Nanoparticle-Mediated Evaporation at Liquid-Vapor Interfaces

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Abstract

Advancing solution-based additive manufacturing of functional materials demands a fundamental understanding of how nanoparticles straddling a liquid-vapor interface influence evaporation. Using many-body dissipative particle dynamics, we model evaporation at liquid-vapor interfaces with adsorbed nanoparticles. We quantitatively characterize the interfacial mechanics and the nanoparticle-mediated evaporation, using a particle-free interface as the reference system. We demonstrate that particle-particle interactions are critical for surface tension reduction induced by nanoparticles. The comparison of evaporation rates measured for different surface coverages with partially-wetted nanoparticles shows that the interface-bound nanoparticles can suppress evaporation through reducing the accessible interfacial area. We also observe reduced evaporation rates when the wettability of nanoparticles is varied from hydrophilic to hydrophobic while the surface coverage is kept approximately constant. This behavior suggests that obstruction in the evaporation path of escaping vapor beads can also inhibit net evaporation. The results also indicate the interfacial mechanics has no direct correlation with evaporation. Further analysis of the evaporation suppression provides important insight that the retardation effect of surface-covering nanoparticles depends on ambient conditions and highlights that the nanoparticle monolayers modulate evaporation in a similar manner as insoluble surfactant monolayers.

Keywords: nanoparticle monolayers; surface tension; evaporation

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Introduction

High-throughput, low-cost coating techniques (dipping, spinning, and spraying) and inkjet printing are important additive processes for manufacturing thin films of functional materials from sol-gel precursors.[1–6] Key to all these processes is to organize building block materials into precise and predetermined nano- or microstructures in order to achieve desired functionalities. However, the self-organization occurs in liquid environments and is accompanied by evaporation to remove solvents. Hence, evaporative effects play a paramount role in determining the final morphology of produced materials and must be treated prudently in manufacturing.[7–9]

In particular, the evaporation-driven self-assembly in deposited liquid masses like sessile droplets[7,10–14] and rivulets[15–17] has received much attention in recent years. The coffee ring effect is a prime example of this burgeoning field, which demonstrates the intricate interplay of fluid dynamics, diffusion, capillarity, and evaporation.[7,8,18–20] Lin et al.[14,21] and Bigioni et al.[10] have reported the formation of close-packed nanocrystal monolayers on the top surface of a volatile sessile droplet that encompasses thiol-capped nanoparticles. As droplet shrinks due to rapid evaporation, the particles impinge the descending liquid-vapor interface and are arrested by the capillary force, given that the interface velocity is fast compared to particle diffusion in the bulk solution. Upon complete evaporation of solvent, solid nanocrystal sheets with long-range ordering can be obtained on the substrate. In contrast, the coffee ring effect prevails over the monolayer growth on the liquid-air interface when the evaporation is slow, thereby forming three-dimensional nanocrystals at the edge of the droplet. While a sufficiently high evaporation rate is required to initiate nanoparticle assembly at the interface, other experiments and computational simulations [22,23] show that slow evaporation rates improve the quality of nanocrystals with less defects and grain boundaries.

These studies have exemplified that manipulating evaporation is critical to better control of the self-assembly dynamics of nano- or microscopic building blocks (e.g., colloidal particles and macromolecules) and the final structure of solid materials in the sol-gel methods.[24] Nevertheless, the existence of nanoparticles will inevitably perturb the evaporation process and present a serious challenge to the evaporation control. Although the effects of evaporation on particle transport and assembly in drying liquid masses have been extensively studied, how nanoparticles influence evaporation remains largely unexplored to date. Some pioneering literature

reports the addition of nanoparticles to bulk solvents can either enhance or suppress evaporate rate depending on the surface chemistry, size, and structure of the particles.[25–27] Other studies show the evaporation of sessile droplets with dispersed nanoparticles in the bulk is enhanced due to the synergistic effect of increased initial spreading, prolonged contact line pinning during evaporation, and greater thermal conduction for phase change.[28,29] Cheng and Grest [23] reported weak blockage effect of nanoparticles on evaporation when nanoparticles assemble into crystalline structures below the liquid-vapor interface. They speculated that the evaporation will slow down significantly when the nanoparticle layer straddles the interface. Although these studies touch upon the evaporation behavior in the presence of nanoparticles, a systematic study to elucidate the modulation of evaporation by interface-bound nanoparticles is still lacking.

Herein we use computational modeling to investigate the nanoparticle-mediated evaporation. We particularly focus on comparing the evaporation kinetics of a variety of nanoparticle-covered interfaces at different evaporation conditions. Below, we first describe the computational approach that allows us to formulate this interfacial system on the mesoscale. Using the newly developed model, we characterize the interfacial mechanics of the liquid-vapor interfaces with adsorbed nanoparticles. We then measure the evaporation of planar liquid-vapor interfaces covered with nanoparticles having specified surface wettability and discuss our findings on the nanoparticle-mediated evaporation. In the discussion, we highlight the importance of ambient vapor pressure and emphasize the analogy between the nanoparticle monolayers and insoluble surfactant monolayers in regulating evaporation.

