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The role of diffusion in the nucleation of calcium carbonate

Xiangyu Dou^{1,2,3,#}, Haoyang Huang^{1,2,#}, Yongsheng Han^{1,2,*}¹ State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China² School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China³ College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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ABSTRACT

Nucleation widely exists in nature, from cloud formation to haze generation. The classical nucleation theory (CNT) was created to describe the nucleation process, but it fails to predict many experimental phenomena due to the short consideration of nanoscale phenomena and macroscale dynamics. Although the attachment and detachment of monomers are considered in the developed model of nucleation, the diffusion of chemicals in the bulk is not valued as supersaturation in the nucleation process so far. Here we employ simulation and experimental approaches to investigate how the diffusion of ions affects the nucleation of calcium carbonate. The diffusion of ions is regulated by the viscosity of solvents and the sonication imposed on the solution. It is found that the nucleation rates increased exponentially with the diffusion coefficient of ions, which is beyond the prediction of CNT. This abnormal finding might be ascribed to the involvement of cluster aggregation in the nucleation of calcium carbonate. This study highlights the significance of chemical diffusion in the nucleation process, which may help to revise the nucleation theory and develop solutions for the rational synthesis of materials, as well as for the control of air pollution.

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1. Introduction

Nucleation is one of the most important phenomena in the world, widely presenting in nature, such as the clouds condensation [1], metal solidification and particles generation [2]. A hundred years ago, the classical nucleation theory (CNT) [3] was created to describe the formation of nuclei, which is based on the principle of thermodynamics. It was proposed that the nucleation proceeds spontaneously when the nucleation free energy gained by volume free energy overcomes the interfacial free energy. An energy barrier was established for a nucleation process. The nuclei become stable after they reach their critical size. The critical sizes and energy barriers are unique in a given system based on the CNT, by which the nucleation is a single-step activated process, but often this is not the case. In the nucleation of calcium carbonate, the so-called pre-nucleation process was observed [4], which led to a two-step or multistep nucleation. The two-step nucleation sheds light on the preservation of these

thermodynamic unfavorable phases in deposits [5–7]. CNT also fails in predicting the supercooling nucleation since CNT model does not consider the slow mobility of liquid molecules at the low temperature [8–10].

To modify the CNT, the dynamical nucleation theory (DNT) [11–13] was developed by utilizing variational transition state theory [14] to provide an expression for the monomer detachment rate. DNT provides a unique and physically consistent value for the cluster constraining volume. The extended modified liquid drop theory and DNT were combined later [15], which successfully predicts the spinodal phenomena. The argon nucleation rate predicted by this new model shows excellent agreement with the simulation results with a deviation of less than one order of magnitude over the studied temperature range, while the deviations calculated by CNT is about 2–7 orders of magnitude in the same temperature range [16]. These results indicated that the dynamics of chemicals plays an important role in the nucleation, which may be underestimated previously. In previous study, the attachment and detachment rates of monomers have been considered in the developed method [17]. In the diffusion-controlled attachment kinetics [18], $D_n = 4\pi D\rho R$ (D_n refers to the attachment frequency, D is a spatial diffusion coefficient which has the same physical meaning as the diffusion regulated in this study, ρ is the concentration of monomer, R is the critical nucleus radius). In the kinetic model of

* Corresponding author at: State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

E-mail address: yshan@ipe.ac.cn (Y. Han).

The first two authors contributed equally to this work.

nucleation, the nucleation rate is linearly dependent on diffusion coefficient when diffusion is limited. However, there is few effort to discover the physical mechanism behind the diffusion effect, especially no analogies with the supersaturation in affecting nucleation process. In an atomic view of nucleation, the diffusion depicts the movement of monomers [19] while the supersaturation reflects the concentration of monomers. Since both concentration and movement determine the collision frequency of monomers, they may have an analogous effect on the nucleation process. This is the main hypothesis of this study. A clarification of this issue may promote our understanding on the nucleation processes and benefit the rational synthesis of materials, as well as to solve the engineering problems [20,21].

In this paper, the molecular dynamics (MD) simulations [22] and transmittance experiments were employed to investigate how the diffusion of chemicals influences the nucleation of calcium carbonate. The diffusion of chemicals was slowed down by adding glycerol into the solution and sped up by giving additional energy to chemicals during nucleation. The OPLS (optimized potentials for liquid simulations) potential [23] and Buckingham potential [24,25] were used in the simulation. The nucleation rate was given by the mean first-passage time method (MFPT) [26,27]. In the experiments, the transmittance of solution was measured as a function of time on a UV-Vis spectrophotometer [28] to calculate the nucleation rate. Both MD simulation and experiments indicated the dependence of nucleation rate on the diffusion of chemicals. The exponential relationship between the nucleation rate and diffusion coefficient was found and discussed in the end.

2. Simulation and Experiments

2.1. Simulation part

Molecular dynamics simulations had been performed by running the LAMMPS [29] package on the Mole-8.5e supercomputer [30]. The interactions among ions and molecules were described by a combination of the OPLS potential [23] and the Buckingham potential [24]. The water and glycerol molecules were described by OPLS force field which is defined as follows:

$$E = \sum_i \sum_{j>i} \left[\frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) \right] + \sum_{\text{bonds}} K_r (r - r_{\text{eq}})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{\text{eq}})^2 + \sum_i \left\{ \frac{V_{1i}}{2} [1 + \cos(\varphi_i)] + \frac{V_{2i}}{2} [1 - \cos(2\varphi_i)] + \frac{V_{3i}}{2} [1 + \cos(3\varphi_i)] + \frac{V_{4i}}{2} [1 - \cos(4\varphi_i)] \right\} \quad (1)$$

The total energy E of the system is the sum of individual energies of Coulomb terms, Lennard-Jones terms, harmonic bond stretching terms, angle bending terms and a Fourier series for torsional energetics. The partial atomic charges q are fixed on each atom's mass center, i and j represent all pairs of atoms ($i < j$), r_{ij} is the distance between atoms i and j . ϵ_{ij} and σ_{ij} represent the Lennard-Jones radii and potential well depth, respectively, which are obtained by the geometric combination rules $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}$ based on the literature [31]. K_r , K_θ and V_{ni} ($n = 1, 2, 3, 4$) are the force constants, and r_{eq} , θ_{eq} and φ_i represent equilibrium values.

