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Kinetic effect of cluster-cluster processes on homogeneous nucleation rates in one- and two-component systems

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Cluster-cluster collisions and cluster dissociation into two smaller clusters have an effect on steady-state size distributions and nucleation rates. Clustering also affects nucleation rates by influencing the saturation vapour pressure, which is often ignored in nucleation studies. Both the kinetic and the vapour pressure effect of clustering on nucleation in one and two component systems are investigated. For water, the effect of cluster-cluster kinetics is in the order of 10%, and the effect via vapour pressure in the order of 100% in nucleation rate. The approximate method [Shugard *et al.*, J. Chem. Phys. **75**, 5298 (1974)] to take the kinetic effect of clustering into account works well for water. In acetic acid vapour the dimer concentrations are an order of magnitude higher than monomer concentrations. Even in this extreme case the approximate way to describe the kinetic effect of clustering gives reasonable estimates of the correct rates. In sulphuric acid-water mixture the kinetic effect is from one to four orders of magnitude in nucleation rate, depending on whether the clustering is accounted for in the saturation vapour pressure or not. The effect of clustering via vapour pressure is 5-10 orders of magnitude, depending on the kinetic model used. The approximate way to describe cluster kinetics works only in some of the cases. © 1997 American Institute of Physics. [S0021-9606(97)52232-X]

I. INTRODUCTION

Thermal collisions are generally used to model the gas-liquid nucleation process. A cluster formed in a collision has a size-dependent probability to live long enough to undergo another collision and grow further before it breaks up. This probability is determined by the formation free energy of the cluster, and it is described by the evaporation coefficient. In a nucleating vapour, a distribution of clusters of different sizes is present. Clusters collide with each other and form larger clusters. In nucleation studies it is usually assumed, that the concentration of monomers is so much higher than the concentration of clusters, that the rate of cluster-cluster collisions is negligible compared to the rate of monomer-cluster collisions. In most analytical and numerical studies (see, e.g., Refs. 1–5), only monomer-cluster collisions and the inverse process, evaporation of monomers, are taken into account in the kinetics. Recently Clement *et al.*⁶ studied the effect of dimer collisions and evaporation of dimers on the nucleation rate in one-component systems. The purpose of this paper is to investigate the effect of cluster-cluster collisions, and cluster decay to two smaller clusters, on steady-state size distributions and nucleation rates, taking all cluster sizes into account.

The monomer vapour pressures both in the saturated and the nucleating vapour are needed to calculate the formation free energy of clusters, and the evaporation coefficients. Usually, only the total vapour pressures (or total molecular concentrations) are known or measurable. In most studies, the effect of cluster distribution on saturated vapour pressure is neglected, and monomer pressures are approximated by the total pressures. Following the pioneering work of Katz *et al.*,⁷ the effect of clustering on vapour pressure can be taken into account by determining the monomer concentra-

tion so that the sum of partial pressures of clusters of all sizes equals the total vapour pressure both in saturated and super-saturated vapours.⁸

The terminology concerning clusters varies in the literature. The smallest clusters are often called associates, especially if they exist in great measure, or are stable. In binary systems having water as one component and, e.g., some acid as the other, small clusters consisting of both water and acid molecules are called hydrates. In this study, all n -mers with n greater than two are called clusters in both one- and two-component systems.

In this paper, two approaches for the saturated vapour pressures and their influence on steady-state distributions and nucleation rates are compared:

- (1) Monomer pressure is approximated by the total pressure.
- (2) Clusters are taken into account in the vapour pressure.

Three models are used for nucleation kinetics:

- (1) Full cluster kinetics, where cluster-cluster collisions and cluster decay to two smaller clusters are incorporated in the birth-death equations.
- (2) Monomer kinetics, in which only monomer-cluster collisions and evaporation of monomers are included.
- (3) Approximate cluster kinetics: Monomer kinetics is used, but the collision rate of monomers is modified to take cluster-cluster processes into account approximately following Shugard *et al.*⁹

The six combinations of the various vapour pressure and kinetic approaches are applied to three example systems: water, in which monomers dominate the total concentration; acetic acid, which is highly dimerized; and the water-sulphuric acid system, in which hydrate formation plays an

important role. In this study the evaporation coefficients are calculated using detailed balance and the classical equilibrium distribution based on capillary approximation. The method described in this paper is not restricted to the classical form of equilibrium distribution, which is used only because better approximations for realistic systems are lacking. Condensation coefficients describing the collision probabilities are taken from kinetic gas theory. The dimerization of acetic acid is not predicted by the classical theory, and is therefore implemented using experimental equilibrium constants. The birth-death equations are solved numerically. Theoretical models for the cluster-cluster kinetics and the effect of clustering on vapour pressure are presented in section II. The numerical results are presented and compared in section III, and the conclusions are drawn in section IV.

II. THEORY

A. One-component system

The rate at which clusters of size i_1 collide with clusters of size i_2 is given by $k(i_1; i_2)c(i_1)c(i_2)$, where $c(i_1)$ and $c(i_2)$ are the number concentrations of clusters of sizes i_1 and i_2 , respectively. The condensation coefficient $k(i_1; i_2)$ is given by kinetic gas theory,¹⁰

$$k(i_1; i_2) = \left(\frac{3}{4\pi}\right)^{1/6} (6kT)^{1/2} \left(\frac{1}{m_{i_1}} + \frac{1}{m_{i_2}}\right)^{1/2} (v_{i_1}^{1/3} + v_{i_2}^{1/3})^2, \quad (1)$$

where m_{i_1} and v_{i_1} are the mass and volume of cluster of size i_1 . The rate at which clusters of size i_1 decay to clusters of size i_2 and clusters of size $i_1 - i_2$ is given by $e(i_1; i_2)c(i_1)$, where $e(i_1; i_2) = e(i_1; i_1 - i_2)$ is the evaporation coefficient for the process $i_1 \rightarrow i_2 + (i_1 - i_2)$.

