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978-0-521-88052-7 — High-Temperature Levitated Materials
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Excerpt
More Information

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Scientific and technological context

The present time appears appropriate for a monograph summarizing the current state of the art of investigation of high-temperature materials with levitation techniques. Although methods for levitating solid and liquid samples in a containerless environment have existed for the best part of the century – the patent for electromagnetic levitation dates back to 1923 – it is only in the past 20 years that their potential has been fully exploited by combining the levitation and heating aspects with new capabilities for structural and dynamic studies at synchrotron X-ray and high-flux neutron sources and refined techniques for thermophysical and transport property studies such as digital imaging, noncontact modulation calorimetry and electrodeless conductivity measurements. There has also been a rapid diversification in the types of levitation methods – aerodynamic, electromagnetic, electrostatic, and others – each of which have special advantages and disadvantages. The 2006 American Physical Society meeting in Baltimore, USA, featured a symposium of invited talks focusing on just one of these methods, electrostatic levitation combined with synchrotron X-ray studies.

Measurements of the structural, dynamical, thermophysical and transport properties of materials at high temperature are important in advancing condensed matter theory, in developing predictive models, and in establishing structure–property–process. Major experimental difficulties are encountered in obtaining reliable data on contained materials at temperatures above 1000 K owing to reactions of the samples with container walls and to the influence of the containers on scattering measurements. These problems are compounded when dealing with high-melting, corrosive liquids. A number of research groups around the world have overcome these difficulties by employing levitation techniques, eliminating container interactions and container-derived impurities and providing rapid access to high temperatures under controlled gaseous environments. Their results have not only advanced our understanding of high-temperature materials and phenomena but also provided important technological information, especially in the aerospace and semiconductor industries.

A special advantage of levitation techniques for high-temperature experiments is the reduction and, in favourable cases, virtual elimination of heterogeneous nucleation, so that normally inaccessible metastable states can be realized. These include not only substantially supercooled liquids – opening up new possibilities for exploring liquid–liquid phase transitions – but also metastable crystalline and glassy solid phases obtained on cooling from these liquids that were not previously available.

The arrangement of the book is quite transparent, starting with a brief description of some of levitation and heating techniques currently in use and proceeding to outline the concepts of the transport, thermophysical, structural and dynamic properties measurement and simulation techniques performed on high-temperature materials, particularly in the liquid state. The aim is to give the non-specialist reader sufficient background to appreciate some of the recent results discussed in the following chapters, devoted to liquid metals and alloys, molten semiconductors and molten oxides. The final chapter presents some subjective ideas on where this field may be heading.

The philosophy is to be illustrative rather than comprehensive, with some arbitrary choices of materials that seem interesting to the author. This applies especially to the chapter on metals and alloys, where an enormous body of research has been carried out with several levitation techniques. At the same time, earlier work on contained samples is included whenever it enhances our understanding.

2
Levitation methods

A variety of levitation techniques are available to the researcher to study high-temperature materials in the normal and supercooled states. The most widely practised techniques at the present time are aerodynamic levitation, in particular conical nozzle levitation (CNL), various kinds of magnetic levitation including electromagnetic levitation (EML), and electrostatic levitation (ESL). Other methods developed for specific applications such as acoustic levitation and gas-film levitation are less widely used and will be discussed only briefly.

In order for levitation to be useful in a scientific experiment, it is important not only to supply a force that can counteract the gravitational field but also to maintain the sample in a configuration that is sufficiently stable to allow the measurements to be performed. The issue of stability may be quite complex. A prime example is the Levitron®, a popular toy in which a spinning magnetic top is suspended above a flat surface of a magnetic material (http://www.levitron.com/). The levitating force is obvious, but the stability requires a complex physical analysis (Berry, 1996; Berry & Geim, 1997).

The variety of methods in current use suggests that each one has particular advantages and disadvantages, depending on the application in hand. CNL is a relatively simple and versatile technique and can be readily incorporated into different kinds of experimental apparatus. EML is restricted to conducting samples, generally metals, in which case relatively large samples (up to 1–2 cm diameter if desired) can be levitated. ESL has the advantage that samples can be held under vacuum, removing the possibility of contamination by a surrounding gas, or alternatively under controlled gas pressures up to a few atmospheres; on the other hand, it involves a relatively complex setup that makes it harder to use with certain spectroscopies. The principles of these techniques are described in the following sections.

