Homogeneous nucleation: Patching the way from the macroscopic to the nanoscopic description

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How and when does water "fracture"? In other words, how and when does a small cavity, or nucleus, form that does not heal but grows to macroscopic size, thus becoming a bubble? This question is important in various areas of technology and nature, affecting, for example, the ability of tall trees to draw sap to great heights (1, 2).

The classical answer, developed by Volmer in the 1930s and described in his monograph (3), implies that, in ideal conditions, it is next to impossible to create a bubble in water because the tension (or negative pressure) required is of the order of thousands of atmospheres (1 atm is about 0.1 MPa; for more modern accounts see refs. 4–6). Although this result had some uncertainties as far as precise numerical values were concerned, the order of magnitude—dictated by the strength of the intermolecular hydrogen bonds—seemed robust. However, it was also in flagrant conflict with experience, because cavitation is often encountered at tensions of the order of one or a few atmospheres, as, for example, in the acoustic cleaning baths used by dentists and jewelers. Even more strange is the embarrassingly wide range of nucleation thresholds reported by different investigators.

The way out of these paradoxes was suggested by Harvey et al. (7), who postulated that in "real life" nucleation in water does not occur in the homogeneous liquid, as postulated in the classical theory, but at "weak spots," such as preexisting small gas pockets trapped on solid walls or on floating motes, hydrophobic nanoparticles, or other impurities. These inhomogeneities become even more important in the presence of large amounts of dissolved air (or any other gas), which may also lead to the formation of surface nanobubbles (8).

Harvey et al.'s (7) insight led to the development of the so-called crevice model, which was later refined by several investigators (9–11). In particular, the form of the model developed in ref. 11 was found in excellent agreement with experiments showing that, for example, a tension of −0.5 MPa is sufficient to generate a bubble from a cylindrical hole of 500-nm diameter, whereas for holes of 10-nm diameter −2.5 MPa is required (12) (Fig. 1) The crevice model rationalizes the differences among reported data in the literature on the nucleation threshold by the variability of the degree of "cleanliness" of the water used in the experiments, which is very difficult to control due to the strong affinity of this liquid for a whole variety of impurities.

Thus, the vast majority of nucleation events in water are heterogeneous, rather than homogeneous, as postulated in the classical theory. Water seems to be "special" in this respect as well, because homogeneous nucleation is found in other liquids, such as helium (2) and some organics.

The question of the "true" nucleation threshold of "pure" water, although somewhat academic,

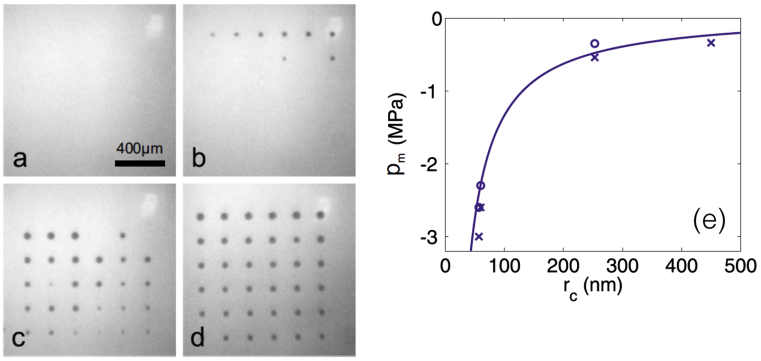

Fig. 1. Cavitation bubbles in degassed water emerging from 6 × 6 cylindrical pits with radius 246 nm, for three negative pressure pulses (applied through a piezoacoustic transducer) with amplitude (*A*) $p_m = -0.24$ MPa, (*B*) $p_m = -0.35$ MPa, or (*C*) $p_m = -0.54$ MPa. The nanoscopic pits, with a depth of 500 nm and separated from each other by 200 μm, were etched into the substrate by a focused ion beam. (*D*) The full bubble pattern can develop when $p_m = -0.54$ MPa is immediately applied, without any preceding less-strong pulses. (*E*) Nucleation threshold as a function of the pit radius for both the crevice theory (line) and experiment (crosses, nucleation and circles, no nucleation). The theoretical line lies perfectly in between the "no nucleation" and "nucleation" symbols. Figure reused from ref. 12.