The non-bonded interaction between Ca^{2+} and CO_3^{2-} ions were given by Buckingham potential, which is defined as follows:

$$E = Ae^{-r/\rho} - \frac{C}{r^6} \quad (2)$$

where C , A , ρ are the parameters for the specified ion pairs. The interaction of ions and water molecules are depicted by Lennard-Jones force [24]. All the force field parameters of atoms and ions

are given in Table S1. The OPLS force field parameters of water and glycerol molecules are from the literature [32] and optimized with the 1.14*CM1A method [33].

The simulation box is a cubic with 8.41 nm in xyz dimension. The box contains 550 Ca^{2+} and 550 CO_3^{2-} , and solution molecules at different glycerol molar fraction in water (from 0% to 20%). Before running simulation, the energy of whole system was minimized for 10,000 steps at most for 10^{-4} energy tolerance and 10^{-6} force tolerance. After the minimization, it was initially equilibrated in the NPT ensemble at 293.15 K and 0.1 MPa for 0.5 ns. After the equilibration, the density of calcium carbonate aqueous solution is $1.05 \text{ g}\cdot\text{cm}^{-3}$ which agrees with the experimentally determined density $1.03 \text{ g}\cdot\text{cm}^{-3}$ of the same solution in the literature [34,35]. The time step of 1 fs was used in all simulations. A cutoff of 1.0 nm was used for the Lennard-Jones potential. A neighbor searching was carried out at the same distance from the central ion and was updated every simulation step. The electrostatic interactions beyond 1.0 nm were accounted for by the computationally efficient K -space method based on particle-particle particle-mesh (PPPM) [36].

The simulations were carried out at 293.15 K and 0.1 MPa in the NPT ensemble using a Nosé-Hoover thermostat for 4 ns. The damping parameter for thermostat is 0.1 ps and for barostat it is 1 ps. To decrease the diffusivity of chemicals, glycerol was added to the CaCO_3 solution. The densities of the CaCO_3 solution at different glycerol ratios are from the experiment work [37]. To increase the diffusivity, the ions (Ca^{2+} and CO_3^{2-}) were given the additional energy with the power from $1.6 \times 10^{-8} \text{ W}$ to $3.2 \times 10^{-7} \text{ W}$ in the Nosé-Hoover thermostat at 10% (mol) glycerol solution. The additional energy was modeled by introducing a thermostating force to the motion equation [38]:

$$g_i = \frac{m_i F_i}{2K_{\text{cent}}} (v_i - v_{\text{cent}}) \quad (3)$$

where i is the index of the nucleation ions, m_i is the mass and the quantity F_i corresponds to the input parameter F , which is the energy flux into the group of nucleation ions. K_{cent} and v_{cent} denote the non-translational kinetic energy and the center of mass velocity of that group, respectively. The additional force does not affect the mass velocity of individual groups and the velocity of entire system molecules.

To determine the diffusivities at different conditions, the mean-squared displacements (MSD) of both ions were separately computed, and the diffusion coefficients (D) were obtained from the standard procedure of taking the slopes of the MSDs over time and divided by six, as shown in the follow equation:

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N \langle [r_i(t) - r_i(t_0)]^2 \rangle \quad (4)$$

where i is the index of nucleation ion, and the $r(t)$ is the location in three dimensions at special time point. For the solution of calcium carbonate, the diffusivity follows:

$$D = \frac{2}{1/D_+ + 1/D_-} \quad (5)$$

where the D_+ is the diffusivity of the Ca^{2+} , and the D_- is the diffusivity of the CO_3^{2-} .

The nucleation rate of calcium carbonates was calculated by a time dependent cluster statistic. The MFPT [39] was used to analyze the cluster statistics. In the MFPT, $t(n)$ is defined as the average time in which the nuclei grow to size n for the first time. via this method, we got $t(n)$ of each nuclei size. Based on the MFPT, $t(n)$ has the relationship with the nucleation time t_j and the critical size n^* , as shown in the below

$$t(n) = \frac{t_j}{2} \left[1 + \operatorname{erf}(\sqrt{\pi} Z(n - n^*)) \right] \quad (6)$$

where $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-k^2} dk$ is the error function and Z is the Zeldovich factor. So a simple three-parameter fitting of the MFPT to Eq. (6) gets the nucleation time t_j and the critical size n^* directly. The nucleation rate is obtained by the following equation:

$$J = \frac{1}{V_s t_j} \quad (7)$$

where J is the nucleation rate and V_s is the volume of the nucleation solution.

2.2. Experimental part

The nucleation rates of calcium carbonate under different diffusion conditions was measured by transmittance experiments. The chemicals used in the experiments were purchased from Xilong Scientific Chemical Co., Ltd. All chemicals were used as received. Deionized water with a resistivity higher than 18.2 MΩ·cm generated by a Milli-Q system (Millipore, USA) was used throughout the experiments. The CaCO_3 solution with supersaturation ratio of 4.449 was prepared by simply mixing Na_2CO_3 (2.529 mmol·L⁻¹, 5 ml) and CaCl_2 (2.523 mmol·L⁻¹, 5 ml) solutions. The transmittance of solution was measured as a function of time on a UV–Vis spectrophotometer (Evolution 600, Thermo Fisher Scientific) using a quartz cuvette with an optical path of 1 cm, and the nucleation time was determined by the time lapse between the mixing of Na_2CO_3 and CaCl_2 solutions and the onset of transmittance's decrease. The wavelength used was in the range from 600 to 605 nm and the transmittance was recorded at each step of 0.1 nm, so 50 data were obtained in one scanning cycle. The average of these 50 data was regarded as the transmittance at one measurement time.