Methodology

We use many-body dissipative particle dynamics (MDPD)[30–35] to model the liquid-vapor coexistence with nanoparticles present at the interface. MDPD is a coarse-grained, particle-based computational method that can effectively simulate multi-phase, multi-component systems on the mesoscale and captures correct hydrodynamic behavior.[25,36–43] MDPD models a volume of fluid as individual beads, and each bead represents a cluster of molecules. The evolution of the entire system over time is dictated by the motion of beads, which is governed by Newton’s equation of motion, $m d\mathbf{v}_i / dt = \mathbf{f}_i$. In particular, the force acting on each bead i from neighboring beads consists of three parts $\mathbf{f}_i(t) = \sum_j (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R)$, each of which is pairwise additive. The

three terms respectively describe the conservative, drag, and random forces. The sum runs over all beads j within a certain cutoff radius r_c from bead i .

In order to achieve liquid-vapor coexistence in MDPD fluids, the conservative force $\mathbf{F}_{ij}^C$ is given by $\mathbf{F}_{ij}^C = A_{ij}(1 - r_{ij}/r_c)\hat{\mathbf{r}}_{ij} + B_{ij}(\bar{\rho}_i + \bar{\rho}_j)(1 - r_{ij}/r_d)\hat{\mathbf{r}}_{ij}$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$. [32] Here, the force contains a repulsive term that depends on local densities $\bar{\rho}_i$ and $\bar{\rho}_j$ as well as inter-bead distance r_{ij} and an attractive term depending only on the distance. The attraction strength $A_{ij} < 0$, the repulsion strength $B_{ij} > 0$, and the repulsion range $r_d < r_c$. The interaction parameters A_{ij} and B_{ij} are given in terms of $k_B T / r_c$, where $k_B T$ is the Boltzmann constant and T is the temperature of the system. The local density for each particle is defined as $\bar{\rho}_i = \sum_{j \neq i} 15 / 2\pi r_d^3 (1 - r_{ij}/r_d)^2$. [32] This many-body conservative force was shown to produce cubic pressure-density equations of state with a van der Waals loop, thereby permitting the liquid-vapor coexistence with a sharp interface and a vapor phase with vanishingly small density. [30,32,34] More importantly, the soft-core repulsive term allows a degree of overlap between beads, in contrast to hard-core potentials (e.g., the Lennard-Jones potential) in which the repulsion diverges at zero inter-bead distance. Consequently, we can apply larger time steps than those typically used in molecular dynamics (MD) simulations, which commonly involve hard-core potentials. Together with the coarse-grained representation of multi-component, multi-phase systems, MDPD can capture physical phenomena occurring on relatively larger length and time scales than those normally captured by MD. These features make MDPD an ideal computational simulation tool to resolve the evaporation mass transfer coupled with nanoparticle dynamics at liquid-vapor interfaces.

The drag force is $\mathbf{F}_{ij}^D = -\lambda \omega_D(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}$, where λ is a simulation parameter related to the viscosity arising from the interactions between the constituent beads of fluid. ω_D is a weight function satisfying $\omega_D = 0$ at $r_{ij} = r_c$, and the relative velocity is $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$. The random force is $\mathbf{F}_{ij}^R = \sigma \omega_R(r_{ij})\xi_{ij}\hat{\mathbf{r}}_{ij}$, where ξ_{ij} is a zero-mean Gaussian random variable of unit variance and σ is the amplitude of the noise. The fluctuation-dissipation theorem relates σ to λ as

$\sigma^2 = 2k_B T \lambda$.[44] Finally, the weight functions take the following form: $\omega_D(r_{ij}) = \omega_R(r_{ij})^2 = (1 - r_{ij}/r_c)^2$ for $r_{ij} < r_c$.[45] The combination of drag force and random force serves as a thermostat applied on the MDPD system for producing the canonical (*NVT*) ensemble.[44–46] These forces act on pairs of neighboring beads such that the momentum is conserved locally, and hydrodynamic behavior emerges in relatively small systems.[46,47]

The equations of motion are integrated in time using the velocity-Verlet algorithm. We take r_c as the characteristic length scale and set the dimensionless value as $r_c = 1$. We choose the corresponding energy scale $k_B T$ at room temperature as the characteristic energy. Thus, we take $k_B T = 1$ at $T = 25^\circ \text{C}$. The characteristic mass is defined as the mass of a MDPD bead and takes the dimensionless value of 1. The characteristic time scale is then defined as $\tau_{\text{intrinsic}} = \sqrt{m r_c^2 / k_B T} = 1$. We use the time step $\Delta t = 0.01 \tau$ for all simulations.[45] The value of λ is chosen as 4.5 to obtain a relatively rapid equilibration of the temperature in the system and to ensure the numerical stability of the simulations for the specified time step. All simulations are performed by modifying and extending the particle dynamics software code LAMMPS.[48]

