Water nucleation in helium, methane, and argon

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Water nucleation in helium, methane, and argon: A molecular dynamics study

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Nucleation of highly supersaturated water vapor in helium, methane, and argon carrier gases at 350 K was investigated using molecular dynamics simulations. Nucleation rates obtained from the mean first passage time (MFPT) method are typically one order of magnitude lower than those from the Yasuoka and Matsumoto method, which can be attributed to the overestimation of the critical cluster size in the MFPT method. It was found that faster nucleation will occur in carrier gases that have better thermalization properties such that latent heat is removed more efficiently. These thermalization properties are shown to be strongly dependent on the molecular mass and Lennard-Jones (LJ) parameters. By varying the molecular mass, for unaltered LJ parameters, it was found that a heavier carrier gas removes less heat although it has a higher collision rate with water than a lighter carrier. Thus, it was shown that a clear distinction between water vapor-carrier gas collisions and water cluster-carrier gas collisions is indispensable for understanding the effect of collision rates on thermalization. It was also found that higher concentration of carrier gas leads to higher nucleation rate. The nucleation rates increased by a factor of 1.3 for a doubled concentration and by almost a factor of two for a tripled concentration. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5021765>

I. INTRODUCTION

Understanding and modeling condensation phenomena plays a crucial role in the field of earth sciences,^{1,2} biomedical research,^{3,4} and industrial processes such as the production of liquefied natural gas (LNG). Prior to liquefaction, impurities like water vapor, carbon dioxide, and hydrogen sulfide need to be removed to avoid blockages in the pipelines and heat exchangers and to prevent damage to the liquefaction equipment. Several removal procedures are available,⁵ but none of them effectively covers all types and concentrations of contaminants. Here we investigate the condensation of water as a first step in a gas treatment process.

Nucleation is the first stage in the condensation process subsequently followed by droplet growth. The nucleation process is called homogeneous when the presence of dust particles and foreign bodies can be excluded and small nuclei of the new phase are formed solely due to statistical thermal fluctuations within the metastable phase. These fluctuations need to overcome an energy barrier in order to form an interface between the gas phase and the new stable nucleus. The height of the nucleation barrier decreases as the degree of supersaturation increases. The supersaturation is defined as $S = \rho^n / \rho_{sat}^n$, where ρ^n and ρ_{sat}^n are the number densities of the supersaturated vapor and saturated vapor at identical conditions, respectively. The nucleation rate (J) is defined as the amount of stable (critical) clusters formed per unit time, per unit volume.

When a cluster catches a new water molecule, it absorbs the latent heat, which subsequently rises the temperature of the cluster. This leads to non-isothermal conditions in the system and highly affects the nucleation rate of the process (as nucleation is very sensitive to temperature changes). In experimental or real-life plants, a carrier gas typically removes the heat through high-frequency molecular collisions. It seems obvious that the more efficient the latent heat is removed from the cluster, the more the nucleation rate will approach the isothermal nucleation rate, where no latent heat is generated at all. Gas pressure also influences nucleation. An early study reported a pressure effect of the carrier gas on nucleation in a thermal diffusion cloud chamber setup.⁶ The pressure effect has been intensively studied both theoretically and experimentally; a detailed review is given by Brus *et al.*⁷ Still, both theoretical model predictions and experimental results are very much controversial. Improved formulations of the classical nucleation theory (CNT^{8–12}) agree on nucleation rates decreasing with increasing pressure of the carrier gas,^{13–15} but Feder *et al.*¹⁶ report the opposite effect. Experimental data show that nucleation rates either increase, decrease, or do not vary at all when the carrier gas pressure increases.¹⁷

The influence of the carrier gas density was previously investigated in molecular dynamics (MD) simulations of argon nucleation by Wedekind *et al.*¹⁸ The authors report an overall increase in nucleation rates with an increasing amount of helium. Their result is consistent with the studies on water nucleation by Zipoli *et al.*¹⁹ at 350 K using the coarse-grained TIP4P model in argon and of Tanaka *et al.*²⁰ using the extended

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simple point charge (SPC/E) water model in argon and temperatures of 275–350 K. Monte Carlo simulations were performed to compute the nucleation barrier of water cluster formation in nitrogen,²¹ where it was found that the nucleation barrier at 240 K is increasing with carrier gas density, while at 298.15 K no effect was found.

