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Tolman Length Effect on Cavitation of a Binary Metallic Liquid under Negative Pressure

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We demonstrate the stochastic nature of cavitation in a binary metallic liquid $Cu_{46}Zr_{54}$ during hydrostatic expansion by employing molecular dynamics (MD) simulations. The activation volume is obtained from MD simulations and transition state theory. Extrapolation of the pressure dependence of the activation volume from our MD simulations to low tensile pressure agrees remarkably with the cavitation experiments. We find that classical nucleation theory can predict the cavitation rate if we incorporate the Tolman length derived from the MD simulations.

Cavitation or the formation of bubbles in metastable liquids, has been investigated experimentally and theoretically since Lord Rayleigh [1–6], yet there remain considerable uncertainties in the underlying descriptions. While it has been exploited for practical uses including ultrasonic cleaning [7, 8] and sonoluminescence [9], cavitation is directly relevant to undesirable natural events including volcanic eruptions and void formation in solids or glasses that degrade their mechanical, physical and chemical properties (e.g., fracture, shear banding and corrosion). In particular cavitation during isochoric cooling of a metallic liquid may lead to voids at grain boundary triple junctions or randomly dispersed in a metallic glass. This has been difficult to characterize for most metallic glasses because they are normally multicomponent. However, bulk binary metallic glasses have recently been developed (e.g., Ni-Nb and Cu-Zr glasses), thus simplifying the analysis for elucidating the physics underlying cavitation in engineering metallic glasses and alloys.

Cavitation in metastable liquid is a fluctuation-driven process that is described using classic nucleation theory (CNT) [10–12]. However, direct application of CNT to cavitation is complex, considering the closeness of the thermodynamic state to the spinodal, and the lack of reliable constraints on such parameters as surface tension. Molecular simulations (molecular dynamics and Monte Carlo method) and statistical theories have provided some insights into this phenomenon at a more fundamental level [13–20]. However, recent molecular dynamics (MD) simulations of cavitation dynamics in a single-component liquid appear to disagree with CNT in the cavitation rate, likely due to uncertainties in estimating the surface tension [13, 14]. In order to connect MD simulations with transition state and nucleation theories and with experiments, we report MD simulations of cavitation in a binary metallic liquid, $Cu_{46}Zr_{54}$, under negative pressure. Our studies shows that cavitation can be described as a random Poisson process. Thus using the activation volume obtained from the transition state theory and the surface energy from the Tolman length model, we find that CNT predicts the cavitation rates in accord with direct MD simulations. We characterize the pressure-dependence of the activation volume within a limited range of pressure and show that the extrapolation to lower pressures leads to good agreement with experiments.

Our MD simulations use the Rosato-Guillope-Legrand potential [21, 22] for Cu-Zr alloy extracted from density functional theory calculations on CuZr compounds and implemented in the ITAP molecular dynamics program [23]. Previous studies [22, 24, 25] showed that this potential is accurate: the predicted glass formation temperature (~700 K), bulk structure, elastic moduli, and viscosity agree with available experiments.

We first construct binary $Cu_{46}Zr_{54}$ systems ranging from 2000 atoms to 54000 atoms with random atom positions. Using an integration time step of 1 fs, we melt the systems at 1200 K and equilibrate them for 100 ps for subsequent cavitation simulations. For tensile loading, we expand the cell at a uniform expansion rate of 2×10^8 s^{-1} at 1200 K using a Nose-Hoover thermostat (constant volume-temperature or NVT ensemble). In order to explore the stochastic nature of cavitation, we carry out 100 independent calculations for a given initial, metastable state. In each of such runs, we change only the initial velocity distributions (via changing the random number seed for velocity assignment) and observe the cavitation dynamics. To calculate the cavity volume within the binary liquids we use a grid-based void analysis method [26].