In this study, each non-deformable nanoparticle is modeled as a cluster of frozen MDPD beads grouped into a rigid body, which consists of 276 interior beads and 162 surface beads.[49] The interior beads are arranged in a face-centered cubic (fcc) lattice structure with a cube side length of 0.7. Surface beads (162) are distributed on a spherical layer of radius 2 units in length to cover the interior beads. The layer is modeled as geodesic grids generated by subdividing an icosahedron, and the surface beads are placed at the vertices of the grids.[49–52] In this manner, the surface beads are uniformly distributed on the surface and the maximum distance between surface beads is minimized. The combination of interior and surface beads generates an impenetrable particle with a well-defined smooth surface, maintaining a high degree of symmetry.[49]

A typical simulation system contains a planar interface along the x and y directions, with periodic boundary conditions applied in these directions. The dimensions of the simulation box used in this study are $L_x \times L_y \times L_z = 40 \times 40 \times 100$. The system is bounded by two walls in the z direction. A wall consists of frozen beads organized in amorphous arrangements, with a height

$h = 1$ and density $\rho_w = \rho_l$, where ρ_l is the number density of the liquid phase detailed below. In addition to the frozen solid wall beads, bounce-back boundary conditions are applied at the prescribed fluid-wall interfaces (located at $z = h$ and $L_z - h$) to prevent the fluid beads from penetrating into the wall regions, and also to produce no-slip boundary conditions with minimal interfacial density oscillations.[52–55]

In the present work, we model the liquid-vapor coexistence with the attraction and repulsion parameters for fluid-fluid interactions, A_{ff} and B_{ff} , of -40 and 40, respectively. The repulsion range r_d is set to be 0.80. This set of interaction parameters leads to equilibrium number densities of $\rho_l = 3.926 \pm 0.004$ and $\rho_v = 0.009 \pm 0.001$. As shown in previous MD and DPD simulations,[49,56–59] surface tensions of both particle-free and particle-laden interfaces can be calculated using the Irving-Kirkwood approach given as $\gamma = L_z \langle P_{zz} - (P_{xx} + P_{yy})/2 \rangle$, where P_{xx} , P_{yy} , and P_{zz} are the diagonal components of the microscopic pressure tensor.[59,60] In this formula, the z-direction of the simulation box is the direction normal to the time-averaged interfaces. The calculated pressure tensor includes a temperature-dependent kinetic energy contribution and a virial contribution induced by pairwise interactions between beads. Since nanoparticles are treated as individual rigid bodies, the intra-particle pairwise forces are internal forces and do not contribute to the dynamics of the system. Consequently, we exclude the internal forces between the beads in the same nanoparticle in the calculation of the virial term. As detailed in Ref. [61], the rigid body contribution to the virial is evaluated from the contribution of the rigid body constraint force applied on each bead. The viscosity of the liquid phase is measured in a separate simulation by imposing a doubly periodic Poiseuille flow.[62] The surface tension and viscosity corresponding to the parameter set are $\gamma_0 = 2.00 \pm 0.07$ and $\eta = 3.510 \pm 0.004$, respectively. The attraction parameters for wall-fluid and particle-fluid interactions are adjusted to control the wettability of walls and nanoparticles, while all repulsion parameters are fixed as 40. The top wall is modeled as hydrophobic with $A_{wf} = 0$ and the bottom wall is modeled as hydrophilic with $A_{wf} = -40$. The particle-fluid attraction parameter A_{pf} is varied in the range from -47.5 to -22.5 to obtain three-phase contact angles θ in the range from 45° to 161° as shown in Fig. 1. Here, the contact angle is defined with respect to the liquid phase through the Young's

equation, $\gamma_{lv} \cos \theta = \gamma_{pv} - \gamma_{pl}$ (see Fig. 1 inset). γ refers to the appropriate interfacial tension and the subscripts l, v, and p represent the liquid, vapor, and particle, respectively. In the simulations, we measure the time-averaged contact angle by using a simple geometric relation based on the time-averaged z -location of the liquid-vapor interface and that of the nanoparticle center.

Figure 1. Time-averaged contact angle of nanoparticle θ at the liquid-vapor interface as a function of the particle–fluid attraction parameter A_{pf} . Error bars indicate the variations among four independent runs. The inset sketches the definition of θ . The line is a guide to the eyes.

Evaporation is simulated by removing vapor beads that enters a deletion zone at specified rates.[23,63] This zone of thickness 10 units in length is located at the top of the simulation box as shown in Fig. 2. The removal of vapor beads decreases the vapor density below the saturation vapor density, thereby inducing net evaporation at the liquid-vapor interface. To control the evaporation rate, n_R beads are removed every N_R time steps, which defines a bead-removal rate as the maximum number of beads removed per unit area and time $j_R = n_R / (L_x L_y N_R \Delta t)$. Typically, $5 \leq n_R \leq 30$ and $N_R = 1000$ are set for the MDPD fluid modeled in this study. The evaporation rate is defined as the number of beads that are actually removed in the deletion zone per unit area and time, which is related to the total number of actually removed beads n_E through

$j_E = dn_E / dt / (L_x L_y)$. The derivative is evaluated using central difference formula. The value of j_R determines the steady-state vapor density in the deletion zone, and thus we can model a system exposed to an ambient environment with varying vapor pressures by assigning different j_R . We note that when j_R is sufficiently large, all beads that enter the deletion zone are removed, which effectively represents a system in contact with a vacuum. In this scenario, the value of j_E can be different from that of j_R .