The role of the carrier gas type was investigated experimentally in a laminar flow diffusion chamber for n-hexanol nucleation.²² The nucleation rates were found to be larger for argon than for helium, with reduced differences at elevated temperatures. However, the nucleation pulse chamber experiments on water nucleation by Viisanen *et al.*²³ show no effect when varying the carrier gas (helium, neon, argon, krypton, or xenon), although a slower droplet growth was observed for heavier carrier gases.

In this paper we aim to understand the effect of the carrier gas on the nucleation process. We study the non-isothermal effect by evaluating the heat and mass transfer. We compute transport parameters such as collision rate and removed latent heat that are sometimes hard to measure in experiments. In a previous work,²⁴ we performed MD simulations of water nucleation in argon. Here we study the nucleation of water (using the TIP4P/2005 model) in helium^{7,25–27} and methane, where the latter is representative for industrial processes.²⁸ To our knowledge, so far no molecular simulation study investigated how the type of carrier gas influences water nucleation. We compute nucleation rates using the mean first passage time (MFPT) method^{29–31} and the Yasuoka and Matsumoto (YM) threshold method.³² We investigate and quantify how the molecular properties such as mass and interaction of the carrier gas define the thermalization behavior, i.e., the capacity to remove heat from the condensing water phase to the thermostated background carrier gas. We run generic simulations where we choose different molecular weights of the carrier gases to observe the effect on the system properties. We also compute the removed latent heat and nucleation rates for different number densities of the carrier gases.

II. PHYSICAL MODEL AND METHODOLOGY

A. MD model

We perform MD simulations using double precision Groningen Machine for Chemical Simulations (GROMACS) 5.0.4 in a $28 \times 28 \times 28$ nm simulation box with periodic boundary conditions³³ for all three dimensions. A leap-frog algorithm³⁴ is used to generate the molecular trajectories, with a time step of 0.5 fs.²⁴ The simulation box contains 5000 molecules of the condensing phase (water) and 5000 molecules of the carrier gas. We use two different carrier gases, helium and methane, both represented by a spherical Lennard-Jones (LJ) potential,

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where ϵ is the depth of the potential well, σ is the atom diameter, and r is the interatomic separation. The water molecules are described by the TIP4P/2005 rigid model³⁵ with an intermolecular potential,

TABLE I. Potential parameters and densities of carrier gases and water. The parameters for methane from Ref. 37 and for helium are from Ref. 38 and for the TIP4P/2005 water model from Ref. 35.

Atom/molecule	ϵ/k (K)	σ (Å)	q_H (e)	ρ (mg cm ⁻³)
CH ₄	148.55	3.7281	...	6.060
Ar	119.8	3.405	...	15.093
He	10.22	2.576	...	1.512
TIP4P/2005	93.2	3.1589	+0.5564	6.806

$$U_{inter} = \sum_{a,b < a} 4\epsilon_{OO} \left[\left(\frac{\sigma_{OO}}{r_{ab}} \right)^{12} - \left(\frac{\sigma_{OO}}{r_{ab}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \sum_{i,j < i} \frac{q_i q_j}{r_{ij}}. \quad (2)$$

The first summation represents the LJ interaction between the oxygen atoms of the water molecule, where ϵ_{OO} , σ_{OO} , and r_{ab} are the interaction strength, the length scale, and the distance between the oxygen atoms, respectively. The second summation represents the electrostatic potential, where ϵ_0 is the electric constant, q_i and q_j are the partial charges, and r_{ij} is the distances between the pairs of charged sites in the water molecule.