If a source produces (only) monomers at rate P , and clusters of size above M are depleted from the system, or their concentrations are negligible, the time evolution of the size spectrum is given by the following set of equations:

$$\frac{dc(1)}{dt} = P - c(1) \sum_{i_2=1}^M k(1; i_2)c(i_2) + \sum_{i_2=3}^M e(i_2; 1)c(i_2) + 2e(2; 1)c(2), \quad (2)$$

$$\begin{aligned} \frac{dc(i_1)}{dt} = & \sum_{i_2=1}^{\text{int}(i_1/2)} [c(i_2)c(i_1 - i_2)k(i_2; i_1 - i_2) \\ & - c(i_1)e(i_1; i_2)] - \sum_{i_2=1}^M c(i_2)c(i_1)k(i_2; i_1) \\ & + \sum_{i_2=0}^{M-i_1} c(i_1 + i_2)e(i_1 + i_2; i_1) \\ & + c(2i_1)e(2i_1; i_1)|_{2i_1 \leq M}, \end{aligned} \quad (3)$$

where $\text{int}(i_1/2)$ is the highest integer value less or equal to $i_1/2$.

At equilibrium, the rate of each process equals the rate of its inverse process, and evaporation coefficients can be calculated from detailed balance,

$$c_e(i_1)e(i_1; i_2) = c_e(i_1 - i_2)c_e(i_2)k(i_2; i_1 - i_2), \quad (4)$$

provided that the equilibrium distribution $c_e(i)$ is known. The self-consistent classical expression for the equilibrium concentration is based on the capillary approximation, and it can be written in the form¹¹

$$c_e^S(i) = \frac{p_1^E}{kT} \left(\frac{p_1^S}{p_1^E}\right)^i \exp\left[\frac{-\sigma A_1}{kT}(i^{2/3} - 1)\right], \quad (5)$$

where p_1^E and p_1^S are the partial pressures of monomers in saturated and supersaturated equilibrium vapours, respectively, σ is the surface tension, and A_1 is the surface area of a monomer. Using the distribution above, the values of evaporation coefficients are independent of the system (i.e., saturated or supersaturated) to which the principle of detailed balance is applied. Saturation ratio is defined as the ratio of total vapour pressure in the nucleating vapour and in the saturated vapour

$$S = \frac{p}{p_s} = \frac{\sum_{i=1}^M c(i)}{\sum_{i=1}^M c_e^{S=1}(i)}. \quad (6)$$

If the effect of clustering on the vapour pressure is neglected, monomer pressures in the equilibrium vapour are approximated by total pressures

$$p_1^E = p_s(T), \quad (7)$$

$$p_1^S = S p_s(T), \quad (8)$$

where $p_s(T)$ is the measurable saturation vapour pressure at temperature T and S is the saturation ratio. To account for the effect of clustering on the vapour pressure, total pressure is taken to be the sum of partial pressures of clusters of all sizes. The partial pressure of monomers in saturated vapour is given by

$$\frac{p_s(T)}{kT} = \sum_{i=1}^M c_e^{S=1}(i) = \frac{p_1^E}{kT} \sum_{i=1}^M \exp\left[\frac{-\sigma A_1}{kT}(i^{2/3} - 1)\right] \quad (9)$$

$$\Rightarrow p_1^E = \frac{p_s(T)}{\sum_{i=1}^M \exp\left[\frac{-\sigma A_1}{kT}(i^{2/3} - 1)\right]}. \quad (10)$$

The partial pressure of monomers in (hypothetical) supersaturated equilibrium vapour is given by the root of the polynomial

$$\frac{S p_s(T)}{kT} = \sum_{i=1}^M c_e^S(i) = \frac{p_1^E}{kT} \sum_{i=1}^M x^i \exp\left[\frac{-\sigma A_1}{kT}(i^{2/3} - 1)\right], \quad (11)$$

where $x = p_1^S/p_1^E$.

Normally the total pressure in the nucleating vapour, rather than the monomer production rate P , is known, and equation (2) cannot be used. If the effect of clustering on the

vapour pressure is neglected and equations (7) and (8) are used, the steady-state monomer concentration is

$$c(1) = S \frac{p_s(T)}{kT}. \quad (12)$$

If the effect of clustering on vapour pressure is taken into account and equations (10) and (11) are used, it is consistent to require that the equation

$$S \frac{p_s(T)}{kT} = \sum_{i=1}^M c(i) \quad (13)$$

holds in the steady-state.

The steady-state concentrations of clusters are the solutions of the non-linear set of equations (3) with $2 \leq i_1 \leq M$ and $dc(i_1)/dt = 0$, together with equation (12) or (13). The nucleation rate J_{nuc} is the number of clusters growing to sizes larger than M (i.e., out of the system) in unit time,

$$\begin{aligned} J_{\text{nuc}} &= \sum_{i_1=1}^M \sum_{i_2=1}^M c(i_1)c(i_2)k(i_1; i_2)|_{i_1+i_2>M} \\ &\quad (\text{each process only once}) \\ &= \sum_{i_1=M+1}^{2M} \sum_{i_2=\max(0, i_1-M)}^{\text{int}(i_1/2)} [c(i_1-i_2)c(i_2)k(i_1-i_2; i_2)], \end{aligned} \quad (14)$$

in the limit where M is large enough so that increase in M does not affect the value of J_{nuc} . By setting $k(i_1; i_2) = 0$

unless $i_1 = 1$ or $i_2 = 1$ (which leads to $e(i_1; i_2 \neq 1) = 0$), one obtains the commonly used approximation, whereby only monomer-cluster processes are taken into account.