Figure 2. Liquid-vapor coexistence of MDPD fluid systems with particle-free interface (left) and particle-laden interface (right). Vapor beads in a deletion zone of thickness 10 units in length at the top of the simulation box are removed at specified rates to model evaporation. The top and bottom walls are not displayed.

The system is typically equilibrated for 2×10^6 time steps before the evaporation process starts. A global thermostat is automatically applied on the entire system during the equilibration, as a result of the combination of the drag and random forces. The characterizations of interfacial mechanics and monolayer structure (described later) are conducted after the system reaches equilibrium. To avoid simulation artifacts affecting the interfacial mass transfer, the global thermostat is turned off during the evaporation process. Only a local thermostat is coupled to a

liquid region that is away from the liquid-vapor interface to keep the bulk temperature constant (defined as the liquid temperature in the thermostat region).[63] In particular, the drag and random forces are removed except for the beads within 10 units in length of the bottom wall. The relative height of the region with respect to the thickness of liquid region is set to be comparable to the one used in previous studies.[63] In all simulations considered in this study, the liquid film thickness decreases less than 10 units in length and the temperature gradient due to evaporative cooling remains the same during the evaporation process, which indicates that the influence of the thermostat region on the evaporating interface is negligible. Evaporation is carried out for at least another 2×10^6 time steps and the evaporation kinetics is monitored.

We can relate the dimensionless simulation parameters to physical values through mapping the properties of the liquid phase of the MDPD fluid to those of water. If we assume that each MDPD bead represents 3 water molecules,[34,64,65] a bead will occupy a volume of $90 \text{ \AA}^3$ (the volume of a water molecule is $30 \text{ \AA}^3$). Correspondingly, the characteristic mass is $m = 54 \text{ Da}$. Since the liquid number density is $\rho_l = 3.926 r_c^{-3}$ and the mass density of water at ambient condition is 997 kg/m^3 , we obtain the unit length $r_c = 0.71 \text{ nm}$. We can also present the characteristic energy at room temperature in SI units as $k_B T = 4.11 \times 10^{-21} \text{ J}$. Knowing the characteristic length, mass, and energy, the time scale of the MDPD simulation is calculated as $\tau_{\text{intrinsic}} = \sqrt{m r_c^2 / k_B T} = 3.3 \text{ ps}$. It is known that MDPD produces accelerated dynamics due to the soft-core potential if the above intrinsic time scale is used.[45,66,67] Because physical phenomena of interest are dictated by certain dynamic properties of the fluid (e.g., viscosity, diffusion coefficient, and thermal diffusivity), the characteristic time needs to be rescaled such that the most relevant dynamic properties of the modeled system match that of a real system.[68–70] In this study, we relate the maximum evaporating mass flux of the particle-free liquid-vapor interface obtained in the simulation, $J_w = m j_w^{\text{max}} = 2.01 \times 10^{-3} m r_c^{-2} \tau_{\text{MDPD}}^{-1}$, to the experimental evaporation rate of water under low-pressure conditions $J^{\text{exp}} = 7.22 \times 10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$. [71] We thus find the characteristic time scale $\tau_{\text{MDPD}} = 0.498 \mu\text{s}$.

Results and Discussion

Interfacial Mechanics and Particle-Particle Forces

To model a nanoparticle-laden interface, N_p partially-wetted nanoparticles ($\theta = 92^\circ$) are placed directly on the interface as the initial configuration with no particles present within the bulk liquid phase. The in-plane structure of the nanoparticle monolayer is characterized using a two-dimensional particle-particle radial distribution function (RDF), which is defined by the geometric centers of particles. The nanoparticle surface coverage is computed as $\phi = N_p \pi d^2 \sin^2 \theta / 4L_x L_y$, where d is the shortest distance between two nanoparticles and is obtained from the position of the first peak in the radial distribution function.[49,59] Figure 3 shows the RDFs at different surface coverages. The patterns of RDFs inform that the monolayer is in an amorphous liquid state at low surface coverages and presents highly ordered, hexagonal packing as ϕ increases. This disorder-to-order transition is consistent with previous experimental and computational observations.[59,72,73] The theoretical limit of surface coverage for two-dimensional close-packing of particles with $\theta = 90^\circ$ is 0.91, and the corresponding maximum number of nanoparticles is 68, which gives $\phi = 0.89$. Further addition of nanoparticles leads to the broadening of the first peak in the RDF (Fig. 3). This behavior indicates buckling of the monolayer and distortion of the interface, which are also illustrated by the snapshot in Fig. 3.

Figure 3. Two-dimensional particle-particle radial distribution functions of interfacial bound nanoparticles with the contact angle $\theta = 92^\circ$ obtained at increasing surface coverage. The inset are the enlargement at short distances and the snapshot of distorted monolayer.