Fig. 1(a) shows the pressure evolution as a function of volume (or bulk strain) for the 54000-atom system under tension at a constant strain rate and fixed temperature (T). With increasing strain, pressure (P) decreases steadily (AB) until it reaches the pressure minimum B. There is a drastic decrease in the magnitude of P after B due to tensile stress relaxation accompanying rapid cavity nucleation and growth (BC). The system then

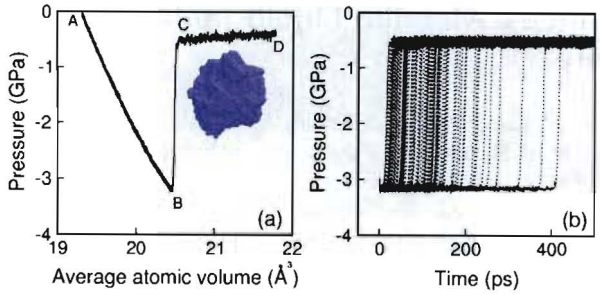

FIG. 1: (a) The pressure–volume plot for the 54000-atom system under hydrostatic tension at 1200 K; inset: an example of the cavity near C ($\sim$1 nm in diameter). (b) Pressure evolutions for 100 independent NVT runs, all started with the same configuration at P=−3.16 GPa in (a).

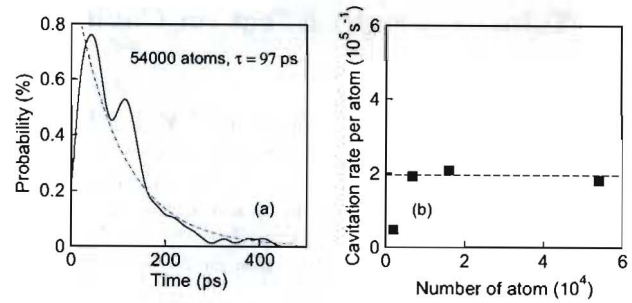

FIG. 2: (a) Probability of cavitation obtained from 100 independent runs on the 54000-atom system (solid line) and Poisson fitting (dashed line). T=1200 K, and P=−3.16 GPa. (b) The cavitation rates (per atom) for four different system sizes at the same loading conditions.

reaches a steady states (CD) where P increases slowly. Cavitation during BCD is confirmed by direct analysis, and an example of the cavity is shown as an inset to Fig. 1(a). The cavity is approximately spherical but with a rugged surface at the MD scales.

In order to analyze the onset of cavitation of this metastable binary liquid we follow its evolution under a fixed bulk volume and temperature. We choose various starting configurations from Fig. 1(a) prior to the pressure minimum B, to explore homogeneous cavitation at different loading conditions. For each such configuration, we perform NVT simulations (with fixed bulk volume and temperature) and observe the cavitation dynamics under the prescribed tensile loading. The point of cavitation is obvious in the change of the instantaneous bulk pressure. Starting from a specific initial configuration [e.g., near B in Fig. 1(a)], we carry out 100 independent NVT runs; for each run, a different random number seed is used for initial velocity assignment. Fig. 1(b) shows the results from 100 runs all starting at a pre-cavitation loading of P=−3.16 GPa. For each run, P remains constant for a while and then increases rapidly as a result of cavity nucleation and growth, finally reaching a plateau in which the stress is in equilibrium [Fig. 1(b)]. The pre- and post-cavitation values of P are the same for all 100 independent runs. However, cavitation occurs at very different individual waiting time ($t_{\rm wait}$). Here $t_{\rm wait}$ is the instant at which the pressure amplitude decreases to 85% of the pre-cavitation value.

For a given pre-cavitation pressure, the statistical runs yield 100 values of $t_{\rm wait}$ used to construct the probability distribution [solid line in Fig. 2(a)]. Here each point was broadened into a Gaussian width of 15 [27]. Fitting the solid line to a Poisson process leads to the dashed line with an expected waiting time τ=97 ps. The nucleation or cavitation rate follows as $\nu\equiv 1/(N\tau)$, where N is the system size. Here we obtain ν=1.9×10^5 s^{-1} per atom for the 54000-atom system at pre-cavitation pressure of −3.16 GPa and 1200 K. To determine whether N=54000 is sufficiently large for studying cavity nucleation, we perform similar simulations for N=2000, 6750 and 16000. Fig. 2(b) shows that ν is similar for three different system sizes with $N\geq$6750 ($\sim$2×10^5 s^{-1} per atom or 10^{34} s^{-1}m^{-3}), indicating that cavity nucleation is a local phenomenon.

