For example, Chung et al. correlated the measurement of droplet shape and interfacial tension to the behavior of capillary wave resonance modes utilizing quasi-elastic laser scattering to measure the resonant frequency. Similar methods have been studied by Wada et al. and Pigot and Hibara. Resonant frequencies are determined by Iino et al. by purposefully exciting standing wave instabilities on an interface within a cylindrical container using electrostatic oscillations. A similar method was later employed by Tsukahara et al., who also related the experimentally determined resonant frequency to the interfacial tension of multiple fluids using expressions for the fluids’ natural frequencies. Non-resonance methods which employ correlation between the appearance of fluid instabilities and surface tension have also been explored.

In this work, a method for the measurement of interfacial tension to the behavior of capillary wave resonance modes utilizing quasi-elastic laser scattering to measure the resonant frequency. Similar methods have been studied by Wada et al. and Pigot and Hibara. Resonant frequencies are determined by Iino et al. by purposefully exciting standing wave instabilities on an interface within a cylindrical container using electrostatic oscillations. A similar method was later employed by Tsukahara et al., who also related the experimentally determined resonant frequency to the interfacial tension of multiple fluids using expressions for the fluids’ natural frequencies. Non-resonance methods which employ correlation between the appearance of fluid instabilities and surface tension have also been explored.

One of the weaknesses in using these types of methods or traditional surface tension measurement methods like pendant drop tensiometers or liquid bridges is their reliance on constrained geometries. This creates significant challenges in using high temperature samples, such as liquid metals. To process these types of samples, advanced techniques such as electrostatic levitation (ESL) have been developed. The use of ESL for containerless processing has allowed for the study of many thermophysical properties for high temperature liquid metals, including density, surface tension, viscosity, and many others. Of particular interest to the current work is the use of ESL for the measurement of surface tension. Traditional methods for this measurement rely on the use of the equation for the natural frequency of a spherical drop, originally derived by Rayleigh and also given by Lamb. Adding a correction to this equation to account for surface charge results in:

$$\omega_n^2 = \frac{n(n-1)(n+2)}{\rho R_0^3} \left( 1 - \frac{Q^2}{64 \pi^2 R_0^2 \sigma \epsilon_0} \right),$$

where $\omega$ is the natural frequency of the drop, $\rho$ is its density, $\sigma$ the surface tension, $R_0$ the drop radius, $n$ is the nth mode of oscillation of the droplet, $Q$ is the drop charge, and $\epsilon_0$ is the permittivity of free space. This equation is derived from inviscid theory, and
approximates the natural frequencies for spherical liquid metal drops due to their low kinematic viscosities. For example, the kinematic viscosity of molten Zr at its melting point is 80% of that of water. In the case of liquid metals, the correction term arising due to interfacial charge is typically very small, resulting in changes to the surface tension on the order of 1%. For this reason, the correction term is ignored in the surface tension measurements shown in the present work.

In typical non-constant forcing experiments, i.e., the pulse-decay method, the drop is pulsed first translating it about its mean position at an assigned frequency. When this assigned frequency is close to the natural frequency, the drop will execute an $n = 2$ mode, at which point the pulsation is ceased. After the imposed pulsation ceases, the amplitude of the oscillatory prolate-oblate deformation of the spherical drop decays with time. Image analysis is used to fit this decay to a sinusoidal, exponentially decaying function with a given frequency, which is then taken to be the natural frequency of the droplet. This frequency is input into Eq. (1) to deduce the surface tension of the material. Since the feedback system to maintain the drop in its levitated state must re-stabilize the drop after this removal, additional perturbations are unintentionally imposed on the droplet during the initial stages of the decay due to control system noise. These perturbations act to excite all manners of modes within the droplet, which can affect the decay response frequency through non-linear interactions between modes. Thus, the natural frequency obtained from the pulse-decay method is a non-linear composite of the natural frequencies for the various modes. The underlying problem with this method is this unintentional excitation of all other modes upon removing the forcing oscillation.