It is known that the mechanical properties of the interface (e.g., surface tension) can be significantly altered by the presence of nanoparticles. In particular, surface tension can decrease as the loading of nanoparticles increases, and the reduction is prominent when the surface coverage is high.[49,51,72,74–77] Figure 4(a) confirms that the surface tension of a particle-laden liquid-vapor interface calculated by the Irving Kirkwood formula reduces as the density of adsorbed particles increases, but discernable reductions only occur at large nanoparticle loadings. Our results show good agreement with previous results.[51,59]

The thermodynamic definition of surface tension is the mechanical work necessary to increase a surface by a unit area. Assuming that inter-particle interactions are negligible, the surface tension of a particle-laden interface can be estimated as,[78]

$$\gamma = \gamma_0 - N_p E_d / L_x L_y, \quad (1)$$

where $\gamma_0 = \gamma_{lv}$ is the surface tension of the particle-free interface, E_d is the desorption energy required to remove one nanoparticle from the interface into the vapor phase. For the chemically homogeneous particles considered in this study, the desorption energy is given as,[79]

$$E_d = \pi d^2 \gamma_0 (1 + \cos \theta)^2 / 4. \quad (2)$$

Thus, the surface pressure of the nanoparticle monolayer can be calculated as,

$$\Pi = \gamma_0 - \gamma = \pi d^2 \gamma_0 (1 + \cos \theta)^2 / 4 \Sigma, \quad (3)$$

where $\Sigma = L_x L_y / N_p$ is the interfacial area per particle. Figure 4(b) plots the surface pressure isotherm as a function of area per particle Σ obtained from the simulations against the theoretical estimation calculated using Eq. (3). The comparison reveals that the theory significant overestimates the surface pressure of the nanoparticle monolayer (i.e., the surface tension reduction in the presence of nanoparticles), especially at high surface coverages. The discrepancy can be attributed to the constant desorption energy of particle used in Eq. (3), which is obtained under the assumption that the number of interfacial nanoparticles increases continuously as the interfacial area increase.[78] However, the variation of the particle number can only be discrete. In particular, the number does not increase until a sufficient amount of interfacial area ($\pi d^2 / 4$) is

created that allows the insertion of a new particle to the interface.[51] Between consecutive insertions, the newly created interface is merely particle-free liquid-vapor interface. Consequently, the true surface tension reduction on average is smaller than the theoretical estimation using constant desorption energy. Our results for liquid-vapor interfaces are in qualitative agreement with reported experiments and simulations performed at immiscible liquid-liquid interfaces.[51,59,80,81]

Figure 4. (a) Surface tension (in units of $k_B T r_c^{-2}$) of the particle-laden interface (contact angle $\theta = 92^\circ$) as a function of surface coverage and (b) surface pressure (in units of $k_B T r_c^{-2}$) as a function of area per particle. Error bars indicate the fluctuation in time. The blue solid lines in (a) and (b) are the theoretical predictions, assuming negligible particle-particle interactions. The insets in (a) and (b) show the top views of the interfaces covered with 68 and 36 nanoparticles, respectively.

The discrepancy between the theory and simulation results suggests that the nanoparticle desorption energy neglecting inter-particle interactions is not directly associated with the surface tension reduction. To provide addition insight, we measure the inter-particle force profile between nanoparticles at the interface by applying a force-calculation method detailed in literature.[51] Briefly speaking, two nanoparticles are placed at the interface, whose geometric centers are connected by a harmonic bond. The separation of nanoparticles is controlled by the equilibrium distance of the bond. When the system is in equilibrium, the effective particle-particle force at each separation is obtained as the average spring force. The force profile is thus obtained by sampling a series of separations. Figure 5 shows that the repulsive inter-particle force experienced by two nanoparticles diverges quickly when the particles are closer than 4.9 units in length. At large separations, the forces approaches zero in the absence of discernable local maxima and minima in the profile. This effective force profile resembles the Heaviside shape of the hard-sphere potential, verifying the rigid nature of the modeled nanoparticle. Strong inter-particle repulsions can prevent particle adsorption and effectively result in lower nanoparticle adsorption energy, which thus yields small surface tension reduction. This force profile provides a qualitative rationale to the discrepancy present in Fig. 4.

Figure 5. Average particle-particle forces (in units of $k_B T r_c^{-1}$) as a function of the separation between the nanoparticle centers. Error bar shows the statistical uncertainty at each data point, whose magnitude is within $4 k_B T r_c^{-1}$.

Figure 6. Evaporation rates j_E (in units of $\tau^{-1} r_c^{-2}$) as functions of simulation time for particle-free systems at different bead-removal rates j_R (in units of $\tau^{-1} r_c^{-2}$). The inset shows the total numbers of removed beads N_E as functions of time.

Notably, DPD simulations often observe solvent effects as simulation artifacts, namely depletion interactions and layering,[82–85] whose range extends beyond the cutoff of the direct pairwise interaction of only 1.0 units in length. In the force-distance profile, the solvent effects are represented by multiple attractive wells and repulsive peaks at large separations. Importantly, Figure 5 demonstrates no maxima and minima at distances larger than 4.9 units in length. Thus, our particle model eliminates the unphysical solvent effects and accurately captures the particle-particle interactions.