2.1 Aerodynamic levitation

Like most of the techniques described in this chapter, aerodynamic levitation has a long history, with, for example, micrometre- to millimetre-sized water drops being studied in a wind tunnel in the late 1960s (Beard & Pruppacher, 1969). The most widely used technique of this kind employed today is CNL, based on the early work of Winborne *et al*. (1976) and Coutures *et al*. (1990) and on subsequent developments by Weber & Nordine (1995), in which a sample is levitated by gas flow in a convergent-divergent nozzle in which Bernouilli forces push it back to the axis of the nozzle. Stable levitated samples can then be heated to temperatures in excess of 2500 K with a laser or RF heating system.

A typical CNL system, developed at Containerless Research Inc. (CRI) in Evanston, Illinois, is schematically illustrated in Fig. 2.1. In the setup shown here the levitation system is combined with laser heating and integrated with an X-ray goniometer for diffraction experiments at a synchtrotron source, to be described in Chapters 6–8. The figure shows all of the key components including two pyrometers, two video cameras and video microscope, curved beryllium window, six-circle goniometer and X-ray detector. The levitation chamber is located at the centre of the goniometer. The heating laser is inclined at 15° with respect to the normal to avoid physical interference with the X-ray detector.

The nozzle and plenum chamber assembly are supported on three tubes connected to three flexible bellow feed-throughs. Two of these tubes circulate water for nozzle cooling, while the third supplies the levitation gas that feeds into the nozzle's plenum chamber. The CNL system is enclosed in an

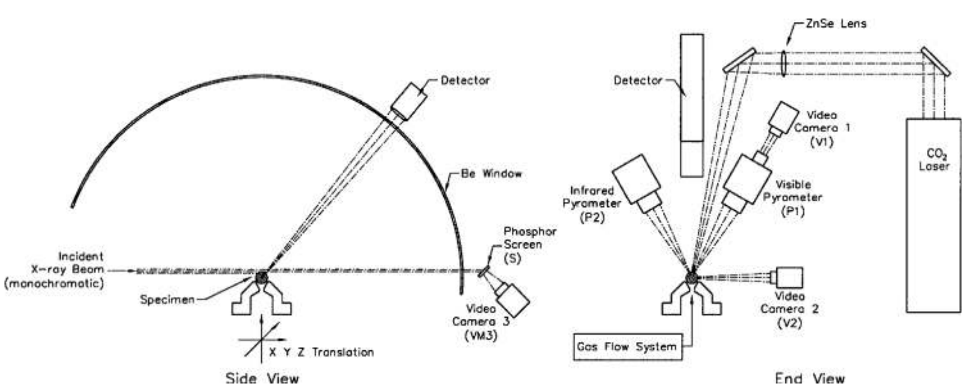

Fig. 2.1. Schematic view of CNL apparatus used by the CRI–Argonne team for measurements of liquid structure, showing two pyrometers (P1, P2), two video cameras (V1, V2) and video microscope (VM3), curved beryllium window, six-circle goniometer and X-ray detector (Krishnan & Price, 2000).

environmentally controlled chamber with suitable ports for laser heating, pyrometry, sample injection and retrieval, and pressure measurements. The upper part of the chamber is a 23-cm diameter sphere. Two beryllium windows are included in this section: a small window for the incident X-ray beam and a larger curved window, approximately 8 mm wide and 0.127 mm thick, subtending an angle of approximately 120° around the nominal sample position at the centre of the chamber. This window extends to about 5° below the normal height of the levitated sample, so that the transmitted part of the direct X-ray beam can pass through.

The gas flow to the CNL system is regulated by electronically controlled mass flow controllers. The chamber is connected to a vacuum system that permits evacuation to about 10^{-5} bar followed by a back-fill with a purified inert gas or other special environment when required. A servo-controlled exhaust throttle valve, placed between the pump and the chamber, enables control of the chamber pressure in the range 0.1–0.8 bar during levitation. The samples are heated with the aid of a 270-W CO_2 laser and the sample temperature is measured with two pyrometers operating at wavelengths of 0.65 and 1–2.5 μm, respectively. Precise sample positioning is achieved by moving the nozzle assembly with a three-axis motorized translator and using a phosphor screen to observe the shadow of the sample in the X-ray beam. Samples can be levitated, heated, melted and positioned stably for up to 3 h with this system.

The condition for levitation is derived from the law of momentum conservation applied to a control volume that contains the sample:

$$\iint \left[\frac{1}{2} \rho u^2 + p \right] dA = Mg, \tag{2.1}$$

where ρ, u and p are the gas density, vertical gas flow velocity and gas pressure, respectively, and Mg is the sample weight. The integral is performed over the surface A of the control volume.

