The oscillation spectrum of a compound drop

I. EGRY
Zentrum für Erstarrung Unterkühlter Schmelzen, ZEUS, Deutsches Zentrum für Luft- und Raumfahrt, DLR, 51170 Köln, Germany

Under microgravity conditions the equilibrium shape of a compound drop, consisting of two immiscible mutually wetting liquids, is given by a spherical liquid core, encapsulated by the second liquid phase. Due to energy considerations, the outer liquid is the one with the lower (vapour-liquid) surface tension. The oscillation spectrum of such a compound drop corresponds to that of two coupled oscillators, one being driven by the surface tension, while the other is due to the interfacial (liquid-liquid) tension between the two immiscible liquids. Therefore, in principle, the values of both, the surface and the interfacial tension, can be derived from the frequencies of the coupled oscillations.
In this paper, an analytic expression is presented, relating the frequency spectrum to the surface and interfacial tension, respectively. In addition, the concept for technical realisation using electromagnetic levitation and copper-cobalt as a model system, is discussed. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

As the temperature of a homogeneous melt of a monotectic alloy is lowered below the binodal temperature, demixing sets in and small droplets of one liquid, L_1, in the matrix of the other liquid, L_2, are formed. These two immiscible liquids do not consist of the pure components, but have concentrations according to the phase boundary of the miscibility gap; therefore, L_1 is rich in component 1, while L_2 is rich in component 2. This initial phase is energetically very unfavourable, due to the high interface area created between L_1 and L_2. In the next stage, Ostwald ripening sets in [1]. This diffusive mechanism leads to the growth of large drops at the expense of the small ones, thereby coarsening the structure of the dispersion (emulsion) and finally leading to two separated liquid phases L_1 and L_2.

In general, the interfacial tension between two liquids is difficult to measure, and only few data exist [2]. The oscillating drop technique [3] is non-contact measurement technique for surface tension measurements of levitated liquid drops. In its original form, it assumes a homogeneous inviscid drop, free of external forces. In this ideal case, the frequency of surface oscillations is simply related to the surface tension σ_0 by Rayleigh's formula [4]

$$\omega_0^2 = \frac{8\sigma_0}{\rho R_0^3} \qquad (1)$$

where ρ is the density of the drop and R_0 its radius. By substituting $M = \rho \, 4 \pi R_0^3/3$, the apparent density dependence of the frequency disappears which makes this equation particularly easy to use. Viscous effects have been included later [5], but can generally be neglected for liquid metals. The influence of external forces, like gravity and the electromagnetic levitation field, is more

severe, because it splits and shifts the single Rayleigh frequency. A correction formula has been worked out by Cummings and Blackburn [6], which has been verified experimentally through a benchmark experiment in microgravity [7].

In this paper, we propose to extend the oscillating drop technique to the measurement of the interfacial tension between two immiscible liquids. We assume that the final structure (after Ostwald ripening has finished) of a compound drop, consisting of two immiscible liquids, wetting each other, will consist of a core of L_1 with density ρ_1, surrounded by a layer of L_2 with density ρ, as shown in Fig. 1. Effects of viscosity and external forces will be neglected. The total surface energy of such a configuration is given by:

$$W = \sigma_0 A_2 + \sigma_{12} A_i \qquad (2)$$

where σ_0 is the surface tension of liquid 2, σ_{12} is the interfacial tension between liquids 1 and 2, $A_2 = 4 \pi R_0^2$ is the surface area of the outer surface, and $A_i = 4\pi R_i^2$ is the interface area between the two liquids. Therefore, in order to minimize this surface energy, the liquid with the smaller surface energy will form the outer layer. If this compound drop is spherical and concentric, the dynamics of its oscillations can be calculated analytically. In fact, Saffren, Elleman and Rhim have calculated the normal modes of a concentric three fluid system [8]. They formulated their theory for a binary compound drop immersed in a third host fluid of infinite extent. The present case of a levitated drop can be derived from their results by setting ρ_0, the density of the host fluid, equal to zero. Also, we are interested in the fundamental $\ell = 2$ mode only. Higher modes are strongly damped, and for concentric, spherical drops, there is no coupling of modes with different ℓ. In the following chapter, we
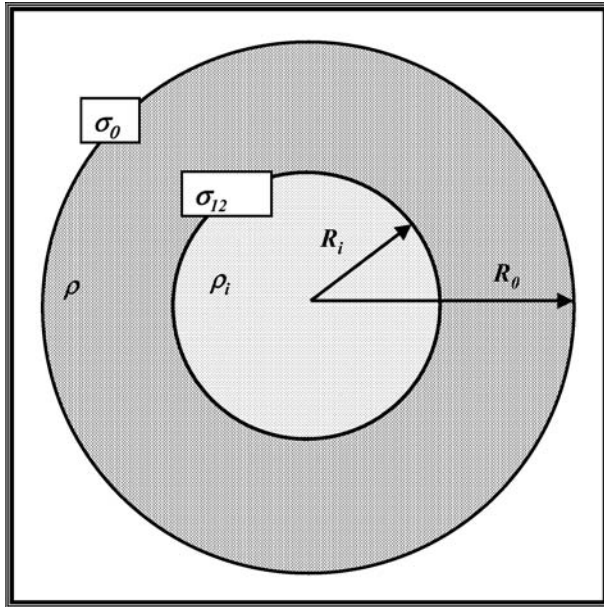
Figure 1 Cross section of a spherical, concentric compound drop consisting of two immiscible liquids with densities ρ_i and ρ, radii R_0 and R_i, surface tension of the outer liquid σ_0, and interfacial tension σ_{12}.