The LJ and the short-range Coulombic interactions are both truncated at a cutoff distance, r_{cut} , of 99 Å. The Particle-Mesh Ewald (PME)³⁶ technique is used for the long-range Coulombic interactions. Lorentz-Berthelot combining rules are assumed between unlike atoms i and j , with $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$. A water molecule is assumed to interact with the carrier gas only through its oxygen site.

In Table I, the values of the potential parameters and the starting densities are given (note that densities change during nucleation). For reference, the values for argon are also included here, as this gas was used in our previous publication.²⁴ In the forthcoming we will validate the water and carrier gases force fields (FFs) at the nucleation temperature 350 K.

B. System and model parameters

As a validation of the nucleation mechanism we examined the water density of the TIP4P/2005 model (Table I) for metastability. MD simulations were carried out in an NVT (i.e., constant number of particles, volume, and temperature) ensemble containing 2500 water molecules at 350 K and densities in the range of 3–33 mg cm⁻³. We use the Berendsen thermostat³⁹ with a relaxation time $\tau = 0.1$ ps and $r_{cut} = 30$ Å for all interactions.

We computed the averaged pressures and used a (cubic) spline interpolation to construct the 350 K isotherm. Note that the pressures are averaged over 20 000 simulation steps with inaccuracies of 0.2–10.9 bars, with large fluctuations at high densities. In Fig. 1, the isotherm from MD is shown together with the binodal line from the IAPWS-95 formulation,⁴⁰ spinodal line and 350 K isotherm from the GERG-2004 equation of state (EOS).⁴¹ We notice that the maximum of the MD isotherm is slightly above the EOS isotherm and quite close to the intersection with the spinodal line. The oscillating points at high densities are a result of the large pressure fluctuations

FIG. 1. Pressure-density diagram of water: binodal curve (IAPWS-95⁴⁰) and isotherm and spinodal curve (GERG-2004⁴¹). The squares represent the 350 K MD simulations of water. A spline fit is added to guide the eye.

in the unstable region. We thus conclude that the prediction of the GERG-2004 spinodal is consistent with our MD results and that the quenching of water at 350 K (6.806 mg cm^{-3}) is in the metastable regime.

To validate the carrier gas models we compute the self-diffusion coefficients (D) in 600 ps NVT simulations of 5000 molecules at 350 K, where we use the corresponding densities (Table I). Here we truncated the LJ interactions at $17 \text{ \AA}$. We compute D using Einstein's relation³³

$$6Dt = \lim_{t \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2, \quad (3)$$

where the right-hand side represents the mean squared displacement (MSD) over all atoms, with N being the number of atoms and $\mathbf{r}_i$ being the position of the atom i at time t . The diffusion coefficient is obtained from the least squares regression of the MSD. We averaged over five independent runs and the results are $D_{\text{He}} = (19.7 \pm 0.4) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{CH}_4} = (2.78 \pm 0.04) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and $D_{\text{Ar}} = (2.23 \pm 0.03)$

$\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The corresponding Reference Fluid Thermodynamic and Transport Properties (REFPROP)⁴² data are $D_{\text{He}} = (22.2 \pm 1.6) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{CH}_4} = (2.89 \pm 0.09) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and $D_{\text{Ar}} = (2.57 \pm 0.06) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The REFPROP values are within the error bars of the MD data for CH_4 and slightly outside for He and Ar. Such discrepancies were reported before for Ar.⁴³

To define condensation, water clusters consisting of two or more water molecules need to be identified. For this we use Stillinger's definition,⁴⁴ who argued that two atoms belong to a cluster if their centres of mass are within a fixed distance r_s . We assume that a water cluster is formed if the distance between two oxygen atoms becomes less than $3.7 \text{ \AA}$ ($\sim 1.17\sigma_{\text{O-O}}$).²⁴