To decrease the diffusion of calcium and carbonate ions in the solution, diverse quantities of glycerol (GI, Aladdin Industrial Corporation) were added into solution. The nucleation times of supersaturated calcium carbonate solutions with 5%–10% mole fraction glycerol was measured. To increase the diffusion of chemicals in solution without significant heat accumulation, pulsed ultrasound with duty cycle of 50% was introduced into supersaturated solution by an ultrasonic cell disruptor (JY92-IIN, Ningbo Scientz Biotechnology Corporation). The nucleation time was measured at the solution with 10% molar fraction of glycerol at different ultrasonic power (0, 1.6×10^{-8} , 5.6×10^{-8} , 8.0×10^{-8} , 1.6×10^{-7} W). It should be noted that the nucleation time is the sum of the experimental data measured by UV–Vis spectrophotometer and the duration of ultrasonic process. All these experiments were conducted at room temperature under the typical atmosphere of a chemical laboratory.

To exclude the effect of solubility variation induced by the addition of glycerol, the saturation concentration of CaCO_3 at different addition of glycerol were measured by electrical conductivity method, referring to the approach [40]. Briefly, the sum of molar ionic conductivity of Ca^{2+} and CO_3^{2-} in solutions with different glycerol fractions was determined indirectly according to the slope of plots reflecting the relationship between the conductivity and concentration of Na_2CO_3 , CaCl_2 and NaCl solutions (Figs. S2 and S3), then the saturation concentration of CaCO_3 could be calculated by considering the sum of molar ionic conductivity, the conductivity of CaCO_3 saturated solution and solvent (Table S4). The results show that when the glycerol fraction increases from 0 to 10% (mol), the saturation concentration of CaCO_3 increases from 2.522×10^{-4} to 2.804×10^{-4} mol·L⁻¹. The change of concentration is tiny. Hence, at the addition of glycerol less than 10% (mol), the effect

of glycerol on the solubility of CaCO_3 could be neglected, and the initial supersaturation ratio could be considered the same.

3. Results and Discussion

3.1. Simulation on the nucleation rates of CaCO_3 at different diffusion of ions

In a nucleation process, the diffusion of monomers determines the collision frequency, which may influence the nucleation rate. This is main hypothesis to be discovered in this paper, as illustrated in Fig. 1A. MD simulation is employed to investigate the nucleation of calcium carbonate at different diffusion conditions. To regulate the diffusion of calcium and carbonate ions, glycerol is added into the solution at different ratios. The diffusion coefficients of calcium and carbonate ions are quantified by MSD method described in Section 2.1, as shown in Fig. 1B. With the increase of glycerol, the diffusion coefficient decrease from 0.995×10^{-10} of pure water to 0.107×10^{-10} m²·s⁻¹ at 20% (mol) ratio of glycerol in water, which agrees well with experiments [41]. To quantify the nucleation rate of calcium carbonate at different solvents, the MFPT method is employed to record the time of nuclei reaching a designed size. Fig. 1C shows the nucleation rates of calcium carbonate at different solvents, which is obtained by calculating the MFPT data in Figs. 1D and Fig. S1. The addition of glycerol leads to a sharp decrease of the nucleation rate of calcium carbonate. In the water solution, the nucleation rate is 8.5×10^{33} m⁻³·s⁻¹ while it decreases to 0.04×10^{33} m⁻³·s⁻¹ at 20% (mol) addition of glycerol. The reduction of nucleation rates is attributed to the diffusion limitation of chemicals in the viscous solvent in which the movement of ions is restricted and the chance to meet other ions or clusters is reduced. In the classical kinetic model of nucleation, the diffusion usually refers to the diffusivity along the nucleus size coordinate [42], often interpreted as an attachment or detachment rate, instead of the displacement coordinate. Here in our study, the diffusion has more clear physical meaning and could be regulated by solvent dynamics.

To confirm the role of diffusion in the nucleation and to exclude the complex effect of glycerol, we designed a simulation in which the movement of ions was speeded up by giving additional energy via a thermostating force. This force is given at the frequency of 0.1 ps with different power from 0 to 3.2×10^{-7} W. The force does not affect the mass velocity of individuals and the whole system. The additional force could be regarded as the energy given by a sonication in a solution, as illustrated in Fig. 2A. With the increase of the additional energy, the diffusion coefficient of ions increases remarkably, as shown in Fig. 2B. Fig. 2C shows the size evolution of clusters at different given energies. The introduction of additional energy speeds up the growth of clusters. At the same size of clusters, higher energy input leads to a shorter time of MFPT. Fig. 2D show the nucleation rate of calcium carbonate at different diffusion coefficient (the MFPT fitting parameters are given in Tables S2 and S3). The nucleation rate increases with the diffusion coefficient, confirming the above finding in the glycerol system.