will derive explicit asymptotic formulae from Saffren's theory which will allow us to measure both, surface and interfacial energy of a compound drop simultaneously.

2. Drop dynamics

Using ref [8] as a starting point, asymptotic relations for the normal mode frequencies ω of a concentric, force-free, inviscid compound drop can be derived.

A number of symbols will be used which are defined as follows:

ω_0 is the unperturbed Rayleigh frequency (Equation 1) of a simple drop with density ρ, radius R_0 and surface tension σ_0 (see also Fig. 1 for the definition of the symbols).

$$\tau = \sqrt{\frac{R_0}{R_i}} \tag{3}$$

is the square root of the ratio between outer and inner radius,

$$\sigma = \sqrt{\frac{\sigma_0}{\sigma_{12}}} \tag{4}$$

is the square root of the ratio of the surface tension and the interface tension, and

$$\Delta\rho_i = \frac{3}{5} \frac{\rho_i - \rho}{\rho} \tag{5}$$

is the weighted relative density difference between liquid L_i and liquid L_0.

In the following, the frequencies will be discussed as a function of σ, with τ and $\Delta\rho_i$ as parameters. First, the asymptotic behaviour of the normal mode frequencies for small interfacial tension σ_{12}, i.e. for $\sigma \to \infty$ are

given by [9]:

$$\omega_+^2 = \omega_0^2 \left(1 - \frac{5}{3}\frac{\Delta\rho_i}{1 + \Delta\rho_i}\tau^{-10}\right) \tag{6}$$

$$\omega_-^2 = \omega_0^2 \frac{3}{5}\frac{\tau^6}{\sigma^2}(1 + \Delta\rho_i)^{-1}$$
$$\times \left[1 - \tau^{-10}\frac{1 + 2\Delta\rho_i}{1 + \Delta\rho_i}\right] \tag{7}$$

We can simplify Equations 6 and 7 for $\Delta\rho_i \ll 1$. They then read:

$$\omega_+^2 = \omega_0^2 \left(1 - \frac{5}{3}\frac{\Delta\rho_i}{\tau^{10}}\right) \tag{8}$$

and

$$\omega_-^2 = \omega_0^2 \frac{3}{5}\frac{\tau^6}{\sigma^2}(1 - \tau^{-10}) \tag{9}$$

The physical meaning of Equation 9 becomes obvious by introducing ω_i as follows:

$$\omega_i^2 = \frac{8\sigma_{12}}{\rho_i R_i^3} \tag{10}$$

which corresponds to the Rayleigh frequency of a single drop with surface tension σ_{12}, radius R_i and density ρ_i. We then have:

$$\omega_-^2 = \frac{3}{5}\omega_i^2(1 - \tau^{-10}) \tag{11}$$

To conclude the discussion of the frequencies, we quote the limiting value of ω_- for $\sigma \to 0$. It is given by [9]:

$$\lim_{\sigma \to 0} \omega_-^2 = \omega_0^2 \frac{\tau^{10} - 1}{\tau^{10} + 2/3} \tag{12}$$

For small $\Delta\rho_i$ the "forbidden band", i.e. the difference $\omega_+^2 - \omega_-^2$ is roughly given by:

$$\omega_+^2 - \omega_-^2 = \omega_0^2 \frac{5/3}{\tau^{10} + 2/3} \tag{13}$$

The asymptotic values for the frequencies, Equation 8 and 9 are shown in Fig. 2 together with the exact solutions as a function of σ for $\Delta\rho_i = -0.01$ and $\tau = 2^{1/6}$.