Analogously to Shugard, Heist and Reiss,⁹ the kinetic effect of clustering is approximately taken into account by using the monomer kinetics, but modifying the monomer collision rate to describe also the cluster-cluster collisions. This is done by replacing $k(i; 1)c(1)$ with $k_h(i)$ and $e(i; 1)$ with $e_h(i)$, where

$$k_h(i) = \sum_{i_1=1}^h k(i; i_1)c_e^S(i_1), \quad (15)$$

$$e_h(i)c_e^S(i) = c_e^S(i-1)k_h(i-1). \quad (16)$$

These equations are based on the assumption, that for smallest clusters ($i < h$) the approximation $c(i) \approx c_e^S(i)$ holds. The value of h , giving the largest cluster taken into account in the kinetics in this approximation, must be chosen small enough to satisfy this condition. The concept of supersaturated equilibrium is necessary only when using this approximation (referred hereafter to as SHR correction or approximation), since the evaporation coefficients can as well be calculated from the saturated equilibrium, as stated after equation (5).

B. Binary system

The time evolution of the concentration of clusters containing i_1 molecules of the first substance and j_1 molecules of the second one, is given by

$$\begin{aligned} \frac{dc(i_1, j_1)}{dt} &= \sum_{i_2=0}^{\text{int}(i_1/2)-1} \sum_{j_2=0}^{j_1} [c(i_2, j_2)c(i_1-i_2, j_1-j_2)k(i_2, j_2; i_1-i_2, j_1-j_2) - c(i_1, j_1)e(i_1, j_1; i_2, j_2)] \\ &\quad + \sum_{j_2=0}^{\text{int}(j_1/2)} [c(i_2, j_2)c(i_1-i_2, j_1-j_2)k(i_2, j_2; i_1-i_2, j_1-j_2) - c(i_1, j_1)e(i_1, j_1; i_2, j_2)]|_{i_2=\text{int}(i_1/2), i_1 \text{ even}} \\ &\quad + \sum_{j_2=0}^{j_1} [c(i_2, j_2)c(i_1-i_2, j_1-j_2)k(i_2, j_2; i_1-i_2, j_1-j_2) - c(i_1, j_1)e(i_1, j_1; i_2, j_2)]|_{i_2=\text{int}(i_1/2), i_1 \text{ odd}} \\ &\quad - \sum_{i_2=0}^M \sum_{j_2=0}^N c(i_1, j_1)c(i_2, j_2)k(i_2, j_2; i_1, j_1) + \sum_{i_2=0}^{M-i_1} \sum_{j_2=0}^{N-j_1} c(i_1+i_2, j_1+j_2)e(i_1+i_2, j_1+j_2; i_1, j_1) \\ &\quad + c(2i_1, 2j_1)e(2i_1, 2j_1; i_1, j_1)|_{(2i_1 \leq M, 2j_1 \leq N)}. \end{aligned} \quad (17)$$

For monomers ($c(1,0)$ and $c(0,1)$), source rates P_i and P_j are added to the left hand side of the equation, and clusters with $i_1 > M$ or $j_1 > N$ are assumed to be depleted from the system. The condensation coefficient $k(i_1, j_1; i_2, j_2)$ for the process $(i_1, j_1) + (i_2, j_2) \rightarrow (i_1+i_2, j_1+j_2)$ is given by an equation analogous to equation (1), and the evaporation coefficients are calculated from detailed balance, analogously to equation (4). For the equilibrium size distribution, the following self-consistent form suggested by Wilemski and Wyslouzil¹² is used

$$\begin{aligned} c_e^{S_i, S_j}(i, j) &= (c_s^1(1,0))^x (c_s^0(0,1))^{1-x} \\ &\quad \times \exp(x\Theta_i + (1-x)\Theta_j - \Theta(i, j)) \\ &\quad \times \left(\frac{c^{S_i, S_j}(1,0)}{c_s^x(1,0)} \right)^i \left(\frac{c^{S_i, S_j}(0,1)}{c_s^x(0,1)} \right)^j, \end{aligned} \quad (18)$$

where $c_s^1(1,0)$ and $c_s^0(0,1)$ are the saturation concentrations of monomers over pure bulk liquids i and j , respectively, $c_s^x(1,0)$ and $c_s^x(0,1)$ are the saturation concentrations of

monomers of type i and j , over bulk liquid with mole fraction $x \equiv x_i = i/(i+j)$, respectively, and $c^{S_i, S_j}(1,0)$ and $c^{S_i, S_j}(0,1)$ are the concentrations of monomers in a vapour characterized by saturation ratios S_i and S_j .

In many-component systems, only the total molecular concentrations of the components, rather than the partial pressures of monomers or clusters of different sizes, are usually known or measurable. The saturation vapour pressures given in the literature are usually the pressures calculated from the total molecular concentrations using the ideal gas law $p = c/(kT)$ with no clustering incorporated. The saturation ratios are thus defined here as the concentration ratios

$$S_i = \frac{c_i^{\text{tot}}(S_i)}{c_i^{\text{tot}}(s)}, \quad (19)$$

$$S_j = \frac{c_j^{\text{tot}}(S_j)}{c_j^{\text{tot}}(s)}, \quad (20)$$

where $c_i^{\text{tot}}(S_i)$ and $c_i^{\text{tot}}(s)$ ($c_j^{\text{tot}}(S_j)$ and $c_j^{\text{tot}}(s)$) are the total number concentrations of molecules of type i (j), in the supersaturated and the saturated vapour, respectively.