3.2. Experimental evaluation of the dependence of nucleation rates on chemicals diffusion

To experimentally confirm the role of chemicals diffusion in a nucleation, we designed two series of experiments by adding glycerol into solution to slow down the diffusion of ions and by introducing pulsed ultrasonic power to speed up the diffusion of ions. The supersaturated calcium carbonate solution ($S = 4.449$) was taken as the initial solution. The transmittance of the solution was recorded during the nucleation process, which is used to cal-

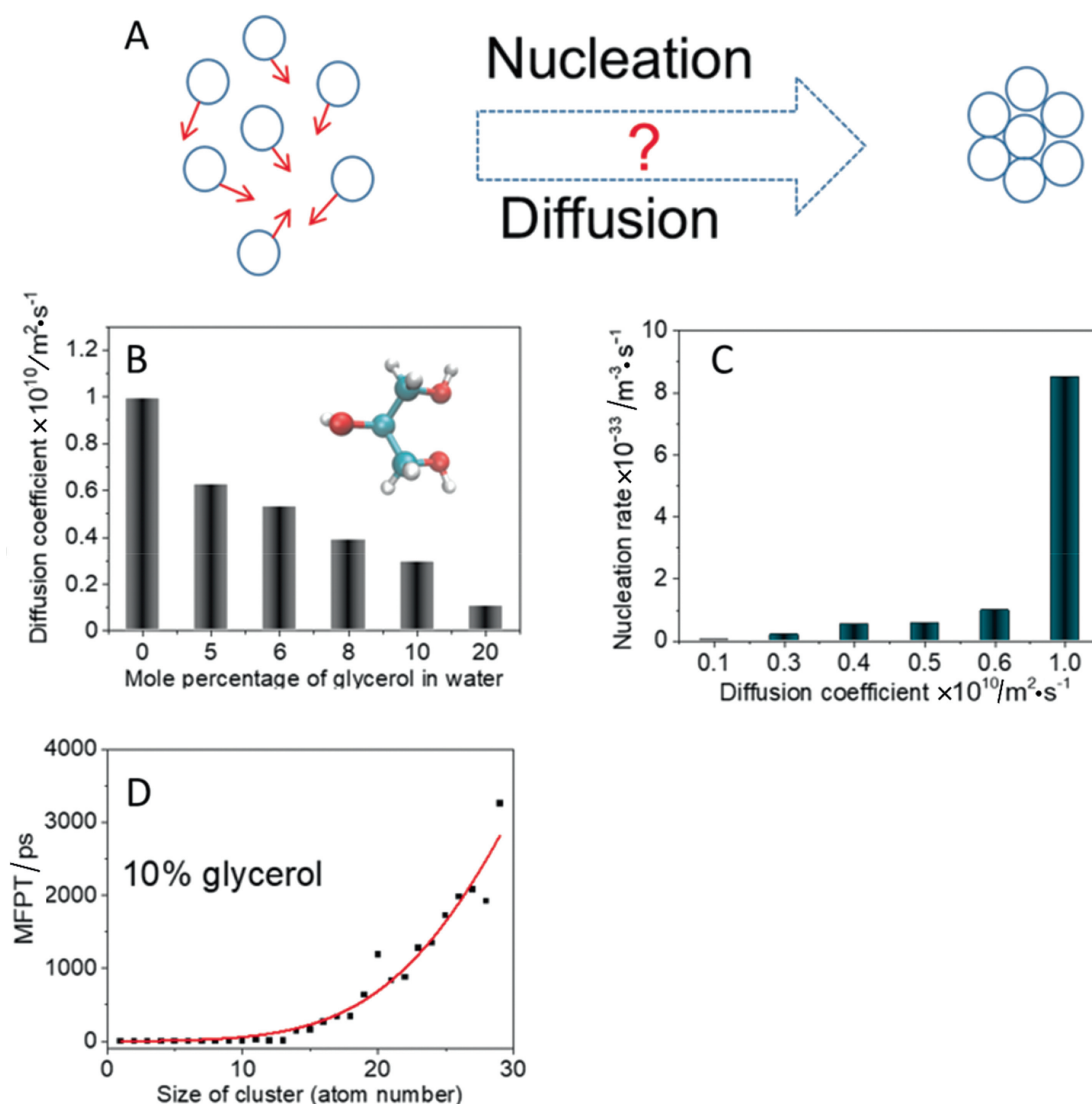


Fig. 1. Simulation of the nucleation of calcium carbonate at different addition of glycerol. Schematic diagram to discover the role of chemical diffusion in the nucleation of calcium carbonate (A). To regulate the diffusivity of calcium and carbonate ions, glycerol is added into the solution, which leads to the decrease of diffusion coefficient (B) and the reduction of nucleation rates (C) which is calculated by MFPT fitting method such as the curve under 10 mol% glycerol addition (D). The inset in B is a molecular structure of glycerol.

culate the nucleation rate. When there is a drop of the transmittance, a nucleation is detected. Although the size detected by light is larger than the critical sizes of nuclei, it could monitor the nucleation and growth process online and evaluate the induction time and the nucleation rate approximately [43].

Fig. 3A shows the transmittance variation over time of the solution at different addition of glycerol. At 10% (mol) addition of glycerol, there is a long platform, indicating a long induction time to form the detectable nuclei. With the decrease of glycerol amount, the platform becomes short. The nucleation rate of calcium carbonate at different glycerol solution is calculated based on the induction time, as shown in Fig. 3B. To keep the data comparable, the diffusion coefficient of ions at different glycerol solution refers to the simulation data. With the increase of diffusion coefficient, the nucleation rate increases remarkably, which agrees well with the simulation results, as shown in Fig. 1C. In the experiments with sonication, the transmittance drops quickly with the increase of the sonication power, as shown in Fig. 3C. When the pulse frequency is 25 kHz and the volume of solution is 10 ml, the energy input by 100 W ultrasound equals to 1.36×10^{-7} W in the simu-

lation box volume. By this conversion, the sonication power is comparable with the simulation data. The increase of sonic power greatly increases the nucleation rate of calcium carbonates, as shown in Fig. 3D, which confirms the simulation results in Fig. 2D. Both the simulation and experiment results show that the diffusion of chemicals play a significant role in the nucleation rate of calcium carbonates.

3.3. The relationship between nucleation rates and chemicals diffusion

In CNT, a linear relationship between the nucleation rate and diffusion coefficient is expected. To examine this supposition, the nucleation rates simulated at different diffusion coefficients were summarized in Fig. 4A. It is found that the linear fitting parameter R^2 is 0.555. However, the exponential fit shows a good accordance, as shown in Fig. 4A. When the nucleation rates take the logarithm, the linear fit could be established with a fitting parameter of 0.905, indicating an exponential relationship between the nucleation rate and diffusion coefficient.