It remains to discuss the contribution of both normal modes to the oscillations of the outer radius, R_0. The normal modes, i.e. the eigenvectors δ_+ and δ_- of the oscillations, are linear combinations of δR_0 and δR_i, where $\delta R_{0,i}$ are the amplitudes of the oscillations around the equlibrium value of the radii in a given direction.

If we express δR_0 in terms of the normal modes as:

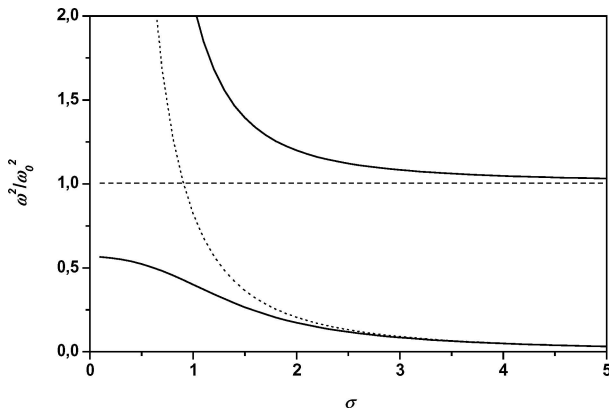$$\delta R_0 = a_{0+}\delta_+ + a_{0-}\delta_- \tag{14}$$

Figure 2 The squared and normalized normal mode frequencies $\omega_{\pm}^2/\omega_0^2$ as a function of σ, the square root of the ratio of surface to interface tension for $\tau = 1.12$ and $\Delta\rho_i = -0.01$. Full lines: exact solutions, dotted line: asymptotic solution for ω_-, Equation 9; dashed line: asymptotic solution for ω_+, Equation 8.
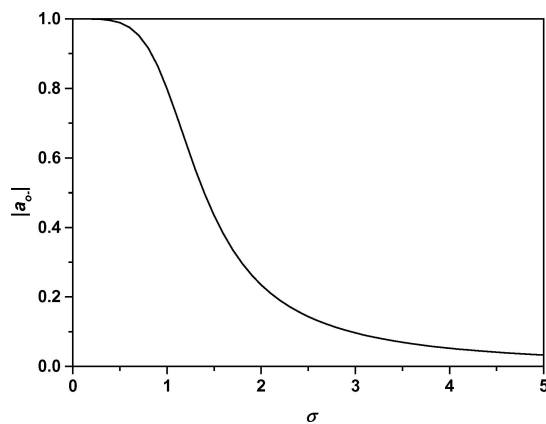

Figure 3 The contribution of the low frequency normal mode to oscillations of the outer radius R_0 as a function of σ, the square root of the ratio of surface to interface tension for $\tau = 1.12$ and $\Delta\rho_i = -0.01$.

then a_{0-} is the contribution of the normal mode with frequency ω_- to the oscillations of the outer radius R_0. Asymptotically, we find for a_{0-} [9]:

$$|a_{0-}| = \frac{1}{2\tau^2\sigma^2} \qquad (15)$$

As is evident, the oscillation spectrum of R_0 is dominated by ω_+ for large σ, but it does contain contributions with frequency ω_-. In Fig. 3, $|a_{0-}|$ is plotted as a function of σ for the same parameters as in Fig. 2.

3. Experimental

The oscillations of a compound drop have been observed and analysed by Saffren *et al.* [8] for transparent water-oil droplets suspended in a neutral buoyancy tank filled with oil. We are interested in liquid metals, for which their method is not applicable, and a levitation technique must be used, in our case electromagnetic levitation. Furthermore, applying the oscillating drop technique [3] to non-transparent metallic drops, it is only possible to observe the oscillations of the outer radius R_0 of a levitated drop. Nevertheless, as shown above, the Fourier transform of the time signal contains
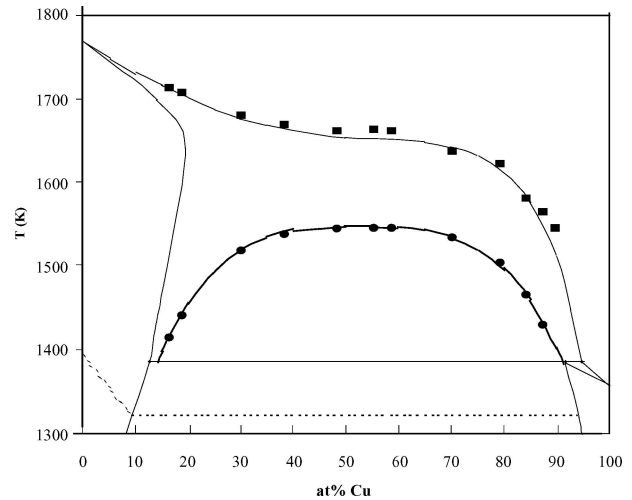

Figure 4 The phase diagram of Cu-Co, showing the experimentally determined liquidus and the metastable miscibility gap.

both normal mode frequencies and therefore all necessary information to measure both, surface and interface tension.