C. Computational approach for nucleation rates

We initially equilibrate the systems over 200 ps during which the gas mixture reaches a stable set temperature of 1000 K and pressure of 63 bars. We first use the Berendsen thermostat³⁹ for the temperature (between 0 and 100 ps) and next use the Berendsen barostat for the pressure (between 100 and 200 ps), both with a relaxation time of $\tau = 0.1 \text{ ps}$. After applying the barostat, the volume of $(28 \text{ nm})^3$ changes by a maximum of 0.25%, which is considered negligible. Next, a 200 ps microcanonical ensemble is used to verify the energy drift of the unperturbed system (between 200 and 400 ps). Then the condensation is triggered by an instantaneous temperature drop (quenching) to 350 K by simple velocity rescaling. During the subsequent condensation period, the carrier gas is kept at 350 K by means of a velocity rescaling thermostat (with $\tau = 0.025 \text{ ps}$) and water is not coupled to any thermostat. Condensation is simulated for a period of 1250 ps.³²

In Fig. 2(a), we show a characteristic number density distribution at the end of the simulation run. In Fig. 2(b), the density distribution in half plane cross sections is shown. We notice in Fig. 2(a) that clusters are formed and in Fig. 2(b) that the maximum number density inside a cluster can reach approximately $3 \times 10^{-4} \text{ nm}^{-3}$, which is in good agreement with the bulk liquid number density of water⁴⁰ ($2.9 \times 10^{-4} \text{ nm}^{-3}$).

FIG. 2. Number density distribution (a) in the simulation box and (b) in half plane cross sections of the box.

FIG. 3. Averaged time development of water cluster thresholds “ n ” in (a) helium and (b) methane. In both figures “ n ”: larger than 20, 30, 40, and 50 molecules. Solid lines are fittings used to measure the nucleation rate.

We compute the nucleation rates by employing two different methods: the threshold method of Yasuoka and Matsumoto (YM method) and the mean first passage time (MFPT) method introduced by Wedekind *et al.*³¹

The YM method is particularly suited to compute nucleation rates in large and highly supersaturated systems,⁴⁵ where a significant amount of clusters is rapidly formed. The method is based on snapshots of cluster size distributions. From the distributions, the number of clusters larger than a threshold value (n_{th}) is plotted over time, where the threshold value should be larger than the critical size. Because we do not have *a priori* information on the critical cluster size, we choose an arbitrary range of values for n_{th} .

In Figs. 3(a) and 3(b), we plot the averaged time evolution of the number of water clusters in helium and methane for different n_{th} . The averaging is over 6 independent runs. During steady-state nucleation, the number of clusters increases linearly with time. This linear regime is followed by a plateau and a subsequent decrease, which suggests that nucleation stopped and droplet growth takes over. Straight lines are fitted through the data points in the nucleation regime in the same way as in our previous publication.²⁴ For any n_{th} larger than the critical cluster size, we expect the lines to run in parallel. According to the YM method,³² the nucleation rate can be determined from the slope of the fitted lines and the simulation box volume. These lines are not parallel for helium nor for methane. To compute the nucleation rates, we will use individual and averaged slopes. The decrease in the slopes of the lines is attributed to the high supersaturation conditions, where a large amount of small clusters are initially formed that later coalesce and grow into larger clusters.

In Fig. 4, we show the number of water monomers in methane and helium. To compute ρ^n we averaged the amount of monomers between 300 and 700 ps.²⁴ Using the TIP4P/2005 saturated density⁴⁶ ($\rho_{sat}^n = 2 \times 10^{-3} \text{ nm}^{-3}$) at 350 K, our systems have supersaturations $S = 51.82$ in helium and $S = 44.50$ in methane. These supersaturations are considerably higher than $S = 11.96$ in helium and $S = 10.27$ in methane when

using the literature data⁴⁰ ($\rho_{sat}^n = 8.7 \times 10^{-3} \text{ nm}^{-3}$), as was also observed by Pérez and Rubio.⁴⁷

At supersaturations of 51.82 (11.96 corresponding literature data) in helium and 44.50 (10.27) in methane, the CNT predictions of the nucleation barriers become $2.16 k_B T$ (5.40) for helium and $2.33 k_B T$ (6.13) for methane, showing that the nucleation mechanism prevails, with a critical cluster size of 1.09 (4.35) for He and 1.22 (5.27) for CH_4 and nucleation rates of $4.44 (613) \times 10^{28} \text{ cm}^{-3} \text{ s}^{-1}$ in helium and $2.74 (172) \times 10^{28} \text{ cm}^{-3} \text{ s}^{-1}$ in methane.