The dimensionless surface energies Θ_i , Θ_j and $\Theta(i,j)$ are given by

$$\Theta_i = \frac{\sigma_i A_i^1}{kT}, \quad (21)$$

$$\Theta_j = \frac{\sigma_j A_j^1}{kT}, \quad (22)$$

$$\Theta(i,j) = \frac{\sigma(i,j)A(i,j)}{kT}, \quad (23)$$

where σ_i , A_i^1 , σ_j and A_j^1 are the surface tension and monomer surface area of pure liquids i and j , respectively, and $\sigma(i,j)$, $A(i,j)$ are the surface tension and surface area of the cluster (i,j) .

Using the distribution above, the evaporation coefficients have the same values independently of the reference state (S_i, S_j) chosen. A saturated vapour over liquid having any mole fraction between zero and one can be used as a reference state to avoid the unphysical concept of supersaturated equilibrium.

If the effect of clustering on vapour pressure is neglected, the monomer concentrations are approximated with the total concentrations

$$c_s^1(1,0) = \frac{p_{si}(T)}{kT}, \quad (24)$$

$$c_s^0(0,1) = \frac{p_{sj}(T)}{kT}, \quad (25)$$

$$c^{S_i, S_j}(1,0) = S_i c_s^1(1,0), \quad (26)$$

$$c^{S_i, S_j}(0,1) = S_j c_s^0(0,1), \quad (27)$$

$$c_s^x(1,0) = \gamma_i(x) x c_s^j(1,0), \quad (28)$$

$$c_s^x(0,1) = \gamma_j(x) (1-x) c_s^i(0,1), \quad (29)$$

where $\gamma_i(x)$ and $\gamma_j(x)$ are the activity coefficients of the substances i and j , respectively. To take the effect of clustering on vapour pressure into account in binary systems, it is required [analogously to equation (11)]^{8,13} that both of the following equations hold:

$$\sum_{i=1}^M \sum_{j=0}^N i c_e^{S_i, S_j}(i,j) = \frac{S_i p_{si}(T)}{kT}, \quad (30)$$

$$\sum_{i=0}^M \sum_{j=1}^N j c_e^{S_i, S_j}(i,j) = \frac{S_j p_{sj}(T)}{kT}. \quad (31)$$

Equations (30) and (31) with $S_i = \gamma_i(x)x$ and $S_j = \gamma_j(x) \times (1-x)$ and $x = i/(i+j)$ ($i=0, \dots, M$ and $j=0, \dots, N$), form a set of non-linear equations, which can be solved to obtain monomer concentrations in saturated vapour, i.e., $c_s^x(1,0)$ and $c_s^x(0,1)$, for all x . Monomer concentrations in saturated vapour are needed for solving the monomer concentrations in supersaturated equilibrium from equations (30) and (31) for arbitrary S_i and S_j . When monomer concentrations are known, equation (18) gives the distribution in either the saturated or the supersaturated state.

Again, usually the total concentrations, rather than monomer production rates are known in the nucleating vapour, and equation (17) can not be used for $(i_1=0, j_1=1)$ and $(i_1=1, j_1=0)$. If the effect of clustering on the vapour pressure is neglected using equations (24)-(29), consistent equations for monomer concentrations in steady-state are

$$c(1,0) = \frac{S_i p_{si}(T)}{kT}, \quad (32)$$

$$c(0,1) = \frac{S_j p_{sj}(T)}{kT}. \quad (33)$$

If clustering is included in the vapour pressure through equations (30) and (31), the following equations hold in the steady-state:

$$\sum_{i=1}^M \sum_{j=0}^N i c(i,j) = \frac{S_i p_{si}(T)}{kT}, \quad (34)$$

$$\sum_{i=0}^M \sum_{j=1}^N j c(i,j) = \frac{S_j p_{sj}(T)}{kT}. \quad (35)$$

Steady-state concentrations are solved from equations (17), with $0 \leq i_1 \leq M, 0 \leq j_1 \leq N$ ($(i_1, j_1) \neq (1,0)$ and $(i_1, j_1) \neq (0,1)$), and $dc(i_1, j_1)/dt = 0$, together with equations (32) and (33), or (34) and (35). The nucleation rate is given by

$$J_{\text{nuc}} = \sum_{i_1=0}^{2M} \sum_{j_1=N+1}^{2N} u(i_1, j_1) + \sum_{i_1=M+1}^{2M} \sum_{j_1=0}^N u(i_1, j_1), \quad (36)$$

$$u(i_1, j_1) = \sum_{i_2=\max(0, i_1-M)}^{\text{int}(i_1/2)-1} \sum_{j_2=\max(0, j_1-N)}^{\min(j_1, N)} v(i_1, j_1; i_2, j_2) + \sum_{j_2=\max(0, j_1-N)}^{\text{int}(j_1/2)} v(i_1, j_1; i_2, j_2) \Big|_{i_2=\text{int}(i_2/2), i_1 \text{ even}}$$

TABLE I. The nucleation rates for pure water calculated with different approaches for kinetics and vapour pressure. The first index refers to the kinetics (c : full kinetics, SHR : SHR corrected monomer kinetics, and m : monomer kinetics), and the second index refers to vapour pressure (c : clustering taken into account, m : clustering neglected).