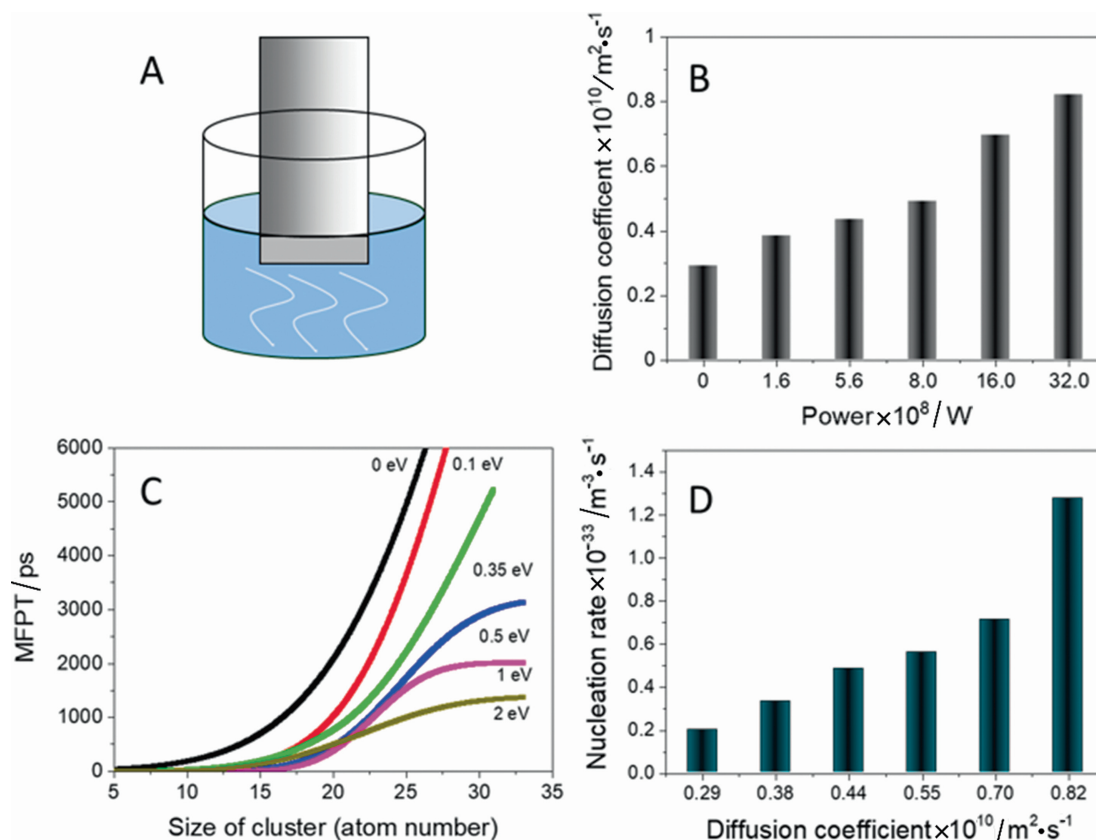


Fig. 2. Simulation of the nucleation of calcium carbonate at the different input of energy. An illustration of introducing pulse energy into the solution to enhance the diffusion of ions in the nucleation of calcium carbonate (A). The change of diffusion coefficient of ions at different power of pulse energy (B). Size evolution of clusters at different energy added (C). The nucleation rate of calcium carbonate at different diffusion coefficient regulated by the additional energy (D).