To analyze the evolution of the mechanism in our simulations, we included typical cluster distributions at three moments. In Fig. 5 at 20 ps (top figure), we notice that very small clusters are getting formed, while later at 300 ps and 700 ps they grow and coalesce into larger clusters.

Another way to compute the nucleation rate is the so-called MFPT method.⁴⁸ In this approach, the time until the largest cluster in the system reaches a given cluster size n is recorded. Next, from the averaged time over replicated simulations, the mean first passage time, $\tau(n)$, is obtained.

FIG. 4. Water monomers time evolution in argon, helium, and methane.

FIG. 5. Cluster size distribution at 20 ps, 300 ps, and 700 ps.

The approach is particularly suited for the study of nucleation in relatively small system sizes and high free-energy barriers. Under these conditions, a large amount of runs is necessary to generate a smooth MFPT curve. In this work, we are dealing with a low free energy barrier in a large system and thus six runs will suffice (nine for the methane-based system).

The results are plotted in Fig. 6, for helium, and in Fig. 7, for methane. We notice that the τ values grow continuously for increasing cluster sizes. This behavior was discussed in depth by Wedekind *et al.*,³¹ Chkonia *et al.*,⁴⁵ and Mokshin and Galimzyanov,⁴⁹ who argued that this is a clear indication that the nucleation and growth processes occur simultaneously for the

largest cluster and that the free-energy barrier for nucleation is relatively low. Yet, it was shown by Wedekind *et al.*³¹ that even for low free-energy barriers the method still provides a very good estimate of the critical size n_τ^* , defined by the inflection point of the MFPT curve: $\partial^2 \tau / \partial n^2 = 0$. Finally, the nucleation rates are given by $1/(V \tau_J)$, with V as the volume of the simulation box and τ_J as the plateau level reached by the curve.

In order to determine the inflection point, in Figs. 6 and 7, we plot the first-order derivative of τ as a function of n for helium and methane, respectively. These plots are obtained from the interpolations of the MD data. The first maximum of the curve (and thus the critical size) is found to be 20 for

FIG. 6. MFPT (τ) and first derivative $\partial \tau(n)/\partial n$ as a function of the cluster size in helium.

FIG. 7. MFPT (τ) and first derivative $\partial \tau(n)/\partial n$ as a function of the cluster size in methane.

helium and 17 for methane. Next, the MD results are correlated with a two-parameter (τ_J and b) least square fit of sigmoidal shape,

$$\tau(n) = \frac{\tau_J}{2} [1 + \text{erf}(b(n - n_\tau^*))], \quad (4)$$

where $\text{erf}()$ is the error function and b is defined by the Zel'dovich factor¹² $Z = b/\sqrt{\pi}$. The fitting domain is between $n = 0$ and $n_{\text{max}} = 2 \times n_\tau^*$, which corresponds to $\tau = 329$ ps for helium and $\tau = 243$ ps for methane. As starting points for τ_J we use the aforementioned τ values and for b we use zero. In Figs. 6 and 7, the resulting curves are plotted (solid lines). Convergence was reached in 6-7 iterations, with values of $\tau_J = 330$ ps and $b = 0.079$ for helium and $\tau_J = 215$ ps and $b = 0.096$ for methane. We use these values to compute the nucleation rates, which are discussed in Sec. III.