T (K)	S	$J_{c,c}$ ($\text{m}^{-3} \text{s}^{-1}$)	$J_{SHR,c}$ ($\text{m}^{-3} \text{s}^{-1}$)	$J_{m,c}$ ($\text{m}^{-3} \text{s}^{-1}$)	$J_{c,m}$ ($\text{m}^{-3} \text{s}^{-1}$)	$J_{SHR,m}$ ($\text{m}^{-3} \text{s}^{-1}$)	$J_{m,m}$ ($\text{m}^{-3} \text{s}^{-1}$)
253.15	5	$0.22 \cdot 10^6$	$0.23 \cdot 10^6$	$0.24 \cdot 10^6$	$0.41 \cdot 10^6$	$0.47 \cdot 10^6$	$0.47 \cdot 10^6$
253.15	6	$0.95 \cdot 10^{11}$	$0.95 \cdot 10^{11}$	$0.99 \cdot 10^{11}$	$0.17 \cdot 10^{12}$	$0.19 \cdot 10^{12}$	$0.18 \cdot 10^{12}$
253.15	7	$0.38 \cdot 10^{15}$	$0.37 \cdot 10^{15}$	$0.36 \cdot 10^{15}$	$0.66 \cdot 10^{15}$	$0.70 \cdot 10^{15}$	$0.69 \cdot 10^{15}$
253.15	8	$0.12 \cdot 10^{18}$	$0.12 \cdot 10^{18}$	$0.12 \cdot 10^{18}$	$0.21 \cdot 10^{18}$	$0.22 \cdot 10^{18}$	$0.21 \cdot 10^{18}$
273.15	5	$0.17 \cdot 10^{15}$	$0.18 \cdot 10^{15}$	$0.17 \cdot 10^{15}$	$0.40 \cdot 10^{15}$	$0.51 \cdot 10^{15}$	$0.50 \cdot 10^{15}$
273.15	6	$0.21 \cdot 10^{19}$	$0.20 \cdot 10^{19}$	$0.19 \cdot 10^{19}$	$0.53 \cdot 10^{19}$	$0.52 \cdot 10^{19}$	$0.51 \cdot 10^{19}$
273.15	7	$0.86 \cdot 10^{21}$	$0.80 \cdot 10^{21}$	$0.76 \cdot 10^{21}$	$0.21 \cdot 10^{22}$	$0.20 \cdot 10^{22}$	$0.19 \cdot 10^{22}$
273.15	8	$0.56 \cdot 10^{23}$	$0.51 \cdot 10^{23}$	$0.49 \cdot 10^{23}$	$0.13 \cdot 10^{24}$	$0.12 \cdot 10^{24}$	$0.12 \cdot 10^{24}$

$$\begin{aligned}
 & + \sum_{j_2=\max(0, j_1-N)}^{\min(j_1, N)} v(i_1, j_1; i_2, j_2) \Big|_{i_2=\text{int}(i_2/2), i_1 \text{ odd}}, \\
 & v(i_1, j_1; i_2, j_2) = k(i_1 - i_2, j_1 - j_2; i_2, j_2) c(i_1 - i_2, j_1 \\
 & \quad - j_2) c(i_2, j_2), \quad (37)
 \end{aligned}$$

with M and N large enough, so that increasing their values does not affect the value of the nucleation rate. Setting $k(i_1, j_1; i_2, j_2) = 0$ if $i_1 + j_1 \neq 1$ and $i_2 + j_2 \neq 1$ (which gives $e(i_1, j_1; i_2, j_2) = 0$ if $i_2 + j_2 \neq 1$) one obtains the commonly used approximation, which takes only monomer-cluster processes into account.

In the SHR approximation, the kinetic effect of hydrate formation is described using monomer kinetics, but modifying the collision rate of type i (acid) monomers by replacing $k(i_1, j_1; 1, 0) c(1, 0)$ with $k_h(i_1, j_1)$ and $e(i_1, j_1; 1, 0)$ with $e_h(i_1, j_1)$, where

$$k_h(i_1, j_1) = \sum_{j=0}^h k(i_1, j_1; 1, j) c_e^{S_i, S_j}(1, j), \quad (38)$$

$$e_h(i_1, j_1) c_e^{S_i, S_j}(i_1, j_1) = c_e^{S_i, S_j}(i_1 - 1, j_1) k_h(i_1 - 1, j_1). \quad (39)$$

The value of h should be small enough so that $c(1, j) \approx c_e^{S_i, S_j}(1, j)$ is valid for $j < h$.

III. RESULTS

The effect of clustering on nucleation rate via both vapour pressure and kinetics was investigated. The numerical calculations were carried out using NAG-library FORTRAN-routine C05NBF.¹⁴

A. Water

Water was studied as an example of a typical case with monomer concentrations much higher than the concentrations of any other clusters. Equation (5) based on the capillary approximation is assumed to give the equilibrium distribution. Comparison to observed dimer mole fractions¹⁵ shows, that equation (5) produces correct order-of-magnitude estimates for the dimerization effect. Surface tension and saturation vapour pressure were taken from Preining *et al.*^{16,17}

Table I shows the nucleation rates for pure water calcu-

lated in a variety of temperatures and saturation ratios using different approaches for the kinetics and for the vapour pressure. The first index refers to the kinetics (c : full kinetics, SHR : SHR approximation, and m : monomer kinetics), and the second index refers to vapour pressure [c : clustering incorporated using equations (10), (11) and (13), m : clustering neglected using equations (7), (8) and (12)]. The calculations were performed with $M = 200$ and checked to give identical results with $M = 300$.

The overall effect of clustering on nucleation rates is rather small; the results from the different approaches lie within 1 order of magnitude. The effect on vapour pressure is seen to be clearly more important than the kinetic effect, as expected. Taking the effect of clustering on vapour pressure into account diminishes the nucleation rate by a factor between 0.4 and 0.6 compared to rates obtained when neglecting this effect. Compared with monomer kinetics, the cluster-cluster kinetics change the nucleation rate by a factor between 0.9 and 1.2, i.e., in the order of 10% rather than 1%, which was approximated to be the kinetic effect of dimers by Clement *et al.*⁶ Cluster kinetics can either increase or decrease the nucleation rate, because the whole distribution is affected. The cluster kinetics is approximated rather well by the SHR correction to monomer kinetics. The SHR approximation is found to be insensitive to the value of $h (> 1)$. $h = 10$ was used in all cases, and it was checked that supersaturated equilibrium distribution approximates the steady-state distribution well for $i \leq h$.