Free-jet and conical nozzle levitation differ in the magnitude of the two components on the left side of Eq. (2.1). Stable free-jet levitation occurs when the gas flow is sufficient to form a free jet with a momentum flow rate equal to about twice the sample weight. Stable levitation in a conical nozzle occurs when the momentum flow is less than the sample weight, and the levitation results mainly from pressure differences over the sample surface. The pressure differences are a small fraction of the total pressure: for example, a 3-mm diameter sphere of liquid aluminium oxide is levitated when the pressure difference across the sample is approximately 0.001 bar, or about 0.1% of the total pressure at one atmosphere.

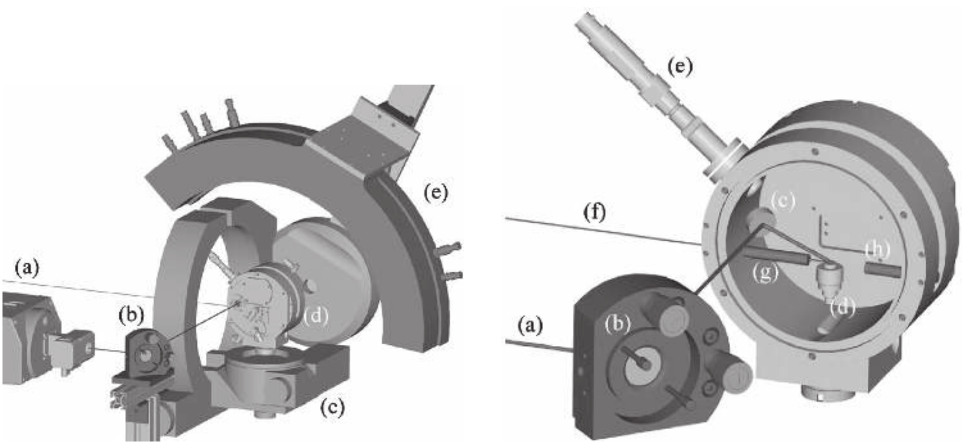

Fig. 2.2. Left: schematic view of the CNL arrangement used by the CRMHT group for measurements of liquid structure, showing the laser head (a), first mirror (b), goniometer (c), high-temperature chamber (d), and curved X-ray detector (e). Right: detailed view of the high-temperature chamber showing the laser beam (a), focusing mirror (b), flat mirror (c), levitator (d), pyrometer (e), X-ray beam (f), X-ray collimator (g) and direct beam stop (h) (Hennet *et al.*, 2002).

For most experiments the chamber is initially pumped down to low pressure and then purged for short durations by flowing through an inert gas such as argon. The chamber is then filled with the gas and maintained at the desired pressure by controlling the throttle valve. Typical flow rates used for metals at 0.4 bar vary from 150 to 600 STP $cm^3\ min^{-1}$. For experiments on metals, UHP argon is generally employed as the levitation gas, and for experiments on ceramics, air, oxygen, nitrogen or a nitrogen/hydrogen mixture can be used.

A CNL system developed independently at the Centre de Recherche sur les Matériaux à Hautes Températures (CRMHT, now CEMHTI) in Orléans, France, is shown in Fig. 2.2. The basic components are similar to the CRI setup shown in Fig. 2.1, but the geometry is somewhat different. This type of arrangement was first used for NMR experiments and subsequently for EXAFS measurements on molten ceramics, to be described in Chapter 8.

One of the drawbacks of the CNL method is that samples have temperature gradients between the laser-beam-heated top of the sample and the bottom of the sample where the cold levitation gas first impinges. Based on observations with the optical pyrometer and the observed maximum undercooling for well-known materials, this difference was estimated to be about 25 K for liquid metals and on the order of 50–75 K for liquid oxides due to their reduced thermal conductivities. The advantage of X-ray diffraction in this context is that the scattering takes place from the region of the sample whose temperature is measured by pyrometry. Temperature gradients become more serious, however, for neutron diffraction and NMR experiments and for X-ray measurements when the X-ray energy becomes sufficiently high to penetrate the interior of the sample. A setup recently developed by the CRMHT group for neutron diffraction experiments (Hennet *et al*., 2006) incorporates a second laser heating the sample from below through a small hole in the conical nozzle in order to reduce temperature gradients.