Evaporation of Particle-Free Interface

We first characterize the evaporation of the MDPD fluid without interface-bound nanoparticles. The bead-removal rate j_R is varied to control the evaporation process and the corresponding evaporate rate j_E is measured. Figure 6 demonstrates the time evolution of j_E for different j_R after evaporation was initiated. In the controlled evaporation regime, in which j_R is small, the evaporation rate shows no time dependence and its value equals the value of j_R . In contrast, at relatively large bead-removal rates, the evaporation rate has large initial values, and

then decreases monotonically over time. This behavior is attributed to the high initial vapor density and the gradual depletion of the vapor beads in the deletion zone. When the bead-removal rate is large, the replenishment of vapor beads in the deletion zone by the net evaporation at the liquid-vapor interface can no longer compensate the loss from bead removal. Eventually, the evaporation rate reaches a steady-state value j_E^s , the limiting value of which is dictated only by the interfacial properties and bulk temperature. Further increase of j_R promotes the initial evaporate rate but has no effect on the steady-state evaporation rate at late time.

For systems undergoing net evaporation, height of the liquid-vapor interface decreases. The time-dependent number density profiles in the z direction are measured to elucidate the displacement of the interface. Figures 7(a) and 7(e) show the evolution of density profiles in time for systems evaporating at different rates. The liquid density exhibits a small increase near the interface by 1% over its equilibrium value, when evaporation is strong ($j_E^s = 2.0 \times 10^{-3}$). However, the relative density enhancement is indiscernible during weak evaporation ($j_E^s = 0.6 \times 10^{-3}$). As pointed out by previous simulations,[63,86] the relative density increase is caused by evaporative cooling of liquid in the interfacial region.

To quantify the evaporative cooling in this nonequilibrium system, two local temperatures as functions of z -position are defined. One is a local absolute temperature defined by the mean kinetic energy of beads, given as $T(z) = m/3N_f k_B \sum_{i=1}^{N_f} |\mathbf{v}_i|^2$. Here, $\mathbf{v}_i$ is the bead velocity and N_f is the total number of beads in a slab of the simulation box from $z - \Delta z$ to $z + \Delta z$, where Δz is 0.5 in length. The other is a local profile-unbiased temperature with possible advection contribution subtracted,[87–91] defined as $T_r(z) = m/(3N_f - 3)k_B \sum_{i=1}^{N_f} |\mathbf{v}_i - \bar{\mathbf{v}}|^2$, where $\bar{\mathbf{v}}$ is the average bead velocity in the slab. Three degrees of freedom are lost due to the computation of the average velocity.[87–91]

The two temperature profiles are plotted for systems evaporating at different rates (see Figs. 7(b,c,f,g)). We observe an approximately 5% evaporative cooling in the liquid region in both profiles at $j_E^s = 2.0 \times 10^{-3}$. Instead, both local absolute and profile-unbiased temperatures in the liquid region are uniform at $j_E^s = 0.6 \times 10^{-3}$. The large fluctuation of temperature in the vapor region is due to the ultra-low vapor density of $\rho_v = 0.009 \pm 0.001$. Driven by the large density

gradient at $j_E^s = 2.0 \times 10^{-3}$, fluid beads in the interfacial region escape from the liquid phase with z -velocities of order $\sqrt{k_B T / m}$ as shown in Fig. 7(d). Hence, the profile-unbiased temperature exhibits a pronounced decrease at the interface (see Fig. 7(c)) compared to the absolute temperature (Fig. 7(b)).

Figure 7. (a,e) Number density, (b,f) temperature defined by the average kinetic energy, (c,g) profile-unbiased temperature with advection contribution subtracted, and mean z -velocity (d,h) as functions of the position in the z -direction for particle-free systems evaporating at rate $j_E = 2.0 \times 10^{-3}$ (a-d) or 0.6×10^{-3} (e-h). From right to left the profiles are plotted every 2500 and 10000 units in time for the left and right columns, respectively. The insets in (a) and (b) are the magnified views of the density increase.

Nanoparticle-Mediated Evaporation

Using the particle-free interface as the reference system, we probe evaporation through a liquid-vapor interface covered by a nearly close-packed nanoparticle monolayer with $\phi = 0.89$. As shown in Fig. 8, the behavior of the evaporation rates j_E at various bead-removal rates is similar to that of a particle-free interface. Namely, j_E is constant and equal to j_R when j_R is relatively small and shows a substantial drop to a j_R -independent steady-state value when j_R is large. Two notable differences between the particle-free and particle-laden interfaces are: (i) faster initial decay to the steady-state value j_E^s (~ 1500 units in time for the particle-laden interface compared to ~ 3000 units in time for the particle-free interface; and (ii) smaller limiting value of j_E^s at large j_R for the particle-laden interface. Both distinctions suggest that evaporation is suppressed by the presence of interface-bound nanoparticles.

Figure 8. Evaporation rates j_E as functions of time for a liquid-vapor interface with a close-packed nanoparticle monolayer at different bead-removal rates j_R . The inset shows the total numbers of removed beads N_E as functions of time.

