Surface tension of undercooled liquid cobalt

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Abstract
This paper provides the results on experimentally measured and numerically
predicted surface tensions of undercooled liquid cobalt. The experiments
were performed by using the oscillation drop technique combined with
electromagnetic levitation. The simulations are carried out with the Monte
Carlo (MC) method, where the surface tension is predicted through calculations
of the work of cohesion, and the interatomic interaction is described with an
embedded-atom method. The maximum undercooling of the liquid cobalt
is reached at 231 K $(0.13T_m)$ in the experiment and 268 K $(0.17T_m)$ in the
simulation. The surface tension and its relationship with temperature obtained
in the experiment and simulation are $\sigma^{exp} = 1.93 - 0.000\,33\,(T - T_m)$ N m^{-1}
and $\sigma^{cal} = 2.26 - 0.000\,32\,(T - T_m)$ N m^{-1} respectively. The temperature
dependence of the surface tension calculated from the MC simulation is in
reasonable agreement with that measured in the experiment.

1. Introduction

Surface tension is a parameter of decisive importance in surface dynamics, which predicts the
actions in the surface, including the Marangoni convection that is the dominant mechanism of
convection under microgravity conditions in outer space, and the phase growth of undercooled
liquid in solidification that resolves the crystal microstructure. Over the years, lots of efforts
have been made to obtain surface tension data for liquid metals [1–3], while little has been
extended to the undercooled region.

In recent years, some advanced experimental technologies have been developed to
measure the surface tension of liquid metal, among which the oscillation drop technique using
electromagnetic levitation takes full advantage of the balance of the electromagnetic force
and gravity to avoid the contact of the sample with the container [4–7]. This measurement
technique is superior to other traditional contact methods in two respects. First of all, the
containerless state of the sample not only eliminates the impact of impurity from the container
wall, but also means that the liquid metal can possibly be undercooled to a high degree, in

which case data on surface tension for both normal and undercooled liquid can be obtained in one experimental process. Secondly, density data are not required to determine the surface tension in this method, thereby improving the accuracy of the data.

On the other hand, with the development of computer science, more researchers are attempting to calculate the thermophysical properties from the statistics of the micro-states for a large number of atoms. In recent years, Monte Carlo (MC) and molecular dynamics (MD) methods have been extensively adopted in many research fields, such as crystal microstructure, adsorption of gas on solid film, and composing proteins. In a MC or a MD simulation, the surface tension can be calculated either from the mechanical expression for the surface stress, or from the viewpoint of surface free energy. In the latter case, the cohesive work required to create a surface in bulk liquid can be directly calculated [8–10].

The aim of this paper is to investigate the surface tension and its temperature dependence for undercooled liquid cobalt by means of a MC simulation along with an experimental measurement using electromagnetic levitation technology. The surface tension is calculated through the work of cohesion, based on a potential of embedded-atom method (EAM) type.

2. Measurement method

The surface tension σ can be determined by measuring the frequency of surface oscillations ω. Provided that the droplet has spherical shape and the surface restoring force is due only to surface tension, σ for a droplet with mass M is related to ω by the Rayleigh equation [11]:

$$\sigma = \tfrac{3}{8}\pi M \omega_R^2. \tag{1}$$

However, under terrestrial levitation conditions, the sample is distorted from its perfect spherical shape owing to gravity and the existence of a strong magnetic field. As a result, the expected single Rayleigh frequency ω_R will shift and split into three to five peaks in the spectrum according to different levitation conditions. Cummings and Blackburn [12] considered the influence of a magnetic field on the split modes and derived the following frequency sum rule for obtaining the Rayleigh frequency:

$$\omega_R^2 = \tfrac{1}{5} \sum_{m=-2}^{m=+2} \omega_{2,m}^2 - 2\bar{\omega}_{tr}^2 \tag{2}$$

where m is the split mode and $\bar{\omega}_{tr}$ is the mean translational frequency of the droplet's centre of mass. Obviously, when all five peaks appear in the spectrum, the Rayleigh frequency and then the surface tension can be determined unambiguously from equation (2) without the assignment of split modes.