III. RESULTS AND DISCUSSIONS

A. Nucleation rates

In Table II, we define the notations and the starting density values of the systems. Here we also added simulations at a slightly lower water density (4.903 mg cm^{-3}) and higher carrier gas concentrations. In Table III, the nucleation rates are given. We obtain $J = 20.4 \pm 1.1 \times 10^{26} \text{ cm}^{-3} \text{ s}^{-1}$ for helium and $28.2 \pm 0.9 \times 10^{26} \text{ cm}^{-3} \text{ s}^{-1}$ for methane, where we averaged over three different slopes $n_{th} = 30, 40$, and 50 (see Fig. 3). Also the values from the individual threshold lines are given in Table III. The uncertainties of the MFPT rates are obtained from the standard deviation of $\tau(n)$ and those of the YM method from the variation of the slopes. Notice that the nucleation rates decrease with increasing n_{th} . The nucleation rates obtained from MFPT are typically one order of magnitude lower than those obtained from the YM method, as was also found in the study by Römer and Kraska⁵⁰ for zinc nucleation in argon. The authors attributed this discrepancy to the coupling of the nucleation and growth processes. The MFPT method considers only the largest cluster. Thus, if this cluster is already in growth stage, the method will overestimate the size of the critical cluster and underestimate the nucleation rate. Yet, the MFPT method predicts a critical cluster size of 20 for helium and of 17 for methane. From this we can confirm that the choice of the threshold values n_{th} in the YM method was correct indeed, as these threshold values should be larger than the critical cluster size.

Remarkably, the three carrier gases (helium, argon, and methane) have similar nucleation rates in spite of the

TABLE II. MD systems and densities (ρ) in mg cm^{-3} from the type and number of molecules of the carrier gas. All systems contain 5000 water molecules.

Carrier gas	No. molec.			
	5000 ^a	5000 ^b	10 000 ^b	15 000 ^b
Helium	S _{0,He} 5.99	S _{1,He} 8.32	S _{2,He} 9.83	S _{3,He} 11.34
Methane	S _{0,CH₄} 9.27	S _{1,CH₄} 12.87	S _{2,CH₄} 18.93	S _{3,CH₄} 24.99
Argon	...	S _{1,Ar} 21.90	...	...

^a $\rho_{\text{H}_2\text{O}} = 4.903 \text{ mg cm}^{-3}$.

^b $\rho_{\text{H}_2\text{O}} = 6.806 \text{ mg cm}^{-3}$.

differences in molecular weight and interaction model parameters (see Table I). This will be discussed in Subsection III B.

B. Thermalization by the carrier gas

The removal of latent heat (thermalization) from the clusters is highly dependent on the collision rate of the clusters with the surrounding carrier molecules. In the study by Wedekind *et al.*¹⁸ on the influence of the carrier gas on argon nucleation, the authors argue that a lighter carrier gas is expected to show better thermalization characteristics than heavier gas, due to higher collision frequency with clusters. The statement is based on the theoretical prediction of Feder *et al.*¹⁶ for monoatomic vapors and gases. We address this by comparing the collision rates, removed energy, and nucleation rates for our three different carrier gases in the S₁ systems.

We compute binary water-carrier gas collision rates (v_{cw}) averaging over the first 600 ps after the quenching with 1 ps time step and we define a collision by an intermolecular distance smaller than 1.12σ . The removed energy (Q) is computed by subtracting the final total energy (at 1.25 ns) from the initial total energy. As the energy in the system is transferred not only through collisions between carrier gas and water molecules but also between the carrier gas molecules among themselves, we also consider the carrier-carrier gas collision rates (v_{cc}) which is averaged over the first 600 ps as well. The results are given in Table IV. We note that the slight discrepancies between nucleation rates are correlated with the amount of removed energy and with the water-carrier gas and carrier-carrier gas collision rates. Apparently the removal of energy is not governed

TABLE III. MD nucleation rate (J) values in $10^{26} \text{ cm}^{-3} \text{ s}^{-1}$ of water in helium, methane, and argon at 350 K.