The Faraday forcing method in this study differs from the conventional pulse-decay technique due to its continuous nature. As the forcing is continuous, the oscillation mode remains excited throughout the course of the measurement at resonant conditions, much like the standing waves observed in traditional Faraday instability experiments. This forcing method is akin to that of ref. and ref., but is utilized at high temperature samples that have already been electrostatically levitated, thus removing sidewall effects from the problem and resultant model. This allows for the determination of the resonant frequency through imaging the droplet’s departure away from a spherical shape. The resonant frequency is taken to be the frequency of forcing where the drop’s deviation from a sphere into prolate and oblate shapes is at its maximum. When utilizing the Faraday forcing method, no curve fitting is required. Since a decaying function is not fit post-experiment, the continuous nature of the Faraday forcing method inherently avoids feedback system interference which is present in traditional methods. In addition, highly viscous samples present difficulties for the traditional method due to fast damping. These problems could potentially be alleviated by utilizing the Faraday forcing method, upon re-deriving an expression similar to Eq. (1), but where viscosity is now taken into account. Notwithstanding the benefits of continuous forcing, the method presented in this study is unable to yield the viscosity of the sample. Thus, the pulse-decay method would be needed in conjunction with the current method for the determination of both surface tension and viscosity.

RESULTS

In each experiment, multiple forcing frequencies are tested at a small, constant amplitude. Images are captured using a high-speed camera and analyzed to quantify the departure of the drop. The diameter of the sample in the absence of any continuous forcing was mm. Maximum disturbance caused through the application of continuous forcing a below the resonant frequency (180 Hz), b at the calculated resonant frequency (185 Hz), and c above the resonant frequency (191 Hz). A video accompanies this study that shows dramatic deviation from the spherical shape at the resonant frequency and the decrease in this deviation both before and after the resonant frequency.
from its spherical shape. Figure 1 describes the change in the deformation of the sample with a slight change in frequency. As can be observed in the figure and in the accompanying video, the magnitude of the maximum departure from the pre-forced spherical shape of a sample is greatly magnified at the resonant frequency. This increase is typically at least 10% greater than the nominal diameter, as seen in Fig. 2.

Table 1 summarizes the surface tension measurements obtained for three samples and companion literature values. Temperatures were chosen in the undercooled region for Zr samples to reduce mass loss via evaporation during the course of experiments, but this was not possible for the Ti39.5Zr39.5Ni21 due to repeated unintentional solidification.

DISCUSSION

As can be observed, the Faraday forcing method yields surface tension measurements which are typically slightly lower than literature values measured using the current pulse-decay analysis. Approximately 1% of the difference could be recovered by taking the charge correction term shown in Eq. (1) into account during our analysis. We attribute the remaining discrepancy to the fact that the pulse-decay analysis inherently involves the excitation of multiple modes upon delivery of the pulse and subsequent feedback control to maintain the drop in its levitated state. This causes the overall response to be comprised of many modes, with \( n = 2 \) decaying the slowest. Non-linear interactions between modes will cause the response frequency to shift upward, resulting in higher surface tension measurements after utilization of Eq. (1). To test this hypothesis, decay experiments were also conducted for all three samples.

