

# Atomic dynamics and Marangoni films during liquid-metal spreading

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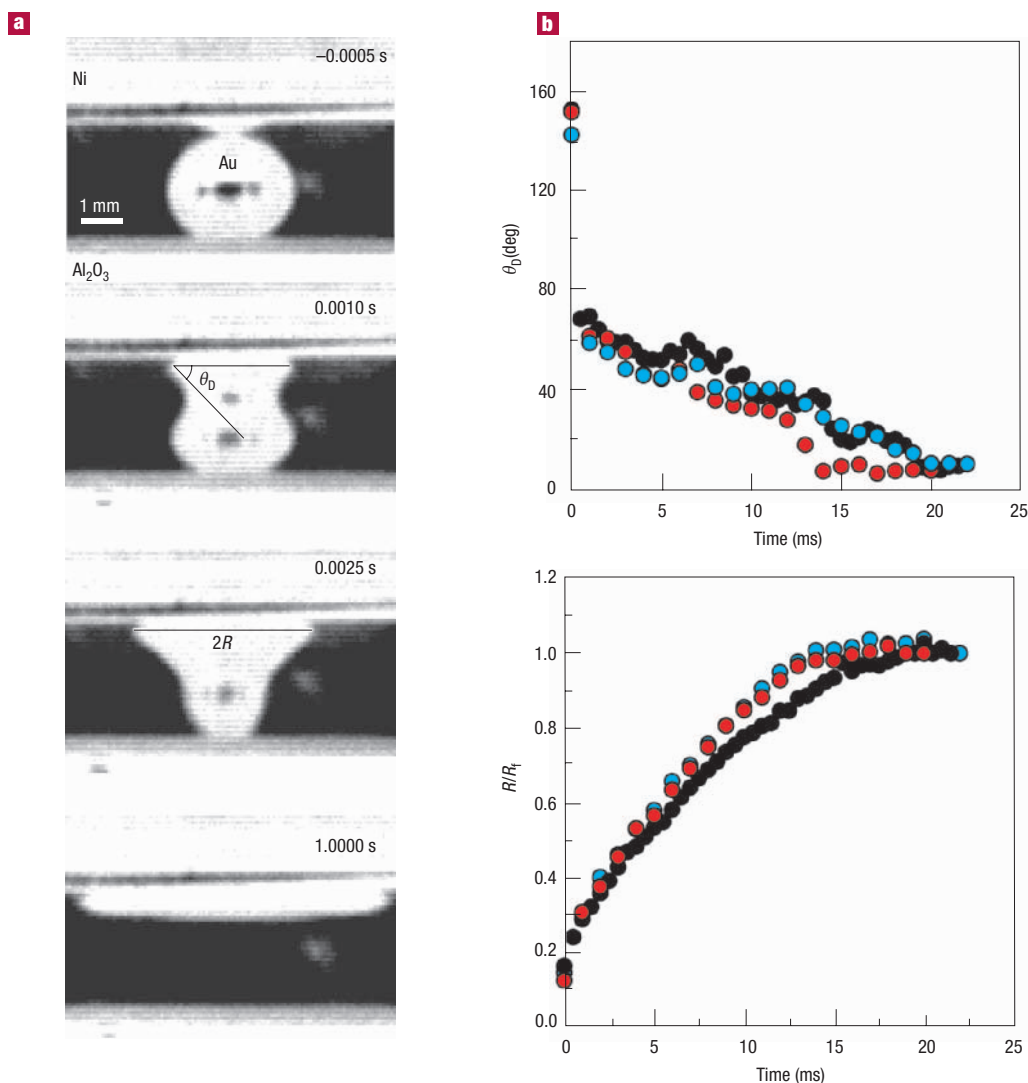
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Published online: 14 November 2004; doi:10.1038/nmat1252

