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Dynamics of Nanodroplets on Vibrating Surfaces
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ABSTRACT: We report the results of molecular dynamics investigations into the behavior of nanoscale water droplets on surfaces subjected to cyclic-frequency normal vibration. Our results show, for the first time, a range of vibration-induced phenomena, including the existence of the following different regimes: evaporation, droplet oscillation, and droplet lift-off. We also describe the effect of different surface wettabilities on evaporation. The outcomes of this work can be utilized in the design of future nanoengineered technologies that employ surface/bulk acoustic waves, such as water-based cooling systems for high-heat-generating processor chips, by tuning the vibration frequency and amplitude, as well as the surface wettability, to obtain the desired performance.

INTRODUCTION
The dynamical behavior of drops and interfaces subjected to free or forced vibrations are classical problems in hydrodynamics, with rich literature dating back to the late 19th century. Early interest was driven by the fundamental science of interfacial instabilities, with the focus on generating analytical expressions for capillary free-surface oscillations and their stability. In the mid 20th century, there were significant theoretical developments in understanding "acoustic streaming", or flow fields generated by sound attenuation within a fluid.

There has been renewed interest in this area in recent years, with experimental research showing that high-frequency bulk/surface vibrations of the supporting substrate can disintegrate liquids into a fine mist of droplets. This has numerous applications in the chemical, medical, and information/communications technology industries. For example, precisely controlling micro/nanoscale droplets inside lab-on-a-chip devices using surface acoustic waves (SAW).

Current experiments on droplet atomization using SAW typically employ frequencies in the MHz–GHz range and amplitudes of nanometres. However, in principle, bulk/surface vibrations in the GHz–THz range are realizable, which is a hitherto unexplored parameter-space that is the subject of this present paper. Existing numerical studies of the effects of vibration on sessile droplets have two drawbacks that make them unsuitable for the problem considered here: first, they are limited to low frequencies, as the time-scale separation (between the rapid acoustics and the slower hydrodynamics) inherent to high-frequency acoustic fluids is challenging to simulate. Second, the droplet interface is typically assumed to be unperturbed throughout the simulation, with the focus on the acoustic streaming within the liquid. No droplet deformation or atomization is considered. In this paper, we address these limitations by using molecular dynamics (MD) to study, for the first time, the behavior of water droplets on vibrating surfaces; there is no other simulation tool that offers the high-fidelity required to resolve these very short spatio-temporal-scales.

MODELING METHODOLOGY
Molecular Dynamics. Molecular dynamics (MD) simulations solve Newton’s equations of motion for each molecule in the domain:

\[
F_i = m_i \frac{dv_i}{dt} = \sum_{j \neq i} -\nabla U_{ij}(r_{ij})
\]

(1)

\[
v_i = \frac{dr_i}{dt}
\]

(2)

where \(F_i\), \(v_i\), and \(r_i\) are the force, velocity, and position, respectively, of molecule \(i\) of mass \(m_i\) at time \(t\), \(N\) is the total number of molecules, and \(U_{ij}(r_{ij})\) is the intermolecular potential between the \(i^{th}\) and \(j^{th}\) molecule, with \(r_{ij}\) the distance between them. In our simulations, all atoms interact using a combined 12–6 Lennard-Jones and Coulomb potential:

\[
U_{ij}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi \epsilon \sigma r_{ij}^{6}}
\]

(3)

where \(\sigma\) is the distance at which the interatomic potential is zero, \(\epsilon\) is the depth of the potential well, \(q\) is the charge of the atomic site, and \(\epsilon_0\) is the vacuum permittivity. The \(\lambda\) parameter in eq 3 allows the solid–liquid interaction strength, and hence the surface wettability, to be modified from superhydrophobic...
The values of \( N \) are identical to the substrate, but with a large artificial interaction strength \( \sigma \). For computational efficiency, we truncate the intermolecular and electrostatic force calculations at radial distances of 1.2 and 1.3 nm, respectively. Long-range electrostatics are incorporated using the particle–particle particle–mesh (PPPM) method, with a relative tolerance of \( 10^{-6} \).