Recall from the introduction how the Faraday forcing method distinguishes itself from the pulse-decay method. To further highlight the difference between the methods, the pulse-decay technique was also analyzed for the tested samples. Figure 3a shows a sample of the data and best fit for a Zr sample at 1800 °C pulsed at a frequency of 185 Hz when using the pulse-decay method. By utilizing the pulse-decay technique, the best fit for an imposed pulsating frequency of 185 Hz would yield a natural frequency of 186.25 ± 0.00697 Hz, which is 0.68% higher than that observed using the Faraday forcing technique. The average measured natural frequency for the 1800 °C Zr sample over all of the tested pulsating frequencies was 186.09 Hz. It should be noted that the instantaneous pulsing of the sample at a frequency above or below the resonant frequency determined by the Faraday forcing method did not substantially impact these results, as shown in Fig. 3b. In fact, the decay analysis provided consistent results for the natural frequency regardless of the pulsating frequency. Though this result was consistent, it was always higher than the frequency which produced the maximum magnitude of departure from each sample’s spherical shape, resulting ultimately in discrepancies for the surface tension measurement of between 1.36% and 4.37% for the tested samples. This analysis effectively shows that the two techniques will produce different results for exactly the same sample, though the sample clearly resonates most strongly at the frequency determined by the Faraday forcing method, i.e., the current method.

The larger discrepancy observed between the Faraday forcing result and the literature values for the Ti39.5Zr39.5Ni21 alloy is attributed to possible oxidation of the sample during testing, as these types of alloys are known to be highly sensitive to oxygen contamination.\(^{19}\) This was evident through the post-processing
Faraday forcing of high-temperature N Brosius et al.

**Methods**

Experiments were conducted using the ESL facility at the NASA Marshall Space Flight Center. Solid samples were initially levitated in vacuum (10^-6 to 10^-7 torr) using multiple electrodes coupled to a feedback controller. A UV beam initialized the charge on the sample prior to levitation and replenished the charge throughout the duration of the experiment. A neodymium-doped yttrium aluminum garnet (Nd:YAG) laser was first used to melt the sample, and then density measurements were conducted by raising the temperature until molten and approximately 50 °C superheated before turning off the laser and recording the droplet shape as a function of temperature. A single wavelength pyrometer (LumaSense Technologies IMPAC IGA 140) was used to measure and record the temperature accurately between 300 and 3000 °C. For the determination of surface tension, the temperature was raised above the melting point before allowing the sample to cool to the desired temperature, either superheated, at the melt point, or undercooled, while remaining in the liquid phase. In the case of Zr, experiments were conducted in the undercooled regimes in order to minimize mass loss via evaporation throughout the course of an experiment. This undercooling was not possible for the Ti50Zr50Ni21 sample due to repeated unintentional homogeneous nucleation. After reaching the desired temperature, a temperature control system maintained the temperature to ensure the sample temperature remained constant during a measurement.

A frequency range is selected by estimating the natural frequency of the material using the measured density and radius of the sample. After the sample is successfully levitated, melted, and cooled to the temperature of interest, an oscillatory forcing is superimposed over the controlled voltage drop at a constant amplitude for all measurements at a given temperature. Each frequency within the expected region is analyzed and the sample response is recorded using a high-speed camera. In the experiments, a camera recording at 1000 fps with a resolution of 512 by 512 pixels was used. The resonant frequency is estimated visually for an initially large frequency step size, as shown in Fig. 2a. After this estimation, a narrow range of frequencies around the estimated resonant frequency is selected for further experiments. Within this narrow range, subsequent experiments are conducted until the uncertainty in the determined resonant frequency reaches an acceptable value. Images collected for all frequencies within the narrow range are analyzed using ImageJ® to determine the frequency.
at which the sample most strongly resonates, i.e., deviates from its spherical shape. The resonant frequency is taken to be the tested frequency which produces the largest prolate and oblate oscillations away from the natural spherical shape of the sample. The smaller the step size, the more accurate the determined resonant frequency. This determined resonant frequency must therefore be the natural frequency of the drop. After obtaining the resonant frequency, Eq. (1) is used to calculate the surface tension of the material for the trial.

Data availability
All relevant data are available from the authors N.B. and R.N.

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AUTHOR CONTRIBUTIONS
N.B. and K.W. took measurements and analyzed the data. M.S., S.M., and R.N. supervised the work and offered expertise to aid in experimental design and operation. All authors contributed to the writing of the manuscript.

ADDITIONAL INFORMATION

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