Figure 1 shows as an example the steady-state size distributions obtained using different models at $T = 253.15$ and $S = 5$. The supersaturated equilibrium distribution is also shown, and for small sizes (actually up to $i = 75$ in this case) it predicts the steady-state distribution well, and the SHR approximation is reasonable. All the distributions calculated with cluster corrected vapour pressure are almost indistinguishable in this scale, and so are all the distributions obtained without cluster correction to vapour pressure. The distributions tend to fall rapidly at $i = M$, which is seen in this figure at size $M = 200$. To make the effect of kinetics on the distributions clearer, Figure 2 shows the ratio of distributions calculated with and without cluster kinetics. At $T = 273.15$ K and $S = 8$, the ratios are above one over the whole size range, and as Table I shows, the nucleation rate is also higher with full cluster kinetics. With $T = 253.15$, $S = 5$, the concentra-

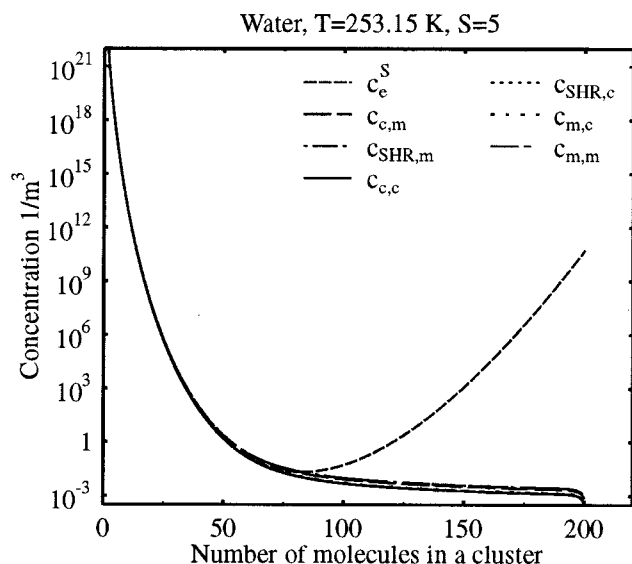


FIG. 1. The size distributions for water obtained using different approaches for kinetics (first index: c : full kinetics, SHR : SHR corrected monomer kinetics and m : monomer kinetics) and vapour pressure (second index: c : clustering taken into account, m : clustering neglected.) The distributions $c_{c,m}$, $c_{SHR,m}$ and $c_{m,m}$ are almost indistinguishable and lie above the distributions $c_{c,c}$, $c_{SHR,c}$ and $c_{m,c}$, which are also seen almost as one line. The supersaturated equilibrium distribution c_e^S is also shown. Temperature is 253.15 K and saturation ratio is 5.

tions with full cluster kinetics are lower than with monomer kinetics over the whole size range, leading to lower nucleation rate.

The system can be closed by setting the condensation coefficients zero for processes that lead to formation of clusters with sizes larger than M . The closed system represents the equilibrium situation, where the flow through the system vanishes, and the distribution is given by equation (5). Distribution (5) is the exact solution of equations (3) for the closed system only if the last term in equation (3) is left out. Leaving this term out means ignoring the fact that decay of even-numbered sizes into two equal parts produces two clusters rather than one. This simplification is often done, particularly in studies in which the limits of the summations are only formally shown, and for water it causes less than 1% error in nucleation rates.

B. Acetic acid

Acetic acid (CH_3COOH) is known to be a highly dimerizing substance.¹⁸ The classical equation (5), however, does not predict this effect at all. Therefore, distribution (5) was used for all other clusters but the dimer, for which the equilibrium constant K_{12} was assumed to determine the equilibrium concentration $c_e(2) = p_2/(kT)$, with $p_2 = K_{12} p_1^2$ and $p_1 = kT c_e(1)$. Surface tension, density, saturation vapour pressure and equilibrium constant were taken from Heist *et al.*¹⁸

With acetic acid, the dimer concentration is an order of magnitude higher than the monomer concentration. Thus only the kinetic effect of clustering was studied, and equa-

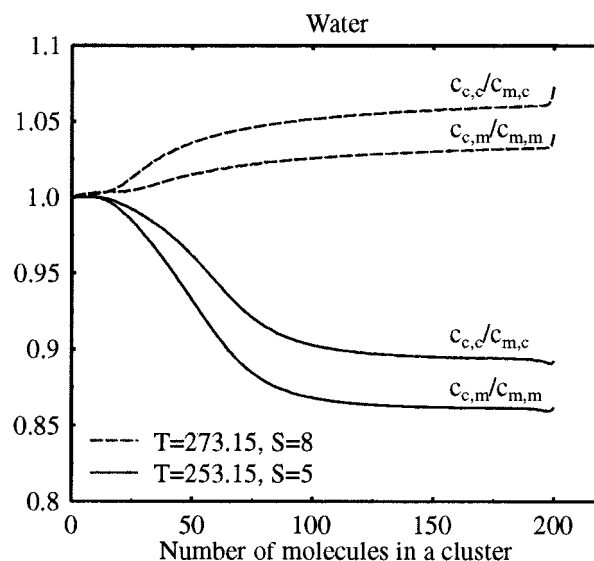


FIG. 2. The ratio of distributions calculated with and without cluster kinetics ($c_{c,c}/c_{m,c}$ with cluster corrected vapour pressure and $c_{c,m}/c_{m,m}$ with clustering neglected in vapour pressure) for water in two cases, $T=273.15$, $S=8$, representing a situation where cluster kinetics increases the nucleation rate and $T=253.15$, $S=5$, a situation where cluster kinetics decreases the nucleation rate.

tions (10), (11) and (13) were used in all calculations. The pure monomer kinetics was found to be numerically unstable, giving unphysical results.