Surface coverage is expected to influence the evaporation process. To explore this behavior, evaporation of interfaces with different nanoparticle loadings is simulated while all other

parameters are held constant. Figure 9(a) plots the steady-state evaporation rate j_E^s as a function of bead-removal rate j_R for different surface coverages ranging from 0 to 0.95. We stress again that the interface having $\phi = 0.95$ is slightly distorted with a buckled nanoparticle monolayer. Regardless of surface coverage, the dependence of j_E^s on j_R consistently exhibits a linear regime and a plateau. The data points for different interfaces collapse onto a master line with a slope of 1 in the linear regime. This confirms that in the controlled evaporation regime, the evaporation rate is completely determined by the bead-removal rate. The plot also reveals the striking fact that the variation of surface coverage ϕ has no discernible effects on evaporation in this regime, which will be further elaborated below. In contrast, the limiting value of j_E^s at relatively large j_R representing the plateau clearly decreases as ϕ increases. Thus, the evaporation rate decreases as the number of nanoparticles increases when ambient vapor pressure is low and evaporation is strong.

Figure 9. (a) Steady-state evaporation rates j_E^s as functions of bead-removal rate j_R for liquid-vapor interfaces with different nanoparticle surface coverages. (b) Relative retardations Φ as functions of surface coverage ϕ for different bead-removal rates j_R . The lines are just guides to the eyes. The red vertical dashed line in (b) marks the limiting surface coverage for two-dimensional close-packing. Error bars represent the magnitude of fluctuations in the time averages of the steady-state evaporation rates.

Figure 10. (a) Steady-state evaporation rates j_E^s as functions of bead-removal rate j_R for liquid-vapor interfaces with monolayers of nanoparticles with different contact angles while keeping the surface coverage constant as $\phi \approx 0.63$. The inset sketches the obstruction in the evaporation path. (b) Limiting value of the steady-state evaporation rate as a function of effective evaporation area fraction $A_{\text{evp}} / L_x L_y$. Error bars represent the magnitude of fluctuations in the time averages of the steady-state evaporation rates.

To quantify the evaporation retardation due to nanoparticle monolayers at the interface, a relative retardation Φ is defined as the ratio of steady-state evaporation rate through a particle-laden interface j_E^s to that of the particle-free interface j_w . As shown in Fig. 9(b), the maximum retardation reaches approximately 50% by having a close-packed nanoparticle monolayer when evaporation is strong. However, an intriguing observation in Fig. 9(b) is the negligible retardation under weak evaporation, even when the interface is fully covered by the monolayer. In summary, the evaporation retardation caused by the interface-bound nanoparticles is influenced by not only the surface coverage but also the evaporation strength of the interface, which depends on ambient vapor pressure and is represented in the simulation by the bead-removal rate j_R .

Besides the surface coverage, the contact angle of nanoparticles is also expected to play a role during evaporation. Through a geometric consideration as shown in the inset of Fig. 10, we note that the nanoparticles with $\theta > 90^\circ$ obstruct the evaporation path of fluid beads escaping from the interface because the cross-sectional area of the evaporation path is now evaluated in the plane of nanoparticle centers, which is smaller than the liquid-vapor interfacial area. Thus, the presence of $\theta > 90^\circ$ nanoparticles introduces a bottleneck that impede the evaporation flux even when the real liquid-vapor interface is large. This blockage effect leads to a decrease in the net evaporation flux. To isolate the effect of contact angle, we simulate evaporation of interfaces with approximately the same surface coverage ($\phi \approx 0.63$) but having particles with different contact angles (63° , 90° , and 120°), under the condition that all other parameters remain the same. Figure 10(a) plots the steady-state evaporation rate j_E^s as a function of the bead-removal rate j_R for different contact angles. Similar to Fig. 9(a), we observe that the evaporation rate is dominated solely by j_R in the controlled evaporation regime. The change in contact angle and the blockage of the evaporation path have negligible effects on the evaporation process at this stage. However, the limiting value of the steady-state evaporation rate decreases with increasing contact angle. Notably, Figure 10 shows that nanoparticles with $\theta = 120^\circ$ inhibit evaporation substantially (about 40% decrease in the evaporation rate compared to the case for $\theta = 63^\circ$). In contrast, reducing the contact angle from 90° to 63° only causes the evaporation rate to increase 8%. To quantitatively characterize the geometric blockage effect at large j_R , we define an effective

evaporation area fraction as the fraction of the total area in the plane of nanoparticle centers that fluid beads can pass through, given as $A_{\text{evp}} / L_x L_y = 1 - N_p \pi d^2 / 4 L_x L_y$. Notably, when the contact angle is larger than 90° , A_{evp} only depends on the number of particle not the contact angle. As the contact angle of nanoparticles increases while holding the surface coverage as constant, the number of nanoparticles on the interface increases, leading to greater evaporation area A_{evp} . To illustrate the contribution of A_{evp} to the reduction of the evaporation, we conduct additional evaporation simulations for $\phi \approx 0.63$ with nanoparticles having contact angles (97° , 102° , 112° , 118°). Figure 10(b) shows that the evaporate rate increases as the effective area fraction increases, which confirm that the obstruction in the evaporation path of escaping vapor beads due to non-wettable nanoparticles with $\theta > 90^\circ$ can significantly suppress the net evaporation. In addition, we observe that there is no statistically significant differences in the surface tension of these interfaces with particles having different contact angles. This result again indicates that the nanoparticle desorption energy neglecting inter-particle interactions, which is a function of wettability, is not directly associated with the interfacial tension reduction.[51] Thus, the surface coverage instead of particle wettability predominately dictates the surface tension of the particle-laden interface. These results indicate that evaporation retardation is primarily affected by the geometry of evaporation pathway and does not depend on the interfacial mechanics.