While the CNL technique appears to have been first used for scientific experiments in the 1970s, the basic aerodynamic principle – the Bernouilli effect – was of course already well known. Paradis *et al*. (1996), who made a detailed study of nozzle behaviour in both terrestrial and microgravity environments, point out that the corresponding hydrodynamic effect was employed in fire hoses early in the twentieth century. Waltham *et al*. (2003) describe a system in which air is blown vertically downwards through a hose that exits in a flat horizontal sheet. Another sheet brought up to the orifice is held in place despite the fact that the air is pushing downwards. The acceleration of the air in the gap causes a drop in pressure that more than compensates for the high pressure in the hose. Weights of 2 kg can be suspended in this way.

The past 30 years have seen a continual improvement in design of the nozzle for CNL, principally by the CRI and CRMHT groups whose systems have just been described. Because of the simplicity of the method, it can be readily combined with other types of apparatus, for example a secondary levitation apparatus, different types of heating or rapid cooling, and probes of structural or physical properties. These cases will be discussed in the chapters that relate to these specific aspects.

2.2 Electromagnetic levitation

'Magnetic levitation' is a general term that can comprise several distinct techniques, in which either:

(a) an inhomogeneous electromagnetic field is generated in a radio-frequency (RF) coil and induces eddy currents in the sample; these interact with the applied magnetic field via a Lorentz force that counteracts gravity; this clearly depends on a significant electrical conductivity in the sample;
(b) a large inhomogeneous magnetic field is generated in a magnet, either conventional or superconducting, and induces a magnetic moment in the sample that

interacts with the applied field; either diamagnetic or weakly paramagnetic samples can be levitated; or

(c) a magnetic field is generated in a magnet, generally a permanent magnet, and induces an electric current in a superconducting sample; this interacts with the applied field via a Lorentz force as in (a).

For convenience we will refer to these three methods as (a) electromagnetic levitation, (b) magnetic levitation and (c) superconducting levitation, although other terms are frequently used in the literature. The three methods are discussed in turn in the present and following two sections.

At this point it is helpful to introduce expressions based on the quasistatic approximation of electrodynamics, valid when the wavelength of the electromagnetic radiation is much greater than the sample size and its frequency is smaller than the relaxation time of the current carriers. Following Enderby *et al*. (1997), we consider an isotropic conducting nonmagnetic sphere of radius a and conductivity σ suspended in a uniform periodic external magnetic field of angular frequency ω. The magnetic response is mainly due to the conduction currents set up in the sphere and can be characterized by a complex susceptibility given by

$$\alpha = \alpha' - i\alpha''. \tag{2.2}$$

The real part is given by

$$\alpha' = -2G\left(\frac{a}{\delta}\right), \tag{2.3}$$

the parameter δ is the skin depth given by

$$\delta = \sqrt{\frac{2}{\omega\mu\mu_0\sigma}}, \tag{2.4}$$

where μ_0 is the magnetic permeability of free space and μ is the relative permeability of the material, and the function G is given by

$$G(q) = \frac{3}{4}\left[1 - \frac{3}{2q}\frac{\sinh(2q) - \sin(2q)}{\cosh(2q) - \cos(2q)}\right]. \tag{2.5}$$

For typical values of $\sigma = 10^4\ \Omega^{-1}\,\mathrm{cm}^{-1}$, $\mu_0 = 1.25\mu\Omega.\mathrm{s.m}^{-1}$ and frequency $\omega/2\pi = 300$ kHz, the skin depth δ is 0.92 mm. The imaginary term in the susceptibility is given by

$$\alpha'' = H\left(\frac{a}{\delta}\right), \tag{2.6}$$

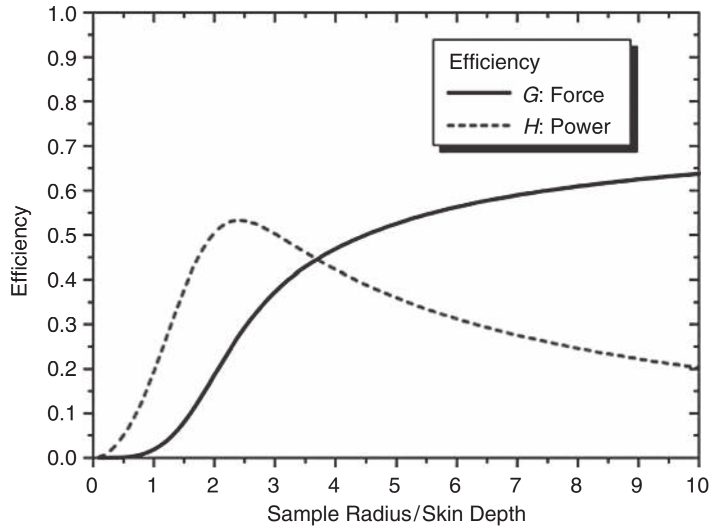

Fig. 2.3. Efficiency of levitation force and inductive heating power as a function of the ratio of sample radius to skin depth (Mathiak *et al*., 2005).

where the function H is given by

$$H(q) = \frac{9}{4q^2}\left[q\frac{\sinh(2q) + \sin(2q)}{\cosh(2q) - \cos(2q)} - 1\right]. \tag{2.7}$$

The dimensionless functions $G(q)$ and $H(q)$ are plotted in Fig. 2.3.