Polar water molecules are modeled using the rigid four-site TIP4P/2005 model;\(^25\) this consists of one oxygen (O) site, two charged hydrogen (H) sites, and one massless charged (M) site located along the bisector of the hydrogen atoms, at a distance of 0.1546 Å from the oxygen atom. The internal geometry of the water molecule is constrained by specifying a fixed O–H bond distance (0.9572 Å) and H–O–H angle (104.52°); this structure is maintained using the SHAKE algorithm.\(^26\) The droplet-supporting substrate consists of seven layers of metal atoms in a FCC lattice, with a lattice constant of 3.92 Å. All the interatomic potential parameters are listed in Table 1. The cross interactions between different atomic sites are specified by the Lorentz–Berthelot mixing rules, \( e_i = \sqrt{e_a e_f} \) and \( \sigma_i = (\sigma_a + \sigma_f)/2 \). Time integration of all molecule trajectories is achieved using the velocity-Verlet algorithm, with a time step of 2 fs. We performed all the simulations using the open-source MD software LAMMPS.\(^27\)

**Simulation Setup.** The initial setup, as shown in Figure 1, consists of a droplet of water molecules initialized on an atomically smooth substrate (S). The domain boundaries are set to be periodic in every direction, and a superhydrophilic barrier is positioned far above the substrate to collect atomized molecules at every time-step. The specified radii \( R \) are calculated assuming a hemispherical shape for each droplet.

One of the key measurements in these simulations relies on tracking how many molecules are “atomized”. We classify a water molecule as atomized if:

1. Its number of neighboring water molecules is fewer than 10 (where two water molecules are considered neighbors if \( r_{ij} < 6.3 \) Å), or
2. Its vertical distance from the top of the substrate is greater than 10 nm.

The first criterion is used to identify vapor molecules,\(^28,29\) while the second accounts for the atomization of liquid molecules en masse; \( N_A \) then represents the total number of atomized molecules at every time-step. Once the atomized molecules are identified, the temperature \( T_f \) of the remaining droplet (comprising nonatomized water molecules) can be calculated using the equipartition theorem:

\[
T_f = \frac{1}{N_f} \sum_{i=1}^{N_f} \frac{2}{3k_B} \sum_{n=1}^{3} \frac{1}{2m} (\bar{v}_{in} - \langle \bar{v}_{in} \rangle)^2
\]

where \( N_f = N_0 - N_A \) is the number of water molecules remaining in the droplet, \( k_B \) is the Boltzmann constant, \( \bar{v}_{in} \) is the velocity of molecule \( i \) in the \( n \) (\( x, y, z \)) direction, and \( \langle \bar{v}_{in} \rangle \) is the average velocity of molecule \( i \).
the mean flow velocity in the n direction due to the induced oscillations. To prevent erroneous temperature values, care must be taken both to exclude the atomized molecules and to subtract the droplet center-of-mass velocity from each water molecule, prior to calculating the temperature.

## RESULTS AND DISCUSSION

**Nanodroplet Evaporation.** Our MD simulations show that when nanoscale droplets or films are exposed to substrate vibrations, atomization occurs primarily due to heating; acoustothermal heating and evaporation has been observed experimentally for microscale droplets and thin films,\textsuperscript{30–32} but here we report it for nanodroplets for the first time. The temperature within the droplet (calculated using eq 4), and the scaled atomization rate $N^* = N_A/N_0$ give an indication of this heating effect. Figure 2(a,b) show these two measurements for a typical case of a droplet evaporating on an oscillating surface (with the vibration and wettability characteristics as specified in the figure caption), while Figure 2(c,f) show temporal snapshots from the MD simulation. In this case, significant heating is observed inside the droplet, with temperatures peaking at 500 K before dropping off to 450 K.

Note that large temperature fluctuations (also known as “thermal noise”) are observed in Figure 2(a) when $t > 0.8$ ns. This is because of the very small number of molecules remaining in the droplet. The fractional error in temperature measurements ($\epsilon_T$) can be calculated as $\epsilon_T = \sqrt{\frac{E_T}{MNc_p}}$,\textsuperscript{33} where $c_p$ is the per-molecule specific heat capacity at constant volume. The thermal noise can only be improved in these tiny residual droplets if many more (i.e., $M$) statistically independent simulations are run and averaged; we instead do not draw any conclusions from our temperature measurements whenever the fractional error $\epsilon_T$ exceeds 0.5 (i.e., a relative error of 50%). This is indicated in Figure 2, and following figures, by the use of light gray lines replacing the original line color when the specified threshold in $\epsilon_T$ is exceeded.

From the MD snapshots, the evaporation process appears to be uniform, and the droplet shrinks evenly without any change in the center-of-mass position relative to the x, z coordinate axes (see Figure 2(c–e)). Movement on the substrate is only observed once the droplet has lost most of its molecules (Figure 2(f)).