Method	S _{0,He}	S _{1,He}	S _{2,He}	S _{3,He}	S _{1,Ar}	S _{0,CH₄}	S _{1,CH₄}	S _{2,CH₄}	S _{3,CH₄}
YM _{30,40,50}		20.4 ± 1.1	28.5	42.6	23.0 ± 1.0 ²⁴		28.2 ± 0.9	36.9	49.5
YM ₂₀		29.1 ± 1.1			...		42.8 ± 0.9		
YM ₃₀		22.6 ± 1.3			25.7 ± 0.9		35.5 ± 1.0		
YM ₄₀		19.3 ± 1.2			22.9 ± 1.0		25.9 ± 0.8		
YM _{20,30,40}	14.5					19.5			
MFPT	1.06	1.37 ± 0.16			1.71 ± 0.50	1.42	2.08 ± 0.27		

TABLE IV. Computational results and reduced mass of the carrier gases, with J_{YM} being the nucleation rate from the YM method.

Carrier gas	CH ₄	Ar	He
$J_{YM(30,40,50)}$ ($10^{26} \text{ cm}^{-3} \text{ s}^{-1}$)	28.2	23.0	20.4
Q (10^4 RT)	3.54	2.96	2.79
v_{cc} (ps^{-1})	79	60	32
v_{wc} (ps^{-1})	56	53.5	44
$m_c/m_{\text{H}_2\text{O}}$	0.89	2.22	0.22

by the molecular mass of the carrier gas (m_c), as the largest energy removal is found for CH₄ with a mass ratio between Ar and He. Obviously these carrier gases differ in other properties as well (see Table I), which could also have an effect on the removal of energy.

We investigate further the mass dependency of water-carrier collision rates and removed energy by varying m_c whilst keeping the other properties of the carrier gases the same. The results are given in Fig. 8. We notice that for variations of m_c , the trends of the energy removal and binary collision rates are opposed, having for a larger molecular mass higher collisions but lower heat transferred. The lower heat transfer of the heavier carrier gas can be explained through an analytical derivation of the centre of mass translational post-collision velocities of water molecules; this was also reported in Ref. 51. The water-carrier collisions consist of interactions of carrier gas molecules not solely with water nuclei but also with water monomers. Due to the low energy transfer, a heavier carrier gas will encounter more water monomers and smaller water clusters to collide with compared to a lighter carrier gas. Thus, the different cluster and monomer distribution evolution in these systems lead to differences in the collision rates. Hence from our simulations the thermalization dependency on m_c is in agreement with Wedekind's statement, as long as the interaction parameters are kept constant.

Figure 8 also shows that $Q_{\text{CH}_4} > Q_{\text{Ar}} > Q_{\text{He}}$ and that $v_{wc}^{\text{CH}_4} > v_{wc}^{\text{Ar}} > v_{wc}^{\text{He}}$ for corresponding molecular masses. In Table V, the nucleation rates for all these masses are

FIG. 8. Removed energy and collision rates as a function of the reduced m_c . Open circles represent true values.TABLE V. Comparison of water nucleation rates for different molecular masses of argon, helium, and methane. Note that the J_{YM} in helium at the largest mass could not be computed due to sparse data points.

$J_{YM(30,40,50)}$ ($10^{26} \text{ cm}^{-3} \text{ s}^{-1}$)	$m_c/m_{\text{H}_2\text{O}}$			
	0.22	0.89	2.22	22.22
CH ₄	30.2	28.2	24.4	3.21
Ar	27.9	26.7	23.0	10.8
He	20.4	14.9	11.0	...

computed. From this table we notice that $J_{\text{CH}_4} > J_{\text{Ar}} > J_{\text{He}}$, except for the highest mass ratio 22.22, where the computation of J becomes ambiguous. At this point we can argue that the mass of the carrier gas is not the only factor in thermalization but also the interaction parameters σ and ϵ play a certain role. Additional simulations were performed where we changed the interaction strength (ϵ) and kept the other properties unchanged. In Fig. 9, we can observe that the increasing strength of the interactions leads to higher energy removal in all carrier gases.

