)g(\nu_1, \nu_2, \nu_3 + 1, \nu_4 - 1, t) - W_4^+(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t) + \\ + W_4^-(\nu_1, \nu_2, \nu_3 - 1, \nu_4 + 1)g(\nu_1, \nu_2, \nu_3 - 1, \nu_4 + 1, t) - W_4^-(\nu_1, \nu_2, \nu_3, \nu_4)g(\nu_1, \nu_2, \nu_3, \nu_4, t), \quad (\text{S5})$$

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  $\text{RO}^\bullet$  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 fourth 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  $\text{RO}^\bullet$  are produced), whereas the third and fourth terms therein are due to the backward sequences (1)-(3) (whereby radicals  $\text{RO}^\bullet$  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 with respect to the variable  $\nu_3$ , while the latter can also change independently due to the direct material exchange between aerosols and air.

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

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

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

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

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

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

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

$$W_i^+(\{\nu\}) = \frac{1}{4} \alpha_i n_i v_{\text{Ti}} S(\{\nu\}) \quad (i = 1, 2, 3), \quad (\text{S9})$$

where  $\alpha_i$ ,  $n_i$ ,  $v_{\text{Ti}}$  ( $i = 1, 2, 3$ ) 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.<sup>23–25</sup> 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  $J_i^e \equiv J_i^e(\{\nu\})$  must be equal to 0.

Applying this principle to the flux  $J_i^e$  ( $i = 1, 2, 3$ ) 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

$$W_i^-(\{\nu\}) = W_i^+(\nu_i - 1, \tilde{\nu}_i) \exp[-(F(\nu_i - 1, \tilde{\nu}_i) - F(\{\nu\}))] \quad (i = 1, 2, 3). \quad (\text{S10})$$

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,  $\nu_i \gg 1$  ( $i = 1, \dots, 4$ ), one can use conventional for CNT approximations

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

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

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

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  $J_4^e$  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):

$$W_4^-(\{\nu\}) \approx W_4^+(\{\nu\})[1 - (F'_3(\{\nu\}) - F'_4(\{\nu\}))], \quad (\text{S13})$$

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) occur via the Langmuir-Hinshelwood mechanism (reactions between species chemisorbed on the surface) or via the Rideal-Eley one (when a chemisorbed species reacts with a fluid-phase species).

In order to obtain eq.(8) from eq.(S8), let us first expand the fluxes  $J_i$  ( $i = 1, \dots, 4$ ) on the RHS of eq.(S8) in Taylor series (in deviations of  $\nu_i \pm 1$  from  $\nu_i$ ):

$$J_i(\nu_i + 1, \tilde{\nu}_i, t) \simeq J_i(\{\nu\}, t) + \frac{\partial J_i(\{\nu\}, t)}{\partial \nu_i} \quad (i = 1, 2, 3), \quad (\text{S14})$$

$$J_4(\nu_1, \nu_2, \nu_3 - 1, \nu_4 + 1, t) \simeq J_4(\{\nu\}, t) - \frac{\partial J_4(\{\nu\}, t)}{\partial \nu_3} + \frac{\partial J_4(\{\nu\}, t)}{\partial \nu_4}, \quad (\text{S15})$$

Here, it is taken into account that nucleating aerosols (in the near-critical region) are large enough so that  $\nu_i \gg 1$  ( $i = 1, \dots, 4$ ) and the terms with the second and higher order derivatives with respect to  $\nu_i$  ( $i = 1, \dots, 4$ ) in the Taylor series expansions can be neglected, as usual in CNT.<sup>23–25</sup>

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):

$$g(\nu_i - 1, \tilde{\nu}_i, t) \simeq g(\{\nu\}, t) - \frac{\partial g(\{\nu\}, t)}{\partial \nu_i} \quad (i = 1, 2, 3), \quad (\text{S16})$$

$$g(\nu_1, \nu_2, \nu_3 + 1, \nu_4 - 1, t) \simeq g(\{\nu\}, t) + \frac{\partial g(\{\nu\}, t)}{\partial \nu_3} - \frac{\partial g(\{\nu\}, t)}{\partial \nu_4}. \quad (\text{S17})$$

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 eqs.(S6)-(S8) and combining together

appropriate terms, one can obtain

$$\begin{aligned}
\frac{\partial g(\{\nu\}, t)}{\partial t} &= \sum_{i=1}^4 W_{ic}^+ \frac{\partial}{\partial \nu_i} \left( F'_i(\{\nu\}) + \frac{\partial}{\partial \nu_i} \right) g(\{\nu\}, t) \\
&+ W_{4c}^+ \left[ \frac{\partial}{\partial \nu_3} \left( F'_3(\{\nu\}) + \frac{\partial}{\partial \nu_3} \right) \right. \\
&\quad \left. - \frac{\partial}{\partial \nu_3} \left( F'_4(\{\nu\}) + \frac{\partial}{\partial \nu_4} \right) - \frac{\partial}{\partial \nu_4} \left( F'_3(\{\nu\}) + \frac{\partial}{\partial \nu_3} \right) \right] g(\{\nu\}, t),
\end{aligned} \tag{S18}$$

This is the kinetic equation of concurrent multicomponent nucleation and chemical aging of an ensemble of model organic aerosols. Its derivation via the Taylor series expansions in the vicinity of the saddle point (involving approximations (S11)-(S17)) and approximation (9) (of the main text) therein require that not only  $\nu_{ic} \gg 1$  ( $i = 1, \dots, 4$ ), but also  $\delta\nu_{ic} \gg 1$  and  $\delta\nu_{ic}/\nu_{ic} \ll 1$ , where  $\delta\nu_{ic} \equiv |a_{ii}|^{-1/2}$  is the half-width of the saddle point vicinity along the  $\nu_i$ -axis [18,19]. Note that the second term on the RHS of eq.(S18) arises because any sequence of reactions (1)-(3) results in the change of not only  $\nu_4$ , but also  $\nu_3$ ; the latter also changes independently via the direct exchange of component 3 between aerosol and air.