Despite its apparent simplicity, spreading of liquid metals at high temperatures has defied description and generalization. Wetting at high temperature is usually accompanied by interdiffusion and chemical reaction, but the forces that drive reactive spreading and the mechanisms that control its kinetics have been very poorly understood. The unsolved challenge has been to link macroscopic measurements such as the dynamic contact angle or the speed of a moving liquid front to phenomena occurring at the microscopic and even atomic level in the vicinity of the triple solid–liquid–vapour junction. We have taken a big step towards meeting this challenge. Our systematic analysis of the spreading of metal–metal systems with varying degrees of mutual solubility allows us to report on the fundamental differences between the mechanisms controlling spreading of organic liquids and liquid metals and on formation of Marangoni films driven by surface-tension gradients in high-temperature systems.

The spreading of liquid metals plays a key role in many modern technologies such as brazing, soldering, thin films, microelectronics, optical and optoelectronic technology, and many others. As a consequence, there is a wealth of empirical data on high-temperature spreading. However, the reported results are inconsistent and very often contradictory. For example, the reported times for the spontaneous spreading of small metal drops range from milliseconds (as can be expected from a comparison with organic liquids of similar viscosity) to minutes and even longer<sup>1–7</sup>. Additionally, in low-temperature systems, there is ample evidence of the existence of two types of thin liquid film that, under certain circumstances, can extend ahead of the main liquid front. In systems with complete wetting (when the final contact angle is 0°), a precursor wetting film a few nanometres thick can extend ahead of the drop during spreading, and if gradients in the surface tension of the liquid develop (due, for example, to temperature gradients or evaporation of a volatile component) the resulting Marangoni stresses can also drive the formation of liquid films typically hundreds of nanometres thick<sup>8–11</sup>. Surprisingly, however, in high-temperature systems there is a lack of evidence of the existence of precursor or Marangoni-driven films. The root of the problem is the difficulty in designing high-temperature experiments in which spreading can be recorded under precisely controlled conditions.

The theoretical analysis of liquid-metal spreading is also challenging. There is no established theory formulating the driving forces for the spreading of reactive liquids, and our latest high-temperature data clearly contradict the prevailing idea that high reactivity enhances spreading<sup>12</sup>. Similar uncertainty exists regarding the main dissipation mechanisms during the spreading of high-temperature liquids. Current theories have identified two main sources of dissipation during spreading: viscous impedance and local dissipation at the triple line. It has been proposed that, except in cases of large angles and fast-spreading velocities, viscous dissipation is the controlling mechanism<sup>13</sup>. However, this may not be true for liquid metals, whose interatomic forces and, consequently, interfacial energies are much greater than those of organic liquids. Additionally, at high temperatures the substrate can no longer be considered as an ideal solid that is perfectly rigid and insoluble because the elevated experimental temperatures allow for some local diffusion or dissolution<sup>5,14</sup>.



**Figure 1** Spontaneous spreading of small metal drops. **a**, Series of photographs showing the transfer of a liquid gold drop from an aluminium oxide substrate (in the bottom) where it exhibits a large contact angle to a Ni substrate approaching from the top. **b**, Variation with time of the contact angle ( $\theta$ ) and of the normalized droplet radius (the radius divided by the final value,  $R_i$ ) for small Au drops spreading on a Ni substrate. Different colours correspond to different experiments. Spreading occurs in a few milliseconds. This is faster than typically observed for spontaneous spreading of small drops of organic liquids at room temperature. From fluid-flow considerations, this can be expected due to the larger surface energy of the liquid metals (typically 1 to 3 orders of magnitude larger). Also, in the molecular-kinetic model, liquids with larger surface energy should spread faster if the wetting activation energies are similar. The final contact angles recorded for the different systems range as follows:  $110^\circ$  for Cu-Nb;  $20\text{--}30^\circ$  for Ag-Mo, Ag-1%Mo/Mo, or Ag-W; and  $\sim 0^\circ$  for fully miscible systems (Ge-Si, Cu-Ni, Au-Ni, 82Au18Ni-Ni). All the experiments were done in flowing Ar-5% $\text{H}_2$  ( $p(\text{O}_2) < 10^{-23}$  atm) to avoid metal oxidation.