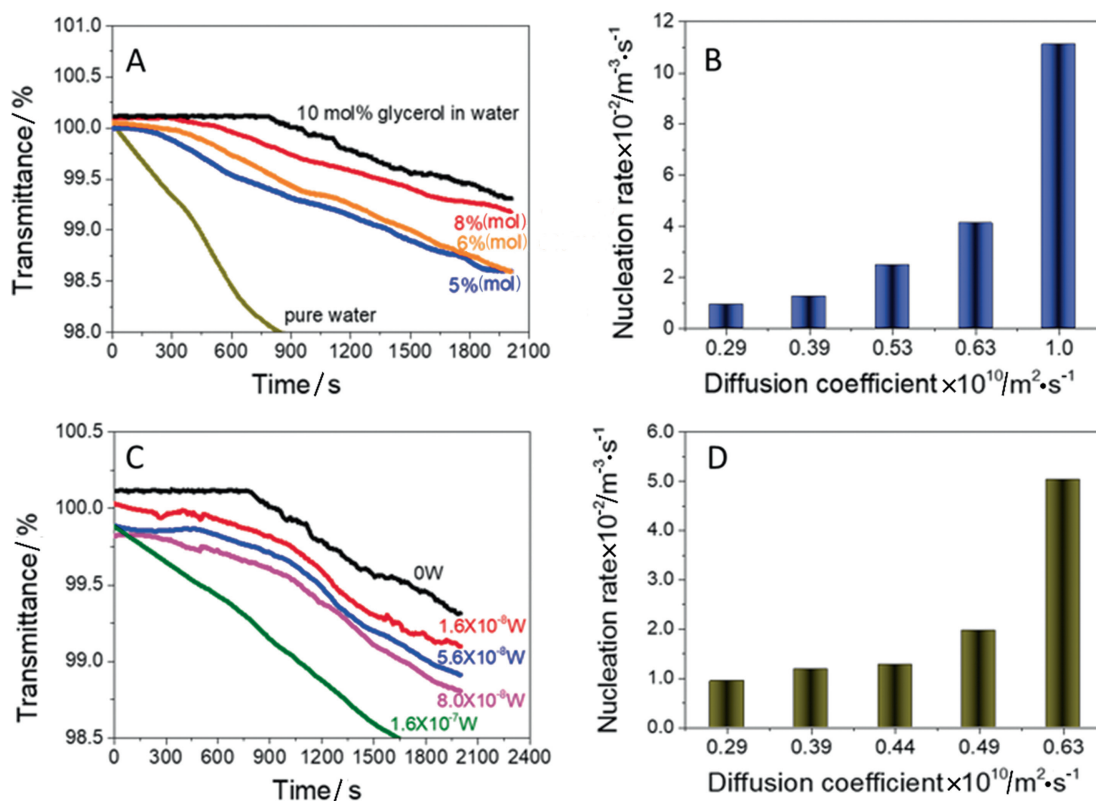


Fig. 3. Experimental evaluation of the role of chemical diffusion in the nucleation of calcium carbonate. The diffusion is reduced by adding glycerol into the solution (A, B) and enhanced by applying sonication to the solution (C, D). The transmittance of the solution (A, C) changes with time, which is used to calculate the nucleation rates of calcium carbonate (B, D).

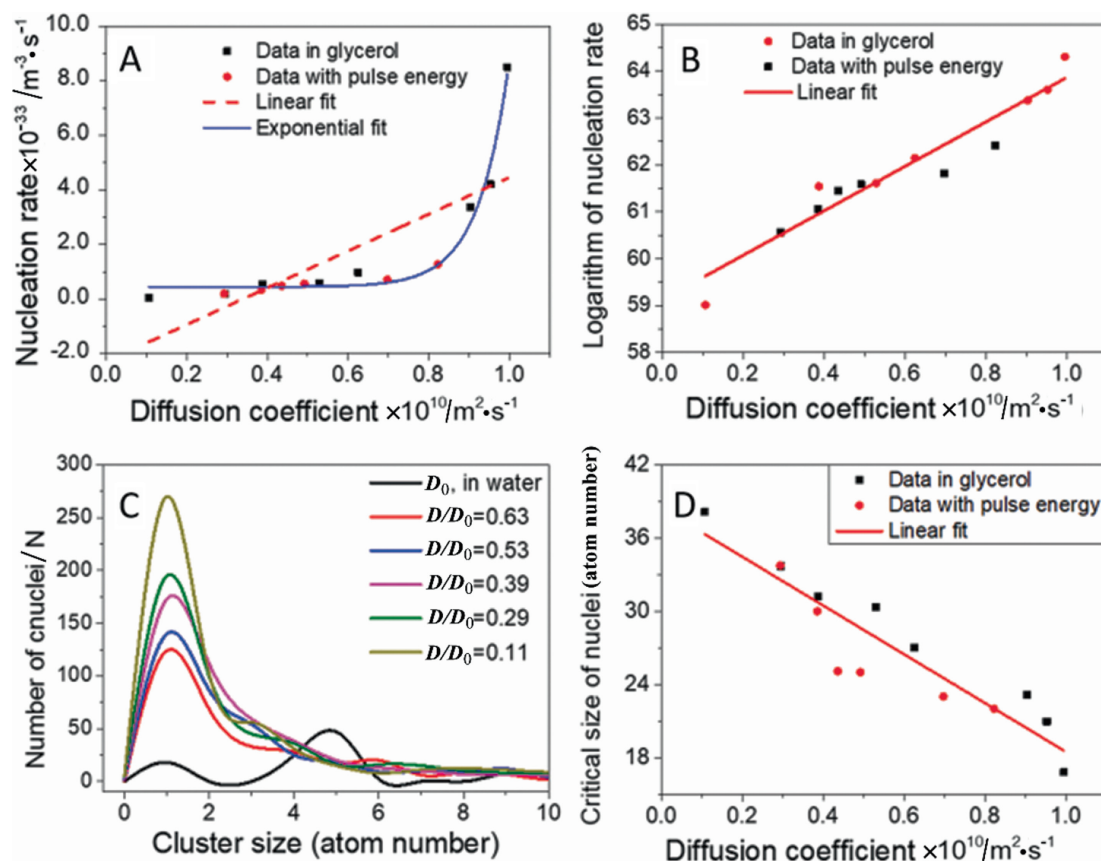


Fig. 4. The relationships between the diffusion coefficients and nucleation rates of calcium carbonates. An exponential relationship between diffusion coefficients and nucleation rates (A) and (B) is found. The exponential relation is attributed to the cluster aggregation in a nucleation, which is supported by the size distribution of nuclei (C). A linear relationship between critical size of nuclei and diffusion coefficient is obtained (D).

In the summary of experimental data, the similar conclusion is obtained, as shown in Fig. S4. The fitting parameter reaches 0.97 after the nucleation rate takes the logarithm. As far as our knowledge can reach, it is the first time to disclose the exponential relationship between nucleation rates and diffusion coefficients in the nucleation process. This finding is beyond the classical nucleation theory since a linear relationship between diffusion and nucleation rate is predicted in a classic nucleation theory. To reveal this exponential relationship, the size distribution of nuclei generated at different diffusion is calculated, as shown in Fig. 4C. At low diffusion coefficients, the unimodal distribution is observed while it changes to multimodal distribution at a high diffusion coefficient. It indicates that nuclei with different sizes are formed at high diffusion, which may result in nuclei aggregation. When the cluster aggregation contributes to the growth of nuclei, a quick formation of stable nucleus and so rapid increase of nucleation rates would be expected. The exponential relationship may be established. Besides, the relationship between the diffusivity and critical size is calculated, as shown in Fig. 4D. With the increase of diffusion coefficient, the critical size of nuclei decreased, which also challenges the classical nucleation theory. A further discovery in this direction is being conducted, in which the collision dependent nucleation model is under developing.

The finding in this study has a significant indication to the air pollution problem. In the summer, the concentration of haze sometimes does not accord with the emission, which is called the anti-season problem. This problem may be caused by the secondary nucleation of haze in the air at a diffusion-enhanced condition. A high temperature and a low atmospheric pressure promote the diffusion of the monomer, which may speed up the nucleation rate of

haze, leading to the anti-season problem. Therefore, to have a reasonable forecast of smog or fog, the dynamic factors should be well considered in the nucleation model.