The samples of pure Co used in the experiments have a purity of 99.999%, and each sample has a mass of 0.8–0.95 g. Experiments were performed with an electromagnetic levitation facility, as shown in figure 1. A 30 kW high-frequency generator operating at 300–450 kHz is used as the power supply, and is connected to a conically shaped coil. The levitation coil is placed in a vacuum chamber, which is evacuated to less than 2.0×10^{-4} Pa and backfilled with a gas mixture of Ar, He, and H_2 in a ratio of 6:3:1. During experiments, the sample was levitated and melted by inductive heating. Then helium with the addition of 22.1% hydrogen, which flowed through liquid nitrogen, was blown toward the sample to achieve high undercoolings. When the sample was undercooled to an expected temperature, the flow rate of the blowing gas was adjusted to maintain this undercooling for 15–40 s. The temperature was recorded by an infrared pyrometer. During the measurement, the temperature had a fluctuation of 3–4 K. The surface oscillations were detected by a photodetector focused on the top view of the sample through a spectroscope. Having passed a low-pass filter with a
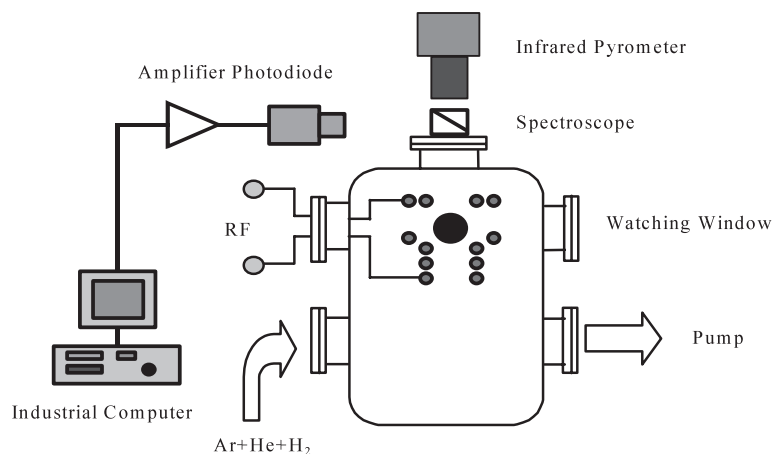
Figure 1. An illustration of the apparatus for measurement of surface tension of undercooled metals.
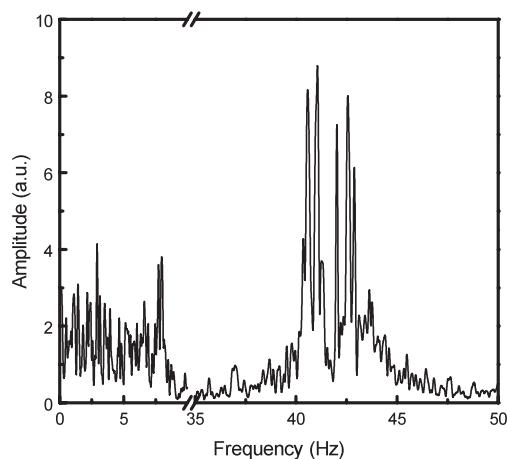
Figure 2. A typical oscillation spectrum of a levitated cobalt droplet after FFT.

threshold of 110 Hz and an amplifier, the signal was recorded with a sampling rate of 800 Hz to avoid aliasing. After analogue/digital conversion with a sampling rate up to 100 kHz, fast Fourier transformation (FFT) was performed off-line to obtain the oscillation spectra.

After signal processing, we obtain a frequency spectrum as shown in figure 2. The Rayleigh frequency splits into five clear peaks around 42 Hz, and the low-lying peaks correspond to the translational frequency. Such spectra are obtained at different temperatures. Using equation (2), the surface tension of the liquid metals can be determined.

3. Monte Carlo simulation

The MC method is based on a stochastic process which generates a Boltzmann-weighted chain of configuration of a given N-particle system by moving atoms randomly, as has been discussed in detail elsewhere [13]. The quantities of interest are obtained as configuration averages for the long chain generated.

Table 1. The model parameters: ϕ_e is in eV; f_e acts as a dimensionless scaling factor; α, β, and γ are dimensionless.