The present investigation concerns the alloy Cu-Co, which shows a metastable miscibility gap, i.e., the melt has to be undercooled before demixing sets in [10, 11]. This alloy is of particular interest because at the concentration $Co_{50}Cu_{50}$ the difference ΔT between liquidus temperature T_l and the critical temperature T_c has a minimum of $\Delta T \approx 100$ K only. The phase diagram including the experimentally determined miscibility gap, is shown in Fig. 4. To measure the interfacial tension in a metastable system is challenging, because nucleation and solidification must be suppressed. Undercooling of metallic melts by containerless processing, using electromagnetic levitation, is possible and has been applied to the alloy Cu-Co [11–13]. The interfacial tension σ_{12} between the two coexisting liquid phases shows critical behaviour near the critical temperature: $\sigma_{12}(T) \propto (T_c - T)^\alpha$, whereas for large undercooling it can be approximated by the difference of the surface tensions of the two liquids: $\sigma_{12} = |\sigma_1 - \sigma_2|$ which implies a linear temperatute behaviour. The critical exponent α has a classical value of 3/2; renormalization theory [14] yields $\alpha = 1.26$.

In the following, we estimate the parameters for the system Cu-Co. The surface tension of this alloy was measured [13] and one can estimate $\sigma_{Co} \approx 1.8$ N/m and $\sigma_{Cu} \approx 1.3$ N/m. Therefore $\sigma_{12} \approx 0.5$ N/m, and $\sigma = (\sigma_{Cu}/\sigma_{12})^{1/2} \approx 1.6$. This value underestimates σ. The densities of liquid copper and cobalt were measured by Saito and coworkers [15, 16]. At the melting point, the quoted values are: $\rho_{Cu}(T_m) = 7.86$ (g/cm^3), $\rho_{Co}(T_m) = 7.75$ (g/cm^3). Therefore, $\Delta\rho_i \approx -0.01$. For the parameter τ we use $\tau = 2^{1/6}$, which corresponds to equal volumes. For these values and $\sigma > 2$, Equation 8 and 18 yield the frequencies with an accuracy better than 20%. For $\sigma > 3$, $|a_{0-}|$ drops below 10%, and ω_- may be difficult to detect in the oscillation spectrum.

In the derivation of the above formulae, the presence of external forces, namely gravity and electromagnetic field, was neglected. As has been discussed in the introduction, these forces lead, in the case of a homogeneous
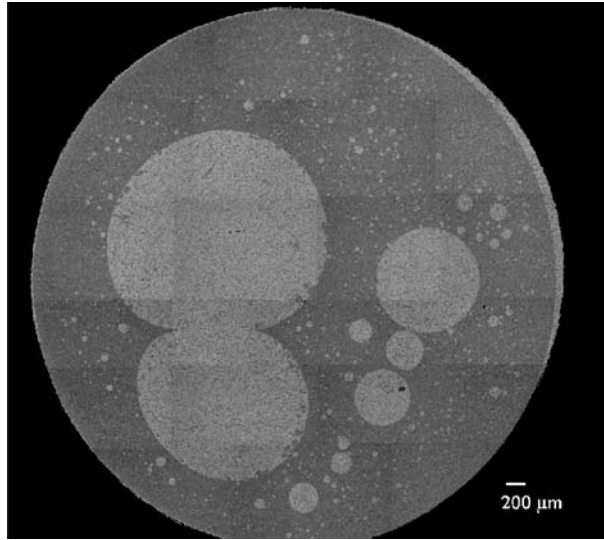
Figure 5 Microstructure of Co-40 wt%Cu sample processed in parabolic flight. Cobalt rich phase is dark, copper rich phase is bright. The sample is covered by a thin Cu-rich layer.
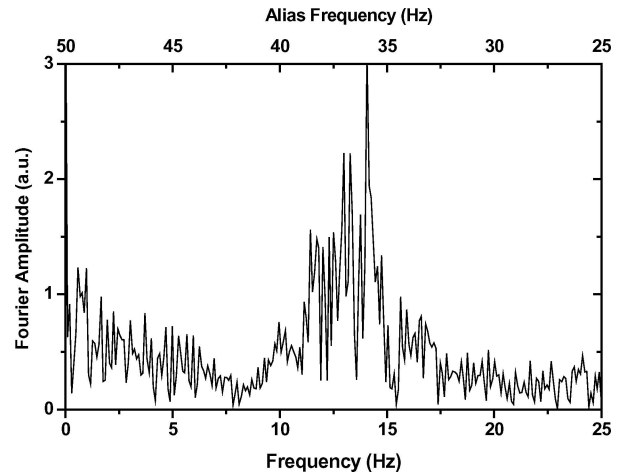