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

$$F(\{\nu\}) = F_c + \frac{1}{2} \sum_{i=1}^4 F''_{ijc} (\nu_i - \nu_{ic})(\nu_j - \nu_{jc}) = F_c + \mathbf{\Delta\nu}^T \mathbf{A} \mathbf{\Delta\nu}, \tag{S19}$$

where  $F''_{ij} = \partial^2 F / \partial \nu_i \partial \nu_j$  ( $i = 1, \dots, 4$ ) and the matrix notation was introduced with a real symmetric  $4 \times 4$ -matrix  $\mathbf{A} = [a_{ij}] \equiv [\frac{1}{2} F''_{ijc}]$  ( $i, j = 1, \dots, 4$ ) and a real column-vector of length 4  $\mathbf{\Delta\nu} = [\Delta\nu_i] \equiv [\nu_i - \nu_{ic}]$  ( $i = 1, \dots, 4$ ); superscript ‘‘T’’ marks the transpose of a matrix/vector. In this approximation, the first derivatives  $F'_i(\{\nu\})$  ( $i = 1, \dots, 4$ ) are linear superpositions of deviations  $\Delta\nu_i$  ( $i = 1, \dots, 4$ ). Thus, the accuracy of eq.(S18) combined with eq.(S19) corresponds to the Fokker-Planck approximation, widely used in the kinetics of the first-order phase transitions.<sup>23–27,39</sup>

Equation (S18) must be solved subject to appropriate boundary conditions. In the framework of CNT, the latter are formulated<sup>22–27,39</sup> by using the equilibrium distribution  $g_e(\{\nu\})$ . In the

near-critical region,  $g_e(\{\nu\})$  can be written as<sup>36,41</sup>

$$g_e(\nu) = (1/w_c) \exp \left[ -F_c - \frac{1}{2} \sum_{i=1}^4 F''_{ijc} \Delta\nu_i \Delta\nu_j \right], \quad (\text{S20})$$

where  $w_c$  is the volume per molecule in the saddle point aerosol (nucleus). As clear, the variables  $\nu_1, \dots, \nu_4$  are not separated in the equilibrium distribution (nor in the kinetic equation (S18)). Hence, they are not convenient to formulate simple enough boundary conditions to the kinetic equation (S18).

The problem can be overcome by using an elegant method of complete separation of variables developed by Kuni and co-workers.<sup>26,27</sup> Its most general presentation can be found in Ref.26.

First, it is necessary to introduce such new variables (instead of  $\nu_1, \dots, \nu_4$ ) that would transform the bilinear form in eq.(S19) into a quadratic one, without cross terms. Let us denote a set of such variables by  $\{x\} = (x_1, \dots, x_4)$  and the corresponding column-vector by  $\mathbf{x} = [x_i]$  ( $i = 1, \dots, 4$ ).

According to the spectral theorem,<sup>38</sup> matrix  $\mathbf{A}$  is orthogonally diagonalizable because it is real and symmetric. Hence, there exists a real orthogonal  $4 \times 4$ -matrix  $\mathbf{P} \equiv [p_{ij}]$  ( $i, j = 1, \dots, 4$ ), such that

$$\mathbf{P}^T \mathbf{A} \mathbf{P} = \mathbf{D}, \quad (\text{S21})$$

where the columns of the matrix  $\mathbf{P}$  are 4 linearly independent orthonormal eigenvectors of  $\mathbf{A}$ , and the diagonal elements of the diagonal matrix  $\mathbf{D}$  are the corresponding eigenvalues  $\phi_1, \dots, \phi_4$  of  $\mathbf{A}$ .

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  $\mathbf{A}$  is negative while all others are positive, so that  $\det(\mathbf{A}) < 0$ . Denoting the negative eigenvalue by  $\phi_1$ , one can thus define the variables

$$x_i = |\phi_i|^{1/2} \sum_{j=1}^4 p_{ji} \Delta\nu_j \quad (i = 1, \dots, 4), \quad (\text{S22})$$



in which the bilinear form (S19) transforms into

$$F(\{x\}) = F_c - \sum_{i=1}^4 \varepsilon_i x_i^2 \quad (\varepsilon_1 = 1, \varepsilon_2 = \varepsilon_3 = \varepsilon_4 = -1). \quad (\text{S23})$$

The transformation of variables (S21) allows one to re-write the kinetic equation of nucleation and chemical aging, eq.(S18), in the canonical form of the multidimensional Fokker-Planck equation

$$\frac{\partial g(\{x\}, t)}{\partial t} = \sum_{i,j=1}^4 b_{ij} \frac{\partial}{\partial x_i} \left( \frac{\partial}{\partial x_j} - \varepsilon_j 2x_j \right) g(\{x\}, t), \quad (\text{S24})$$

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

$$b_{ij} = |\phi_i \phi_j|^{1/2} \left[ \sum_{k=1}^4 W_{kc}^+ p_{ki} p_{kj} + W_{4c}^+ (p_{3i} p_{3j} - p_{3i} p_{4j} - p_{4i} p_{3j}) \right]. \quad (\text{S25})$$

Equation (S24) is eq.(8) of the main text.