We now proceed to discuss EML, which is one of the oldest techniques used for containerless experiments. The method was patented by Muck (1923) and developed further in the 1950s (Okress *et al*., 1952). The Lorentz force that can act to counteract gravity can be expressed, to lowest order in a multipole expansion, as (Jacobs *et al*., 1996)

$$F = -\frac{\nabla B^2}{2\mu_0}\frac{4\pi}{3}a^3 G\left(\frac{a}{\delta}\right). \tag{2.8}$$

The sample to be levitated is positioned in a potential well generated by the electromagnetic (e-m) field **B**. Accordingly, the sample will perform oscillations about its equilibrium position with a frequency that is determined by the spring constant of the field and its mass. In addition, liquid samples will display free surface oscillations with a restoring force due to the surface tension. In particular applications it may be important to design the setup to minimize both types of motion (Jacobs *et al*., 1996). On the other hand, it may be useful to study these oscillations to derive information about the

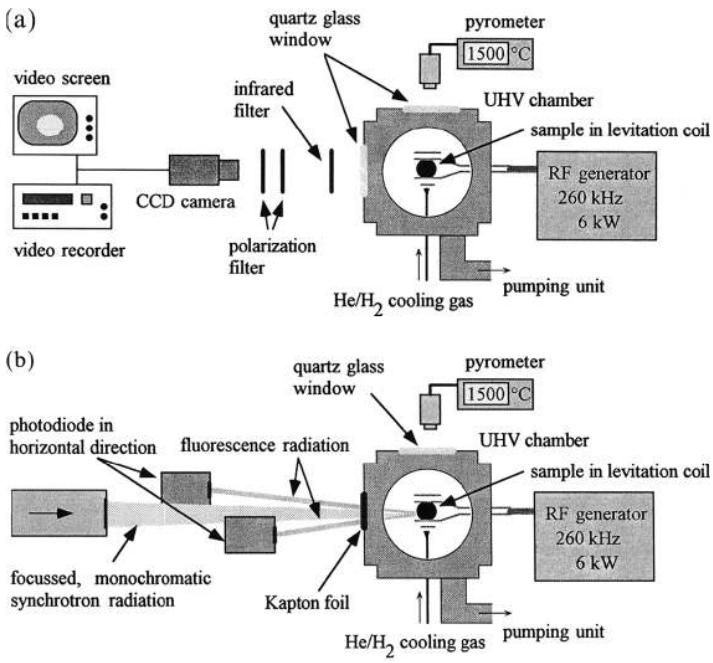

Fig. 2.4. Schematic view of EML apparatus used by the DLR (Germany) group for (a) optical measurements to determine sample density and (b) fluorescence radiation measurements in an X-ray beam to obtain EXAFS spectra (Jacobs *et al.*, 1998).

physical properties of the levitated sample. Investigations of this kind will be discussed in Chapter 6.

A typical EML apparatus, developed by the group at the Institut für Raumsimulation, Deutsche Forschungsanstalt für Luft- und Raumfahrt (DLR) in Cologne, Germany, is shown in Fig. 2.4. Two setups are shown, (a) for optical measurements to determine the sample density and (b) for fluorescence radiation measurements in an X-ray beam to obtain EXAFS spectra. The levitation coil, fed by an RF generator with 260-kHz frequency and 6-kW power, is built into a vacuum chamber that is equipped with quartz windows in setup (a) and Kapton® windows in setup (b). The temperature is measured by a pyrometer viewing the sample from above through a quartz window from the top of the chamber and is controlled by a variable flow of cooling gas, making it possible to maintain a constant sample temperature for several hours.

EML apparatus was also developed in the group of the late J. L. Margrave at Rice University and subsequently at CRI for measurements of the optical properties of liquid metals, to be described in Chapter 6 (Krishnan *et al.*, 1993; Krishnan & Nordine, 1993).