Figure 6 Oscillation spectrum of a liquid Co-40 wt%Cu sample processed in parabolic flight. Due to the low sampling rate, there is aliasing, and higher frequencies are folded back onto the low frequency range. The real frequency of the aliased peaks is shown on the top scale.

drop, to a splitting of the Rayleigh frequency into up to $2\ell + 1 = 5$ peaks and an additional shift of the mean frequency. We expect a similar behaviour for a compound drop, namely a splitting of both, ω_+ and ω_-, into up to 5 frequencies in the oscillation spectrum of such a drop. In fact, Brooks *et al.* have reported a frequency spectrum of 9 peaks for a levitated sample of a multi-component industrial alloy [17]. This complication can be avoided by performing the experiment under microgravity conditions, where both the gravitational and the electromagnetic field are negligibly small. In fact, such an experiment is planned in the framework of an ESA-project [18] for the International Space Station. A preliminary experiment was performed during a parabolic flight campaign [19]. A Co-40 wt%Cu sample of 0.8 g mass was positioned, melted and undercooled during app. 20s of microgravity. While in the liquid phase, the drop was subjected to short heating pulses which triggered oscillations. The oscillations were recorded by a standard CCD camera with 50 frames per second. Due to the short time available, a complete Ostwald ripening was not achieved, as shown in Fig. 5. The resulting liquid drop consists of several copper rich droplets inside a cobalt-rich host fluid. For such a case, we expect a frequency distribution instead of a single frequency ω_-, dominated by the radius distribution of the droplets. The frequency spectrum of the oscillation is shown in Fig. 6 as a function of the natural frequency $\nu = \omega/2\pi$. A broad peak is visible around 14 Hz. Due to the low sampling rate of the video camera, this peak is an alias of the real frequency which can be obtained by mirroring the spectrum around the sampling frequency: $\nu_{real} = 50 - \nu_{apparent}$. The real frequency is therefore around 36 Hz. This peak corresponds to ω_+, or, approximately, to the Rayleigh frequency ω_0, Equation 1. Inserting the mass of the drop into this equation, we obtain for the surface tension of the drop $\sigma_0 = 1.27$ N/m, in reasonable agreement with published data [13].

In order to estimate the position and strength of the second frequency, ω_-, we need to calculate τ. From

Equation 3 we obtain:

$$\tau^6 = 1 + \frac{M_{Cu}}{M_{Co}}\frac{\rho_{Co}}{\rho_{Cu}} \qquad (16)$$

Inserting the numerical values given above, and inserting Equation 16 into Equation 9, we get:

$$\nu_- = 0.47\nu_+ \approx 17 Hz \qquad (17)$$

Unfortunately, this region overlaps with the alias of the Rayleigh peak and can therefore not be evaluated. In view of the microstructure, Fig. 5, it seems unrealistic to expect a single peak anyway.

For the oscillation strength, Equation 15, we obtain

$$|a_{0-}| = \frac{1}{2\tau^2\sigma^2} \approx 0.16 \qquad (18)$$

If the cobalt core consisted of a single drop, the amplitude of this oscillation would be about 16% of the surface oscillation. As can be inferred from Fig. 6, the noise level in the frequency spectrum is about 10%, and this peak should be detectable. However, for incomplete demixing, the oscillation strength is spread over a broad frequency band, defined by the size distribution of the droplets, as stated above.

4. Summary

We have presented explicit expressions for the normal mode frequencies of a concentric spherical compound drop, which is the prevailing geometry under microgravity conditions. The dependence of these frequencies on the ratio between surface and interface tension was discussed, and the asymptotic behaviour for large values of this ratio was derived. Considering the eigenvectors of the normal modes it was shown that both frequencies can be determined from recording the oscillations of the (outer) radius of the compound drop. Preliminary results from an experiment with a Co-40 wt% Cu sample during parabolic flights were reported,

indicating that 20 s are insufficient for complete phase separation and ripening. For long duration experiments on board the ISS, the numerical estimates fo Co-Cu hint towards the feasibility of this concept.

Acknowledgement

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