Table II shows the nucleation rates calculated with cluster kinetics and with the SHR corrected monomer kinetics. Calculations with $M=300$ and $M=400$ were checked to give identical results. The SHR approximation produces nucleation rates within an order of magnitude from the cluster-cluster rates, but the agreement is not as good as with water. The SHR approximation is not sensitive to the value of h , if $h \geq 2$. $h=10$ was used in all cases, and it was checked that $c(i) \approx c_e^S(i)$ is well satisfied for $i \leq h$. The ratio of distributions calculated with full cluster kinetics and SHR corrected monomer kinetics oscillates between values above and below 1, varying between 0.75 and 1.38.

TABLE II. The nucleation rates for acetic acid calculated with full kinetics, $J_{c,c}$, and SHR corrected monomer kinetics, $J_{SHR,c}$, in different temperatures and saturation ratios. Clustering is taken into account in vapour pressure in both cases.

T (K)	S	$J_{c,c}(\text{m}^{-3} \text{s}^{-1})$	$J_{SHR,c}(\text{m}^{-3} \text{s}^{-1})$
300.15	4	$0.11 \cdot 10^1$	$0.19 \cdot 10^1$
300.15	5	$0.11 \cdot 10^{10}$	$0.78 \cdot 10^{10}$
300.15	6	$0.11 \cdot 10^{15}$	$0.54 \cdot 10^{14}$
300.15	7	$0.17 \cdot 10^{18}$	$0.69 \cdot 10^{17}$
310.15	4	$0.38 \cdot 10^7$	$0.54 \cdot 10^7$
310.15	5	$0.89 \cdot 10^{14}$	$0.61 \cdot 10^{14}$
310.15	6	$0.12 \cdot 10^{19}$	$0.56 \cdot 10^{18}$
310.15	7	$0.50 \cdot 10^{21}$	$0.20 \cdot 10^{21}$

TABLE III. The nucleation rates for sulphuric acid - water mixture calculated using different models for kinetics and vapour pressure, with different saturation ratios for sulphuric acid (S_a) and water (S_w) at temperature 203.15 K. The first index refers to the kinetics (c : full kinetics, SHR : SHR corrected monomer kinetics, and m : monomer kinetics), and the second index refers to vapour pressure (c : clustering taken into account, m : clustering neglected).

$T(K)$	S_a	S_w	$J_{c,c}(m^{-3} s^{-1})$	$J_{m,c}(m^{-3} s^{-1})$	$J_{c,m}(m^{-3} s^{-1})$	$J_{SHR,m}(m^{-3} s^{-1})$	$J_{m,m}(m^{-3} s^{-1})$
203.15	9	9	$0.13 \cdot 10^7$	$0.11 \cdot 10^8$	$0.40 \cdot 10^{17}$	$0.81 \cdot 10^{17}$	$0.31 \cdot 10^{13}$
203.15	9	10	$0.77 \cdot 10^8$	$0.13 \cdot 10^8$	$0.74 \cdot 10^{17}$	$0.26 \cdot 10^{18}$	$0.97 \cdot 10^{13}$
203.15	9	11	$0.11 \cdot 10^9$	$0.16 \cdot 10^8$	$0.12 \cdot 10^{18}$	$0.80 \cdot 10^{18}$	$0.14 \cdot 10^{14}$
203.15	10	9	$0.16 \cdot 10^7$	$0.14 \cdot 10^8$	$0.49 \cdot 10^{17}$	$0.11 \cdot 10^{18}$	$0.39 \cdot 10^{13}$
203.15	10	10	$0.95 \cdot 10^8$	$0.16 \cdot 10^8$	$0.87 \cdot 10^{17}$	$0.34 \cdot 10^{18}$	$0.12 \cdot 10^{14}$
203.15	10	11	$0.14 \cdot 10^9$	$0.20 \cdot 10^8$	$0.14 \cdot 10^{18}$	$0.10 \cdot 10^{19}$	$0.17 \cdot 10^{14}$
203.15	11	9	$0.20 \cdot 10^7$	$0.17 \cdot 10^8$	$0.58 \cdot 10^{17}$	$0.14 \cdot 10^{18}$	$0.49 \cdot 10^{13}$
203.15	11	10	$0.11 \cdot 10^9$	$0.20 \cdot 10^8$	$0.10 \cdot 10^{18}$	$0.44 \cdot 10^{18}$	$0.14 \cdot 10^{14}$
203.15	11	11	$0.17 \cdot 10^9$	$0.24 \cdot 10^8$	$0.16 \cdot 10^{18}$	$0.13 \cdot 10^{19}$	$0.21 \cdot 10^{14}$

The nucleation rate obtained leaving out the last term of equation (3) differs by a factor between 1.5 and 6 from the rate obtained using full equation (3).

C. Sulphuric acid - water

In sulphuric acid-water vapour the concentrations of hydrates (small clusters containing both acid and water molecules) exceed the concentration of acid monomers. This effect is at least qualitatively predicted by equation (18). The surface tension of the mixture was taken from Sabinina and Terpugow,¹⁹ the saturation vapour pressure for pure water from Preining *et al.*^{16,17} and for pure sulphuric acid from Ayers *et al.*,²⁰ the density of the mixture from Jaeger-Voirol²¹ and the activity coefficients from Taleb *et al.*²²

Table III shows the nucleation rates calculated using different models for the kinetics and for the vapour pressure, with different saturation ratios for sulphuric acid and water at 203.15 K. The first index refers to the kinetics (c : full cluster kinetics, SHR : SHR corrected monomer kinetics, and m : monomer kinetics), and the second index to the vapour pressure [c : clustering taken into account using equations (30), (31), (34) and (35) m : clustering neglected using equations (24)–(29)].