4. Conclusions

The role of chemical diffusion in the nucleation of calcium carbonate was investigated in this study. MD simulation was employed to discover the nucleation of calcium carbonate at different chemical diffusions. The diffusion is regulated by the viscosity of solvents and a sonication to the solution. The simulation results showed that the nucleation rate of calcium carbonate increased with the diffusion coefficient of ions, which was confirmed by the designed experiments. The increase followed an exponential relationship, which was against with the linear relationship predicted by the classical nucleation model. This exponential relationship may be attributed to the cluster aggregation in a nucleation process at high chemical diffusion. This study confirms the dominant role of chemical diffusion in a nucleation process, which may help to formulate a route for the rational synthesis of materials and to find a solution for the air pollution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.03.039>.

References

- [1] J. Lee, J. Yang, S.G. Kwon, T. Hyeon, Nonclassical nucleation and growth of inorganic nanoparticles, *Nat. Rev. Mater.* 1 (8) (2016) 1–16.
- [2] T. Lapidot, O.K. Matar, J.Y.Y. Heng, Calcium sulphate crystallisation in the presence of mesoporous silica particles: Experiments and population balance modelling, *Chem. Eng. Sci.* 202 (2019) 238–249.
- [3] J.Y. Weng, Y.P. Huang, D.L. Hao, Y.H. Ji, Recent advances of pharmaceutical crystallization theories, *Chin. J. Chem. Eng.* 28 (4) (2020) 935–948.
- [4] A.F. Wallace, L.O. Hedges, A. Fernandez-Martinez, P. Raiteri, J.D. Gale, G.A. Waychunas, S. Whitlam, J.F. Banfield, J.J. De Yoreo, Microscopic evidence for liquid–liquid separation in supersaturated CaCO_3 solutions, *Science* 341 (6148) (2013) 885–889.
- [5] W.H. Sun, S. Jayaraman, W. Chen, K.A. Persson, G. Ceder, Nucleation of metastable aragonite CaCO_3 in seawater, *Proc. Natl. Acad. Sci. U.S.A.* 112 (11) (2015) 3199–3204.
- [6] P. Raiteri, J.D. Gale, Water is the key to nonclassical nucleation of amorphous calcium carbonate, *J. Am. Chem. Soc.* 132 (49) (2010) 17623–17634.
- [7] C. Lindenberg, M. Mazzotti, Continuous precipitation of L-asparagine monohydrate in a micromixer: Estimation of nucleation and growth kinetics, *AIChE J.* 57 (4) (2011) 942–950.
- [8] J.J. Chen, E.B. Zhu, J. Liu, S. Zhang, Z.Y. Lin, X.F. Duan, H. Heinz, Y. Huang, J.J. De Yoreo, Building two-dimensional materials one row at a time: Avoiding the nucleation barrier, *Science* 362 (6419) (2018) 1135–1139.
- [9] K.P. Hapgood, J.D. Litster, R. Smith, Nucleation regime map for liquid bound granules, *AIChE J.* 49 (2) (2003) 350–361.
- [10] K.H. Yu, T. Xu, X. Wu, W. Wang, H. Zhang, Q.B. Zhang, L.P. Tang, L.T. Sun, *In situ* observation of crystalline silicon growth from SiO_2 at atomic scale, *Research (Wash D C)* 2019 (2019) 3289247.
- [11] G.K. Schenter, S.M. Kathmann, B.C. Garrett, Dynamical nucleation theory: a new molecular approach to vapor–liquid nucleation, *Phys. Rev. Lett.* 82 (17) (1999) 3484.
- [12] S.M. Kathmann, G.K. Schenter, B.C. Garrett, Dynamical nucleation theory, in: B. N. Hale, M. Kulmala (Eds.), *Nucleation and Atmospheric Aerosols*, 2000, pp. 197–200.
- [13] M. Vazquez-Pufleau, M. Yamane, Relative kinetics of nucleation and condensation of silane pyrolysis in a helium atmosphere provide mechanistic insight in the initial stages of particle formation and growth, *Chem. Eng. Sci.* 211 (2020) 115230.
- [14] S. Luo, Z.S. Wei, D.D. Dionysiou, R. Spinney, W.P. Hu, L.Y. Chai, Z.H. Yang, T.T. Ye, R.Y. Xiao, Mechanistic insight into reactivity of sulfate radical with aromatic contaminants through single-electron transfer pathway, *Chem. Eng. J.* 327 (2017) 1056–1065.
- [15] D. Reguera, H. Reiss, Extended modified liquid drop-dynamical nucleation theory (EMLD-DNT) approach to nucleation: a new theory, *J. Phys. Chem. B* 108 (51) (2004) 19831–19842.
- [16] J. Wedekind, J. Wölk, D. Reguera, R. Strey, Nucleation rate isotherms of argon from molecular dynamics simulations, *J. Chem. Phys.* 127 (15) (2007) 154515.
- [17] T. Liu, X.Y. Dou, Y.H. Xu, Y.J. Chen, Y.S. Han, *In situ* investigation of dynamic silver crystallization driven by chemical reaction and diffusion, *Research (Wash D C)* 2020 (2020) 4370817.
- [18] N.E. Zimmermann, B. Vorselaars, D. Quigley, B. Peters, Nucleation of NaCl from aqueous solution: critical sizes, ion-attachment kinetics, and rates, *J. Am. Chem. Soc.* 137 (41) (2015) 13352–13361.
- [19] T. Meincke, H.X. Bao, L. Pflug, M. Stingl, R.N. Klupp Taylor, Heterogeneous nucleation and surface conformal growth of silver nanocoatings on colloidal silica in a continuous flow static T-mixer, *Chem. Eng. J.* 308 (2017) 89–100.