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The authors declare no conflict of interest.

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remains, however, a scientifically important one, and the work of Menzl et al. (13) represents a significant step toward its resolution. These authors performed very sophisticated molecular dynamics (MD) simulations of homogeneous bubble nucleation in water with a hybrid Monte Carlo scheme. The use of an isothermal–isobaric ensemble permitted cavities to grow and the total volume of the system to vary. To identify the probability of formation of the larger bubbles, which do not form spontaneously on the timescale of the simulation, they carried out umbrella sampling simulations with a bias on the volume of the largest bubble. They adopted ingenious ways to deal with several delicate aspects of the simulation such as the identification of hydrogen bonds and the calculation of formation rates and of the diffusion coefficient along the "coordinate" of the bubble volume, which they used as order parameter.

A crucial ingredient is, of course, the model used for the interaction potential of the water molecules. Choosing the appropriate one is nontrivial because it is virtually impossible, using the same potential, to get all water properties right in MD simulations—density, surface tension, boiling and freezing points, latent heat, and any other material properties, including their temperature dependence. Despite this and several other difficulties, Menzl et al. (13) succeeded in obtaining nucleation thresholds and rates similar to those found in the best available data obtained in water inclusion experiments in quartz, in which a homogeneous nucleation threshold of –140 MPa was found (14). In addition, they were able to determine the values of the parameters appearing in the classical theory, for some of which there was some uncertainty, as mentioned before.

The key finding of Menzl et al. (13) is that the classical nucleation theory fails quantitatively because it ignores all microscopic information such as the curvature dependence of surface tension and the thermal fluctuations that affect the bubble expansion at the nanoscopic scale. The former can be expressed in terms of the so-called Tolman length δ, which, divided by the radius of curvature of the bubble interface, quantifies the effect of the surface curvature on the magnitude of the surface tension coefficient. This length can be calculated thermodynamically (15, 16). By a fit to their numerical results, Menzl et al. (13) find $\delta \simeq 0.195$ nm, which, being positive, reduces the surfaces tension coefficient, thus helping cavitation. Next, thermal fluctuations must be included into the Rayleigh–Plesset dynamics (17) for the bubble radius $R(t)$, in which, given the small energies involved, inertia can be omitted. This can be done by adding an extra random force (Gaussian white noise), with an amplitude given by the fluctuation-dissipation theorem.

The simultaneous use of MD simulations and of the continuum (extended) Rayleigh–Plesset equation is an interesting solution to a multiscale problem that extends the classical nucleation theory toward the microscopic world. It represents another indication of the fact that continuum equations can be useful down to the nanoscale if fluctuations are properly taken into consideration with the help of the dissipation-fluctuation theorem, as also found by other authors. A prior example is Eggers's extension of the slender jet approximation (18) for the calculation of the jet breakup toward nanoscopic jets (19): By embodying thermal fluctuations into the hydrodynamic equations for the jet velocity and the jet radius, he succeeded in quantitatively describing the pinch-off dynamics of a nanojet, as obtained from MD simulations (20).

These activities directed to finding efficient and physically sound ways to "patch" continuum mechanics and molecular dynamics (for a few additional examples see, e.g., refs. 21–24) will lead to better and more efficient ways to calculate the interaction of fluid flow with the nanoscopic structures encountered in an increasing number of important areas such as nanofluidics, biology, and medicine.

Acknowledgments

This work was supported through Netherlands Center for Multiscale Catalytic Energy Conversion, which is supported by Netherlands Organisation for Scientific Research (D.L.), and National Science Foundation Grant CBET 1335965 (to A.P.).

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