Atom	Model parameter					
	E_c	f_e	ϕ_e	α	β	γ
Co	4.43	0.49	0.33	5.52	5.26	21.0

3.1. Embedded-atom method

Daw and Baskes [14, 15] developed an empirical potential based on density functional theory known as the EAM potential. In the EAM, the energy of an arbitrary configuration of atoms is a unique function of the electron distribution, which is subdivided into embedding energies. That is, it is the sum of the energies required to 'embed' each atom into the local electron density derived from all other atoms, plus a short-range doubly screened pair interaction that accounts for the core–core repulsion. The total energy is taken as

$$E_{total} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{ij, i \neq j} \phi_{ij}(r_{ij}) \tag{3}$$

$$\rho_i = \sum_{j \neq i} f_j(r_{ij}) \tag{4}$$

where F_i is the energy for embedding atom i in an electron density ρ_i; ϕ_{ij} is a short-range pair interaction (core–core repulsion); r_{ij} is the separation of atom i and j; ρ_i is the total local electron density at atom i, computed as a superposition of the atomic electron densities of the rest atoms in the system; $f_j(r_{ij})$ is the atomic electron density of atom j due to atom i. The sums are over all atoms.

In his work [16], an analytic nearest-neighbour model for fcc metals developed by Johnson was adopted:

$$f(r) = f_e \exp[-\beta(r/r_{1e} - 1)] \tag{5}$$

$$\phi(r) = \phi_e \exp[-\gamma(r/r_{1e} - 1)] \tag{6}$$

$$F(\rho) = -E_c \left[1 - \frac{\alpha}{\beta} \ln\left(\frac{\rho}{\rho_e}\right) \right] \left(\frac{\rho}{\rho_e}\right)^{\alpha/\beta} - \Phi_e \left(\frac{\rho}{\rho_e}\right)^{\gamma/\beta}. \tag{7}$$

Here $\rho_e = 12 f_e$, $\Phi_e = 6\phi_e$, f_e, ϕ_e, α, β, and γ are model parameters. r_{1e} is the equilibrium nearest-neighbour distance in perfect crystal. All of the model parameters used [17] are listed in table 1.

### 3.2. Methods of surface tension calculation

Some statistical quantities such as the free energy and entropy cannot be obtained directly from a MC calculations, since these quantities cannot be expressed directly as ensemble averages. Therefore, simulation of the work of cohesion is employed in this paper to calculate the surface tension.

In figure 3, we show the process of producing two new interfaces from a pure liquid column with unit cross-section. This provides us with a possible approach for molecular simulation of surface tension [9]. For the separation process, it is necessary to know the quantity of heat entering the system to obtain equilibrium, Q (a quantity almost impossible to measure), and the entropy increase during the surface formation, S:

$$\Delta G = 2\sigma_A = W_{AA} + Q - TS. \tag{8}$$
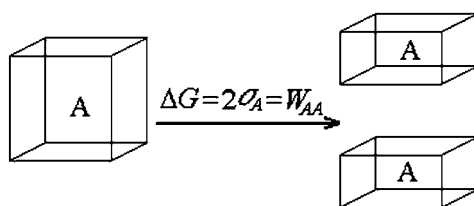
Figure 3. The process of producing two new interfaces from a liquid column.
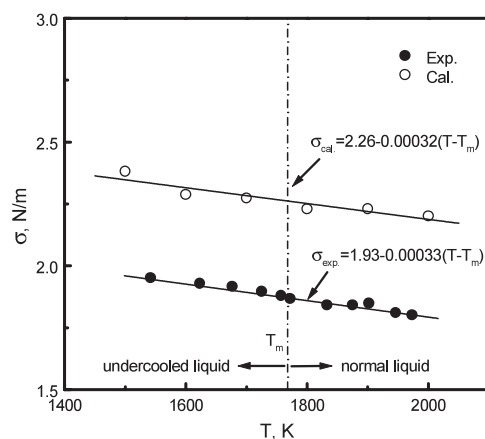
Figure 4. Comparison between the simulated and measured surface tensions of undercooled liquid cobalt.

However in the calculation of the surface tension, it was found to be reasonable to omit the last two terms in equation (8), implying that the quantities Q and TS are numerically equal and cancel each other. The quantity W_{AA} is known as the work of cohesion.

The simulation system is a cubic box with periodic boundary conditions. It is assumed that there exists an interface in the box, which is parallel to the x- and y-axes and perpendicular to the z-axis. Then the work of cohesion can be calculated through the statistics of the interaction between pairs of atoms on different sides of the interface.