We can characterize the acoustothermal evaporation of these nanoscale droplets by the ratio of the force applied by the vibrating substrate, given by $F_{vib} \approx m_f f a^2 (2\pi f)^2$, to the resulting viscous dissipation of the applied vibrations, as defined by the internal energy gained by the water molecules, given by $F_{vis} \approx m_p \mu \nu_{ref}^2 t_a/L_{ref}^3$. Here, $m_p$, $\mu$, $t_a$, $\nu_{ref}$ and $L_{ref}$ are the mass of the droplet, fluid viscosity, acoustic time scale ($t_a = 1/f$), reference velocity scale ($\nu_{ref} = \sqrt{k_B T_0/m_f}$), and reference length scale ($L_{ref} = \sqrt{\mu/2\rho f}$), respectively. This ratio of competing vibration/dissipation forces produces a nondimensional acoustothermal atomization parameter:\textsuperscript{34}
A nondimensional scaling prefactor $K$ has a nondimensional scaling prefactor $K$. Physically, increasing $A^*$ can be interpreted as increasing the energy added to the fluid by the vibrating substrate. If this scaling is appropriate, then the evaporation dynamics for a fixed $A^*$ should be independent of the values of the vibration parameters $a$ and $f$.

To test the validity of this scaling for acoustothermal droplet evaporation, multiple cases with a fixed $A^*$ were simulated, but with different combinations of $a$ and $f$. The temporal evolutions of the atomization and droplet temperature are plotted in Figure 3. Despite the large variation in acoustic parameters (for example, $f$ is varied from $\sim 60–292$ GHz), the evaporation rate (Figure 3(a)) and temperature profiles (Figure 3(b)) are identical for all cases, therefore validating our proposed scaling relationship for evaporating nanodroplets.

**Nanodroplet Oscillation: Approaching Lift-Off.** It has recently been shown in macroscale experiments$^{35}$ that the apparent wettability of a surface increases linearly with vibration amplitude $a$, but is independent of the vibration frequency $f$. Similarly, the magnitude of the (acoustic) pressure field within a macroscale drop increases during unidirectional motion of the substrate, and depends on the amplitude of vibration. The increase in acoustic pressure is higher at larger amplitudes and lower frequencies, but the acoustic pressure does not build for higher frequencies.$^{31}$

The impact of acoustic pressure on nanodroplet vibration can be evinced by comparing the extremal cases from Figure 3, namely those corresponding to $a = 0.1$ nm (small amplitude, high frequency) and $a = 1.1$ nm (large amplitude, low frequency), for which the evaporation rates are identical. Snapshots of the latter case are shown in Figures 4(a−f). (The dynamics of the $a = 0.1$ nm case are qualitatively similar to the case in Figure 2, and are therefore not included here.) From Figure 4, when the droplet is vibrated at large amplitude with low frequency, significant oscillation of the contact line is observed. These oscillations can be seen in both the side and top views of the droplet, and resemble the “rocking mode” of vibration experimentally observed for macroscale drops.$^{36}$

For these oscillating nanodroplets, the effects of amplitude and frequency on quantitative measures of interest (i.e., atomization and temperature) are shown in Figure 5. In Figure 5(a), the vibration amplitude is held constant at $a = 0.5$ nm and $f$ is varied from $60–140$ GHz, while in Figure 5(b), the vibration frequency is held constant at $f = 200$ GHz and $a$ is varied from $0.1–0.4$ nm (which is a range of subnanometre vibration amplitudes typical of SAW devices$^{13}$). For the most part, the line-plots for the individual cases seem to follow expectations. With increasing $f$ or $a$, an increase is observed both in the temperature within the droplet and the number of molecules atomized outside it. However, this trend is reversed for the cases with the largest $a$ (with fixed $f$) and largest $f$ (with fixed $a$). For example, for $f = 140$ GHz in Figure 5(a) and $a = 0.4$ nm in Figure 5(b) the droplet temperature appears to be lower when compared to the other cases, or mostly unchanged from the initial thermal condition of 300 K. The atomization
The behavior of oscillating droplets on a surface can indicate the consequence of the breaking of the solid–liquid intermolecular forces and the droplet "lift-off" the surface (see Figure 6(b)). In the absence of gravitational forces, which are negligible at these scales, there is no restoring force preventing the droplet from continually rising until it collides with the superhydrophilic barrier at the top of the MD domain (Figure 6(c,d)). As a consequence of the breaking of the solid–fluid interaction, negligible heat is transferred to the droplet and its temperature is effectively unchanged from its original value of 300 K, as seen in Figure 6(e).