Using transition state theory, we can write the cavitation rate as $\nu\propto\exp(-\Delta G^{\ominus}/k_BT)$, where k_B is the Boltzmann constant. The Gibbs energy of activation $\Delta G^{\ominus}=\Delta\Omega^{\ominus}{\rm d}P-\Delta S^{\ominus}{\rm d}T$ if we neglect the minor composition change near the cavity. The activation volume $\Delta\Omega^{\ominus}=(\partial\Delta G^{\ominus}/\partial P)|_T$, and the activation entropy $\Delta S^{\ominus}=(\partial\Delta G^{\ominus}/\partial T)|_P$. Our simulations are performed at a fixed temperature, so the $\Delta S^{\ominus}$ term can be neglected. From transition state theory and the definition of ν ($1/N\tau$), we obtain

$$\Delta\Omega^{\ominus}=\frac{\partial(k_BT\ln\tau)}{\partial P}\Big|_T. \quad (1)$$

Thus, given τ for various tensile loading, $\Delta\Omega^{\ominus}$ can be obtained as a function of P. (Similarly, the activation entropy can be obtained via varying temperature at a fixed pressure.) For the 54000-atom system, we also perform runs at lower tensile loading to obtain longer waiting time τ. Fig. 3 shows the plot of $k_BT\ln\tau$ vs P, and its slope is the activation volume. Assuming a linear dependence of activation volume on P, we fit the $k_BT\ln\tau$–P data points with a quadratic function. This leads to $\Delta\Omega^{\ominus}$=820.7+229.3P at T=1200 K where pressure is in GPa and volume in Å^3. For a pre-cavitation pressure P=−3.16 GPa, the activation volume is 94 Å^3 at 1200 K, corresponding to about 5 vacancies.

The cavitation nucleation experiments were carried on CuZr metallic liquid to form cavities by rapid cooling, which created negative hydrostatic pressure inside the capsule; cavities formed within a timescale of 7 s at 1173 K and P=−0.5 GPa (triangle, inset to Fig. 3) [28]. To compare with the experiments, we extrapolate the fitted $k_BT\ln\tau$–P relation to lower pressures, and the extrap-

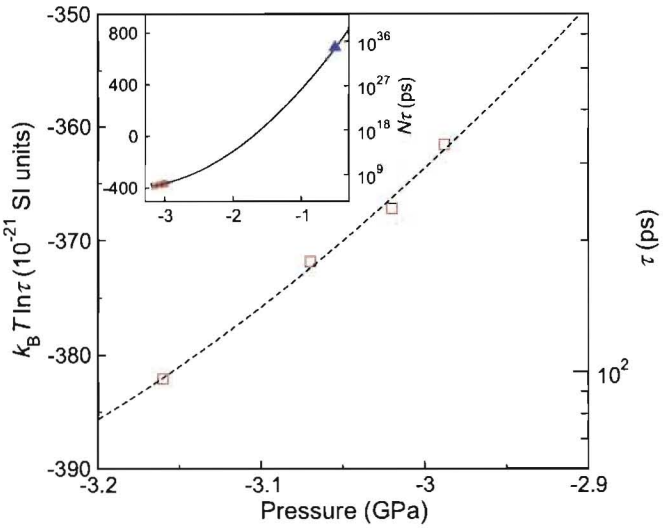

FIG. 3: $k_B T \ln\tau$ (left axis) and τ (right axis) as a function of initial pressure P for the 54000-atom system at 1200 K. MD results: squares; dashed line: quadratic fitting. Inset: Extrapolation of MD results to experimental scales. The experiment point (triangle) has $\tau\sim7$ s for a system size of 10^{22} atoms.

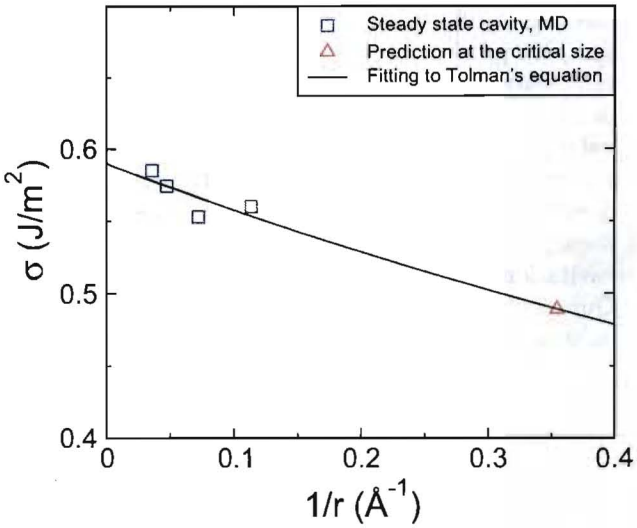

FIG. 4: Surface energy σ vs inverse cavity size (r^{-1}).

olation is in accord with the experiments (Fig. 3 inset). This agreement between the experiments and direct MD simulations lends support to the transition state theory analysis. Note that the local strain rate or the cavity growth rate is different in our MD simulations with different loading and in experiments. The higher the pre-cavitation tensile loading, the higher the growth rate. In Fig. 3, the rate effect is implicitly incorporated in the pre-cavitation pressure.