4. Results and discussion

By using the electromagnetic levitation technique introduced above, the surface tension of pure cobalt was measured. Figure 4 presents the relationship between the surface tension and the temperature of pure liquid cobalt, where the experimental temperature ranges from 1541 to 1973 K. This means that a maximum undercooling of 231 K ($0.13T_m$) is achieved. The linear regression of the data is given as

$$\sigma_{Co}^{exp} = 1.93 - 0.000\,33\,(T - T_m)\,\text{N m}^{-1}. \tag{9}$$

From this relationship, it can be deduced that the surface tension of liquid cobalt at the fusion temperature 1768 K is 1.93 N m^{-1}, and its temperature coefficient of surface tension is 0.33 mN m^{-1}. This relationship is reliable for the undercooled liquid cobalt, because the surface contamination of the sample is decreased greatly in the containerless state. Owing to the lack of experimental data on the undercooled regime, comparison of the present study with

other investigations is limited to the temperature range above the melting point. Keene [18] collected some existing data and gave the mean σ–T relation as

$$\sigma_{Co} = 1.88 - 0.000\,34\,(T - T_m)\,\text{N m}^{-1}. \tag{10}$$

This is in good agreement with present experiment for the normal liquid state.

The MC simulation result on the surface tension for liquid cobalt is also illustrated in figure 4. In the calculation, the system starts in a $5 \times 5 \times 5$ lattice cubic box with a face-centred configuration; each basic lattice contains four atoms and the total number of atoms in the system is 500. Periodic boundary conditions are applied in the x-, y-, and z-directions. Simulations are carried out in NVT ensembles. In the computation of surface tensions at different temperatures, the densities of liquid cobalt at different temperature are determined from the relationship [19]

$$\rho_L = 7.79 \times 10^6 - 0.988 \times 10^3\,(T - T_m)\,\text{g m}^{-3}. \tag{11}$$

In order to achieve a completely equilibrated liquid phase, each simulation runs up to 5×10^5 MC steps, and generates 5.4×10^7 configurations. After achieving equilibrium in the system, 50 000 MC steps are used to calculate the surface tension and other properties of the system.

Figure 4 shows the simulated surface tension of liquid cobalt in the temperature range of 1500–2000 K. This corresponds to undercooling of 268 K ($0.15T_m$) and heating to 232 K above the melting point. According to these simulated results, the relationship between the surface tension of pure liquid cobalt and temperature is fitted as

$$\sigma_{Co}^{cal} = 2.26 - 0.000\,32\,(T - T_m)\,\text{N m}^{-1}. \tag{12}$$

The surface tension of liquid cobalt at the fusion temperature is 2.26 N m^{-1}, which is 17% larger than the experimental result. However, the temperature coefficient of surface tension is 0.32 mN m^{-1}, which is very close to the measured data.

The reason for the discrepancy between the simulated and measured surface tensions might be:

(1) The different external pressure. During the MC simulations, the external pressure of the system is zero from start to finish, while the environmental gases gave at least a 10^4 Pa external pressure in the measuring process.
(2) The metal purity of samples. In the simulation, the purity of liquid cobalt is 100%, which is completely impossible to realize in the experiment.
(3) The influence of oxidization in the experiment. During the experimental processing, the impurity of environmental gases and that of the samples result in the oxidization of the surface occurring very easily at high temperature, which leads to experimental errors.
(4) The potential function. Even the most successful potential function has an approximation to the real interaction between the metal's atoms.
(5) The limited particle numbers in the simulation. In the simulation, the particle number is an important parameter that influences the efficiency of the calculation.

The simulation time might increase exponentially with increase in number of particles. In this simulation, the effect of the limited size on the simulated result might cause some discrepancy.

5. Conclusions

Surface tension of pure liquid cobalt is measured with the oscillation drop technique using electromagnetic levitation. Meanwhile, it is predicted with a MC simulation, through the calculation of the cohesive work. On the basis of the experiment and the simulation, the

temperature dependence of the surface tension of undercooled liquid cobalt is determined; the results are $\sigma^{exp} = 1.93 - 0.00033\,(T - T_m)\,\mathrm{N\,m^{-1}}$ and $\sigma^{cal} = 2.26 - 0.00032\,(T - T_m)\,\mathrm{N\,m^{-1}}$, respectively. Within the temperature range covered by the experimental work, the dependence of surface tension on temperature is determined as $0.33\ \mathrm{mN\,m^{-1}}$, while the simulated temperature coefficient of surface tension is $0.32\ \mathrm{mN\,m^{-1}}$, which shows a reasonable agreement with the experimental result. However, the simulated surface tension shows a 20% overestimation when compared with the experiment. The discrepancy might arise from the potential model adopted in the simulation, the limited size of the simulated system, the oxidization and impurity of the sample, and the impurity of the environmental gases in experiments.

Acknowledgments

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