We systematically investigated the effect of vibration amplitude and frequency on this early droplet lift-off phenomenon, and the results are plotted as a phase map in Figure 7, with a resolution of 2 GHz and 0.1 nm. Open blue symbols represent cases where no lift-off is observed; solid teal symbols represent the threshold for lift-off; and solid purple symbols represent additional cases we simulated to confirm the lift-off threshold. The dotted line connecting the symbols divides the domain into "attached" and "lift-off" regions. The threshold frequency for lift-off is inversely dependent on the amplitude, monotonically decaying from ~180 GHz for \( a = 0.4 \) nm to 84 GHz when \( a = 1.0 \) nm. Note that, due to the computationally expensive nature of these MD simulations, this phase map was developed for the smallest nanodroplet used in our study, with \( N_p = 1000 \). However, it is expected that any differences for larger nanodroplets would be limited to the (quantitative) threshold values for lift-off, while the qualitative variation in the stability threshold with amplitude would remain unchanged. Note that lift-off is more easily observed for low substrate wettabilities, i.e., low values of \( \lambda \).

**Effect of substrate wettability.** The role of surface wettability in vibration-induced atomization is investigated next. We conducted MD simulations for substrates with \( \lambda = 0.25, 0.5, 0.75, \) and 1.0. It is not straightforward to predict a priori how changing the wettability of the substrate will impact droplet atomization or lift-off. For example, it could be argued that the atomization process is controlled by the efficiency of energy transfer into the droplet, which is determined by the strength of the solid/liquid van der Waals forces. This would imply that the higher the wettability (\( \lambda \)), the stronger the interaction of the water molecules with the surface molecules (and so a larger contact area), and therefore a greater energy transfer and atomization rate. This argument has been shown to be correct in MD studies that focus solely on thermal energy transfer to a nanodroplet from a heated surface (with no vibrations): the higher the wettability, the higher the rate of the boiling/evaporation that can be achieved.45

Conversely, for any given water molecule, the energy barrier needing to be overcome for atomization would reduce with a weaker solid/liquid interaction. For low wettabilities (i.e., low \( \lambda \)), the liquid molecules require less energy to be dislodged from the solid and enter the vapor phase. This is consistent with observation of vibration-induced cavitation on patterned hydrophobic/hydrophilic surfaces: cavitation preferentially occurs on the hydrophobic sections,38 indicating that vapor formation is quicker at lower wettabilities. This second argument would therefore imply that as wettability increases, the atomization rate should decrease.

As Figure 8(a) shows, both of these arguments are essentially correct, but they depend on the value of \( \lambda \) considered. As \( \lambda \) increases from 0.15 to 0.25, and from 0.25 to 0.50, the atomization rate increases, as is apparent when the values of \( N^* \) at any given time \( t \) are compared for \( \lambda = 0.15 \).
There are several new and fundamental insights. First, for nanodroplet evaporation, a universal scaling can be formulated, and the evaporation dynamics collapse onto a master curve for a fixed scaling parameter, \( A^* \)—the acoustothermal parameter. Second, nanodroplet oscillation is observed at large vibration amplitudes, likely due to high acoustic pressures being generated within the droplet. This produces a periodic rocking motion reminiscent of that seen in macroscale drops. Third, for larger vibration amplitudes or frequencies, the droplet is observed to take off from the surface entirely, particularly if the surface has a low wettability. A phase map has been developed to characterize this lift-off phenomenon, and shows that the threshold frequency of lift-off is inversely dependent on amplitude. Finally, evaporation is shown to be a slower process on a superhydrophobic or a superhydrophilic surface, and the optimal wettability for vibration-induced evaporation is neither too hydrophobic nor too hydrophilic.

The results presented in this paper can provide insight into the use of surface acoustics for numerous novel applications, for example:

- Acoustothermal droplet evaporation in evaporative self-assembly using nonvolatile solutes (nanotubes, nanowires, nanoparticles), as a simple route to creating highly ordered and complex structures.

- Enhancing mixing within surface nanodroplets, with application to analytical chemistry.

- A better understanding of how droplets can be shaken off surfaces is relevant to the development of acoustically enhanced self-cleaning\(^{40}\) or ultrasonic drying.

- The lift-off phenomenon could be a method for supplying cool droplets to hot spots in high heat-generating processor chips, circumventing the long timescales required for sessile droplets to coalesce and jump.\(^{41,42}\)

- Tuning the evaporation characteristics via surface wettability is key to controlling energy dissipation in nanoscale devices,\(^{43}\) or thermal management involving surface-driven phase change.\(^{44}\)

This work can be developed in several directions. For example, the parametric study could be extended to include the effects of surface roughness and nanodroplet size on the phenomena observed; alternatively, mathematical models could be developed to predict the lift-off threshold or oscillation frequency as a function of the simulation parameters.

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**Notes**

The authors declare no competing financial interest.

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