Regardless of the surface coverage and contact angle of interface-bound nanoparticles, above results confirm no evaporation retardation for weak evaporation conditions, in other words, at high ambient vapor pressure. The dependence of evaporation retardation on the magnitude of the evaporation rate of the particle-free interface resembles the behavior observed for insoluble surfactant monolayers.[92,93] The effective permeation resistances of nanoparticle monolayers can be analyzed using the analogy with electrical resistance and Ohm's law, similar to that of surfactant monolayers.[92] According to the calculation detailed elsewhere,[92] the relative retardation Φ is given as

$$1/\Phi = 1 + (r_m / \Delta\rho_v) j_w. \quad (4)$$

Here, r_m is the effective permeation resistance of the nanoparticle monolayer and $\Delta\rho_v = \rho_v^{\text{eq}} - \rho_v$ is the difference between the current vapor density in the deletion zone and the saturation vapor

density in equilibrium, serving as the driving force for net evaporation. Therefore, r_m should be a constant for a given monolayer characterized by the surface coverage ϕ , and the inverse of the relative retardation $1/\Phi$ should be a linear function of j_w .

Figure 11. (a) Inverses of relative retardations $1/\Phi$ for monolayer-covered interfaces having different surface coverages as functions of the evaporation rate of the particle-free interface j_w . Dashed lines represent least squares fittings. (b) Permeation resistance of nanoparticle monolayers and critical particle-free evaporation rate as functions of surface coverage. Error bars indicate the standard deviations of the slopes obtained in least square fittings.

The results for monolayers with various surface coverages are plotted in Fig. 11(a). The existence of critical evaporate rates of the particle-free interface j_w^{thresh} is observed, below which the presence of nanoparticles does not influence the evaporation process at all. If j_w is greater than

j_w^{thresh} , the linear relation between $1/\Phi$ and j_w was verified for all particle-laden interfaces considered in this study. The slope of the linear fitting provides a quantitative measurement of the permeation resistance of the monolayer. The intersection of the fitting and $1/\Phi = 1$ line yields the critical particle-free evaporation rate j_w^{thresh} . Figure 11(b) summarizes the monolayer resistances and j_w^{thresh} of monolayers at different surface coverages ϕ . The resistance and critical evaporation rate respectively increases and decreases as the surface coverage increases, and the changes are approximately linear. These results provide evidence that interface-bound nanoparticles suppress evaporation of liquid by reducing the accessible interfacial area for evaporation given that the contact angle is held constant.[92] Namely, increasing surface coverage reduces the effective interfacial area for evaporation, and thereby leads to higher monolayer permeation resistances and smaller evaporation rates.

Conclusions

We utilize MDPD simulations to investigate how nanoparticle monolayers reduce surface tension and influence evaporation at a liquid-vapor interface. The measured surface tensions and evaporation rates for the nanoparticle-laden interfaces are compared with those of the nanoparticle-free interface. The characterization of the interfacial mechanics indicates that to correctly predict surface tension reduction in the presence of nanoparticles it is necessary to include particle-particle interactions, especially at high loadings of nanoparticles at the interface. The evaporation results clearly show that when the bead-removal rate is relatively large, the steady-state rate of the nanoparticle-mediated evaporation is smaller than that of the nanoparticle-free evaporation. This difference confirms that the presence of nanoparticles alters the interfacial mechanics and influences the evaporation.

For nanoparticles with the same contact angle, the steady-state evaporation rate decreases as the nanoparticle surface coverage increases. When the contact angle varies (63° , 90° , and 120°) while holding the surface coverage constant ($\phi \approx 0.63$), the evaporation rate decreases as the wettability of the nanoparticle changes from hydrophilic to hydrophobic. We interpret this behavior in the light of the kinetic theory. In detail, the cross-sectional area of the evaporation path changes accordingly as the contact angle varies. When $\theta > 90^\circ$, the presence of nanoparticles reduces the effective area of the evaporation path, thereby leading to a decrease in net evaporation

flux. However, when evaporation is weak (i.e., the system is not far from equilibrium), we observe that nanoparticle monolayers show negligible effects on the evaporation process regardless of the surface coverage and contact angle.

Our results reveal that the evaporation retardation caused by the nanoparticle monolayer is influenced by both the surface coverage and the bead-removal rate, indirectly representing ambient vapor pressure. Importantly, the surface tension reduction induced by interfacial particle shows no explicit influence on evaporation retardation. Further discussion demonstrates that nanoparticle monolayers serve a similar role in suppressing evaporation as insoluble surfactant monolayers, where both exhibit the dependence of retardation on the evaporation rate of the particle-free interface. The permeation resistance of the monolayer and the critical evaporation rate increases and decreases respectively when the surface coverage increases. The findings of this work present unique insight into the evaporation mass transfer through particle-laden interfaces and provide useful guidelines for harnessing interface-bound nanoparticles to control evaporation.

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Graphical Abstract