Finally, the interplay between mass and interaction parameters of the carrier gases supports the small discrepancies in the nucleation rates. This explains why CH₄ having optimal parameter values has the largest nucleation rate.

C. Effect of the carrier gas concentration

We now investigate the effect of the carrier gas concentrations on the latent heat removal for different carrier gases. The amount of water molecules in the computational box is always 5000, but the amount of carrier gas molecules is varied between 2500 and 15 000.

The results are given in Fig. 10. It is clear that for higher carrier gas densities more latent heat is removed from the formed water clusters due to the increasing amount of collisions. The differences between helium and argon are marginal, whereas methane is clearly able to remove more latent heat than the other two carrier gases. The (average) pressure range

FIG. 9. Removed energy as a function of interaction strength (ϵ) of methane, helium, and argon.

FIG. 10. Removed energy as a function of number density of the carrier gas: methane, helium, and argon. The data points correspond to 2500, 5000, 7500, 10 000, and 15 000 molecules, respectively. In all cases, there are 5000 water molecules present.

of the systems is in between 14 and 38.5 bars for helium and between 12.5 and 36 bars for methane.

We also computed the nucleation rates, averaged over 6 simulations, of these concentrations by using the YM method averaged over $n_{th} = 30, 40, 50$. The results are included in Table III. By doubling the carrier gas concentration (10 000), our nucleation rates increase by a factor of 1.3, for both helium and methane. These results are consistent with a study on coarse-grained TIP4P in argon,¹⁹ where the increase factor was 1.6.

By tripling the carrier gas concentration (15 000), the nucleation rates have increased by almost a factor of two for both helium and methane. This confirms our intuitive notion that the presence of more carrier gas molecules enhances the removal of latent heat from the condensing water phase and also increases the nucleation rates, as also known from the simple collision theory prediction, where the rate of collision between two gases is linearly proportional to the carrier concentration.

IV. CONCLUSIONS

Molecular dynamics simulations were conducted to analyze the influence of the molecular properties and concentration of the carrier gas on water condensation at 350 K. We used the TIP4P/2005 water model and the LJ potential for helium, methane, and argon. We applied the mean first passage time (MFPT) and Yasuoka and Matsumoto (YM) methods to compute the nucleation rates. We found that the MFPT results are typically one order of magnitude lower than the YM method for all carrier gases. This is in agreement with earlier results from the literature.

Surprisingly, it was found that the nucleation rates of water in the three carrier gases did not show large differences, although those for methane were found systematically higher. We found that these slight differences are clearly correlated with the amount of removed latent heat and with the water-carrier gas and carrier-carrier gas molecular collisions.

Despite having a mass between argon and helium, methane leads to the highest nucleation rate showing that thermalization is not governed by the molecular mass of the carrier gas.

We varied the molecular mass of the carrier gases while keeping the rest of the properties constant. By increasing the mass of the carrier, we found that the water-carrier gas binary collisions increase while the heat removal decreases and thus nucleation rates decrease as well. From the cluster distribution in these simulations, more water monomers and smaller water nuclei are found in a heavier carrier gas than in a lighter carrier gas. Moreover, for corresponding masses, the different interaction parameters of the carrier gases also lead to discrepancies in thermalization efficiency showing that interaction parameters also play a role in thermalization. Finally, true methane, in comparison to argon and helium, has optimal values of mass and interaction parameters rendering higher nucleation rates.

The concentration of the carrier gas was also varied. Upon increasing the background concentration of the carrier gases, both the thermalization efficiency and nucleation rates increased. For a doubled carrier gas concentration, the nucleation rates increased by a factor of 1.3, slightly less than in the study of Zipoli *et al.*¹⁹ Whereas for tripled carrier gas concentration, the nucleation rates have increased by almost a factor of two.

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