For *steady* states where a cavity is in equilibrium with the surrounding liquid, the surface energy (σ) is $\sigma=\Delta P/2r$, where ΔP is the pressure difference across the cavity surface and r is the radius of the cavity at steady state. We construct a cavity within the liquid at 1200 K, vary the bulk volume and let the system achieve equilibrium, and then measure the steady-state cavity size and pressure to calculate the corresponding σ. The results of σ for different cavity sizes are shown in Fig. 4 (squares), which can be fitted with the Tolman equation:

$$\sigma(r) = \frac{\sigma_0}{1+\frac{2\delta}{r}}, \qquad (2)$$

where the Tolman length δ=0.3 Å, and σ_0=0.59 J m^{-2} is the surface energy for a planar surface (Fig. 4). We apply the Tolman equation to both steady and transient states. For P=−3.16 GPa and T=1200 K, $\Delta\Omega^{\ominus}$=94 Å^3 and r=2.8 Å; the surface energy corresponding to this activation volume is σ=0.49 J m^{-2} from Tolman equation (triangle in Fig. 4).

In classical nucleation theory, the driving force for cavity nucleation is $\Delta G=4\pi r^2\sigma + \frac{4}{3}\pi r^3 P$, where the first (surface) term is the free energy gain due to surface tension of a cavity and the second (volume) term is the reduction while creating the cavity. ΔG peaks at the critical value (ΔG^*) with the critical radius $r^*=2\sigma/P$, and $\Delta G^*=16\pi\sigma^3/3P^2$. Assuming the activation volume at P=−3.16 GPa and T=1200 K is the corresponding critical nucleus size, we have r^*=2.8 Å, σ=0.49 J m^{-2}, and ΔG^*=1.23 eV.

Given ΔG^* at P=−3.16 GPa and T=1200 K, CNT allows us to estimate the nucleation rate at the critical point: $\nu=\nu_0 \exp\{-\Delta G^*/k_B T\}$. Considering that the cavitation in vitreous liquids is related to the spontaneous and cooperative reorganization of individual clusters name shear transformation zones (STZs), we also believe that the kinetic feature of liquid is related to the merging of α and β relaxations in high temperatures [29]. So the prefactor ν_0 is related to the maxwell relaxation time [30], configurational entropy of critical cavity and the size of STZ zones. Thus, the prefactor $\nu_0=(1/N^*)(\mu/\eta)\exp\{n\Delta S/k_B\}$. Here μ is the shear modulus, η is the viscosity, μ/η is the Maxwell relaxation frequency, N^* is the number of atoms in the STZs (around 100 atoms as for glass [31]), ΔS is the configurational entropy per atom, and n is the number of atoms occupying the same volume as the critical cavity. From our previous MD study [25], μ=2 GPa and η=0.2 Pa s under similar conditions. We assume ΔS is about 1 k_B, similar to the entropy of fusion according to Richard's rule, and n=5 as shown above. It follows that ν_0 is about 1.48×10^{10} s^{-1}, and ν is $\sim1\times10^5$ s^{-1} per atom which agrees well with our direct MD simulations (2×10^5 s^{-1}). This agreement shows that the cavitation rate can be predicted from CNT with remarkable accuracy if the Tolman length is considered.

Our systematic study shows that cavitation in a binary

metallic liquid is a random Poisson process, and such complex processes can be well described by the transition state theory and classical nucleation theory. We demonstrate the methodology of obtaining the activation volume (or entropy) indirectly from MD simulations and the transition state theory, and deducing cavitation rate directly from MD simulations. The classical nucleation theory converges with the simulations in describing the cavitation rate if the Tolman length effect is considered. Our results also bear implications to broadly defined nucleation and growth processes.

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