The lower limits of M and N at which the nucleation rate becomes insensitive to their values vary a lot depending on the case. In the cases studied, the typical values were $M=4$ and $N=30$ when calculating $J_{m,m}$, while for $J_{c,c}$ they were $M=6$ and $N=100$. It was necessary to choose a low temperature and high supersaturations to make the values of M and N sufficiently small, so that the system of equations was numerically stable and the computing times reasonable.

The kinetic effect of clustering depends essentially on the model used for the vapour pressure. If clustering is neglected in the vapour pressure, the rates calculated with the cluster kinetics are about four orders of magnitude higher than the rates obtained using monomer kinetics. The SHR correction overestimates the rates somewhat compared with full cluster kinetics, but stays within an order of magnitude. h was chosen so that $c(1, j) \geq 0.99 c_e^{S_i} c_e^{S_j}(1, j)$ for $j \leq h$. The results are quite insensitive to the value of h .

Compared with rates calculated neglecting the effect of clustering on vapour pressure, the rates obtained with the cluster correction are significantly lower. If clustering is included in the value of vapour pressure, the rates calculated with cluster kinetics differ only by about 1 order of magnitude from the rates given by monomer kinetics. The effect can be either increasing or decreasing. To use the SHR approximation, the condition $c(1, j) \approx c_e^{S_i} c_e^{S_j}(1, j)$ should hold for some region $0 \leq j \leq h_j$, but in this case it holds only for a single value of j far from 0. If nevertheless calculated, the SHR rates are orders of magnitude higher than the correct rates with all choices of $h_j > 0$.

The saddle point region is essential in the nucleation process,^{2,4} and it is significantly shifted if clustering is taken into account in the vapour pressure as noted in earlier studies (see, e.g., Ref. 13). Also the downhill in formation free energy from the saddle point to larger sizes becomes less steep, which has a lowering effect on the nucleation rate. If clustering is taken into account in the vapour pressure, the overall cluster concentrations are much lower than if the clusters are neglected. This is a consequence of the restriction of total molecular concentrations in equations (34) and (35), while equations (32) and (33) do not restrict the total concentrations at all. When less clusters exist, their kinetic effect is smaller and the small difference between $J_{c,c}$ and $J_{m,c}$ is understandable.

When using cluster corrected vapour pressure, the free monomer concentrations in a vapour in equilibrium with bulk liquid having sulphuric acid mole fraction x , are solved from equations (30) and (31) at all $x = i/(i+j)$. Figure 3 shows the ratios of free monomer concentration to total number concentration of sulphuric acid and water as functions of liquid mole fraction at 203.15 K. The results do not change noticeably when changing M and N , if their values are high enough. $M=4$ and $N=40$ were found to be sufficient. Due to the non-ideal properties of the mixture, the vapour pressure of water decreases rapidly when sulphuric acid mole fraction increases in the liquid. Increased vapour pressure of acid does not compensate for the decrease in vapour pressure of water. A lower vapour pressure leads to decreased clustering, and when the mole fraction is high, almost all water

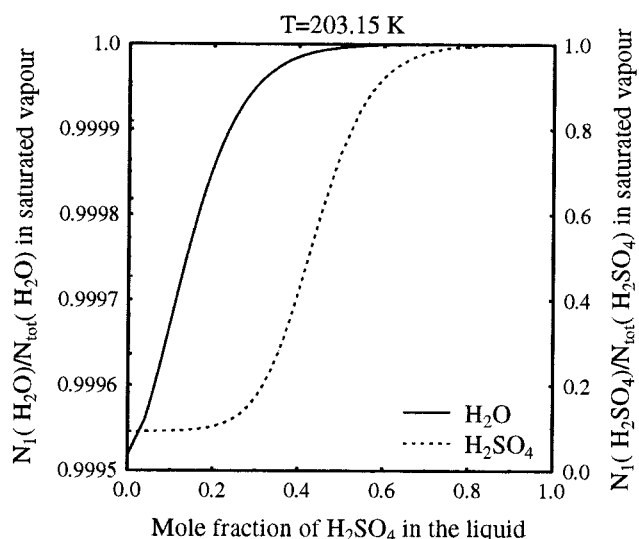


FIG. 3. The ratio of free monomer concentration to total number concentration for sulphuric acid and water in a saturated vapour over bulk liquid having different mole fractions of sulphuric acid. Temperature is 203.15 K.

and acid molecules are free. At low mole fractions almost all the acid molecules are bound to hydrates.

Again, the supersaturated equilibrium distribution is the exact solution of equations (17) for the closed system only if the last term of equation (17) is left out. Leaving this term out results in less than 1% difference in the nucleation rate.

IV. CONCLUSIONS

For water, the effect of clustering via change of vapour pressure is an order of magnitude higher than via kinetics. The kinetic effect can either increase or decrease the nucleation rate. Rates calculated with SHR correction give good approximations to correct rates for water and also for the highly dimerized acetic acid.

For sulphuric acid - water mixture, the kinetic effect of clustering depends on the model used for vapour pressure. If clusters are neglected in the vapour pressure, the kinetic effect increases the rates by 3-4 orders of magnitude, and SHR corrected monomer kinetics approximates the full cluster kinetics rather well. If clusters are taken into account in the

vapour pressure, the nucleation rates are 5-10 orders of magnitude lower than the rates calculated without cluster correction. The rates obtained using full kinetics differ only about 1 order of magnitude from the rates obtained using monomer kinetics. In this case, taking cluster-cluster processes into account can either increase or decrease the nucleation rate. The SHR correction to the kinetics overestimates the kinetic effect of clustering by orders of magnitude. SHR corrected kinetics should not be used without testing that the assumptions behind it are valid.

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