- [20] J.Y. Mo, R.D. Groot, G. McCartney, E.Y. Guo, J. Bent, G. van Dalen, P. Schuetz, P. Rockett, P.D. Lee, Ice crystal coarsening in ice cream during cooling: A comparison of theory and experiment, *Crystals* 9 (6) (2019) 321.
- [21] W.Q. Huang, L.R. Cai, H.F. Dang, Z. Jiao, H.B. Fan, F.L. Cheng, Review on formation mechanism analysis method and control strategy of urban haze in China, *Chin. J. Chem. Eng.* 27 (7) (2019) 1572–1577.
- [22] S.Y. Liu, J.C. Chai, X.N. Yang, B-diketones at water/supercritical CO_2 interface: a molecular dynamics simulation, *Chin. J. Chem. Eng.* 17 (6) (2009) 990–998.
- [23] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids, *J. Am. Chem. Soc.* 118 (45) (1996) 11225–11236.
- [24] R.A. Buckingham, The classical equation of state of gaseous helium, neon and argon, *Proc. Royal Soc. Lond. Ser. A Math. Phys. Sci.* 168 (933) (1938) 264–283.
- [25] P. Raiteri, J.D. Gale, D. Quigley, P. Mark Rodger, Derivation of an accurate force-field for simulating the growth of calcium carbonate from aqueous solution: A new model for the calcite/water interface, *J. Phys. Chem. C* 114 (13) (2010) 5997–6010.
- [26] S.A. Davari, D. Mukherjee, Kinetic Monte Carlo simulation for homogeneous nucleation of metal nanoparticles during vapor phase synthesis, *AIChE J.* 64 (1) (2018) 18–28.
- [27] M.X. Gu, H.F. Shi, K. Ling, A. Lv, K.W. Huang, M. Singh, H. Wang, L. Gu, W. Yao, Z. F. An, H.L. Ma, W. Huang, Polymorphism-dependent dynamic ultralong organic phosphorescence, *Research (Wash D C)* 2020 (2020) 8183450.
- [28] X.Q. Wang, S.Y. Li, L. Zhao, C.M. Xu, J.S. Gao, A DFT and TD-DFT study on electronic structures and UV-spectra properties of octaethyl-porphyrin with different central metals (Ni, V, Cu, Co), *Chin. J. Chem. Eng.* 28 (2) (2020) 532–540.
- [29] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.* 117 (1) (1995) 1–19.
- [30] J. Xu, X.W. Wang, X.F. He, Y. Ren, W. Ge, J.H. Li, Application of the Mole-8.5 supercomputer: Probing the whole influenza virion at the atomic level, *Chin. Sci. Bull.* 56 (20) (2011) 2114–2118.
- [31] Q. Li, S. Tan, L.L. Li, Y.Y. Lu, Y. He, Understanding the molecular mechanism of pulse current charging for stable lithium-metal batteries, *Sci. Adv.* 3 (7) (2017) e1701246.
- [32] D.A. Jahn, F.O. Akinkunmi, N. Giovambattista, Effects of temperature on the properties of glycerol: A computer simulation study of five different force fields, *J. Phys. Chem. B* 118 (38) (2014) 11284–11294.
- [33] L.S. Dodda, J.Z. Vilseck, J. Tirado-Rives, W.L. Jorgensen, 1.14*CM1A-LBCC: localized bond-charge corrected CM1A charges for condensed-phase simulations, *J. Phys. Chem. B* 121 (15) (2017) 3864–3870.
- [34] L. Negadi, B. Feddal-Benabed, I. Bahadur, J. Saab, M. Zaoui-Djelloul-daoudaji, D. Ramjugernath, A. Negadi, Effect of temperature on density, sound velocity, and their derived properties for the binary systems glycerol with water or alcohols, *J. Chem. Thermodyn.* 109 (2017) 124–136.
- [35] X.Y. Dou, Y.X. Chen, Y.S. Han, Modification of glycerol force field for simulating silver nucleation under a diffusion limited condition, *Colloids Surf. A: Physicochem. Eng. Aspects* 592 (2020) 124574.
- [36] T.W. Sirk, S. Moore, E.F. Brown, Characteristics of thermal conductivity in classical water models, *J. Chem. Phys.* 138 (6) (2013) 064505.
- [37] Z. Kolská, M. Černoušek, M. Staszek, J. Leitner, V. Švorčík, Study of binary system glycerine-water and its colloidal samples of silver nanoparticles, *J. Mol. Liq.* 218 (2016) 363–372.
- [38] P. Wirsberger, D. Frenkel, C. Dellago, An enhanced version of the heat exchange algorithm with excellent energy conservation properties, *J. Chem. Phys.* 143 (12) (2015) 124104.
- [39] N. Kalantar, D. Segal, Mean first-passage time and steady-state transfer rate in classical chains, *J. Phys. Chem. C* 123 (2) (2019) 1021–1031.
- [40] A. Dominguez, A. Fernandez, N. Gonzalez, E. Iglesias, L. Montenegro, Determination of critical micelle concentration of some surfactants by three techniques, *J. Chem. Educ.* 74 (10) (1997) 1227.
- [41] H. Wang, Q. Lin, X.Y. Dou, T. Yang, Y.S. Han, A different view of solvent effects in crystallization, *Crystals* 7 (12) (2017) 357.
- [42] M.A. Rohrdanz, W.W. Zheng, M. Maggioni, C. Clementi, Determination of reaction coordinates via locally scaled diffusion map, *J. Chem. Phys.* 134 (12) (2011) 124116.
- [43] N. Lyczko, F. Espitalier, O. Louisnard, J. Schwartzentruber, Effect of ultrasound on the induction time and the metastable zone widths of potassium sulphate, *Chem. Eng. J.* 86 (3) (2002) 233–241.