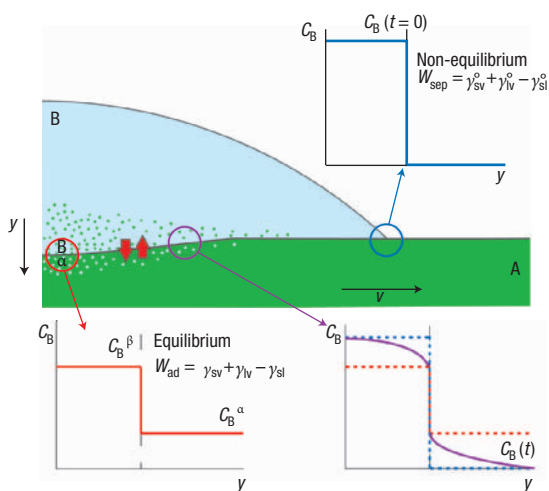
Despite these difficulties, there are great benefits to solving these problems, such as aiding in the theoretical analysis of non-equilibrated interfaces and developing new technologies with smaller relevant dimensions that will require a higher degree of spreading control. At this stage, a unifying approach describing the dynamics of high-temperature wetting is still missing, but our laboratory has recently achieved great progress in this direction. This work provides seminal ideas and data needed to raise the underlying physics of high-temperature spreading to the sophisticated level of knowledge already achieved for low-temperature systems. This article discusses these unique results.

#### DYNAMICS OF LIQUID-METAL SPREADING

A novel drop-transfer setup has been used to study the spontaneous spreading of liquid-metal drops in metal-metal systems with different

degrees of mutual solubility<sup>6</sup>. The systems vary from couples with low mutual solubility and slow dissolution kinetics (Ag-Mo, Ag-W) to fully miscible systems (Cu-Ni, Au-Ni, Ge-Si). All the metal drops spread to a stationary angle in 10 to 30 milliseconds (Fig. 1), unlike most of the data reported in the literature, where spontaneous spreading took minutes or longer<sup>1-6</sup>. Systems with low solubility typically reach finite contact angles, whereas the values for fully miscible systems are close to  $0^\circ$ . All the recorded velocities for liquid metals fall into a narrow band independent of their mutual solubility. The maximum spreading velocities are of the order of  $1 \text{ m s}^{-1}$  for all systems. These fast velocities and normalized behaviour are consistent with a liquid front spreading on a flat substrate<sup>5</sup>.

There are no theoretical models specifically developed for high-temperature systems, but in principle the spreading of liquid metals and organic fluids are quite similar. Therefore, we have compared our data to existing theories that try to establish a correlation between



**Figure 2** Schematic depicting the fast spreading of a liquid on a substrate with mutual solubility. An instantaneous driving force for spreading can be calculated if non-equilibrium interfacial energies can be defined that correspond to the phase composition at the triple line. The composition at the triple line depends on the relative speeds of spreading and interdiffusion. The figure shows a simplified schematic for spreading in systems with limited mutual solubilities when the velocity of spreading is much faster than interdiffusion and the pure phases A and B are in contact close to the triple line. The concentration profile of element B as we move from the liquid to the solid across the interface between the pure phases is represented by the blue line. In this case, the associated non-equilibrium interfacial energies are related to the work of separation ( $W_{\text{sep}}$ ). Far behind the triple junction, enough interdiffusion has occurred for the equilibrium concentrations to be observed across the interface (as it is represented by the red line with  $\alpha$  and  $\beta$  being the saturated phases in equilibrium) and the corresponding interfacial energies can be used to calculate the thermodynamic work of adhesion,  $W_{\text{ad}}$ . Intermediate situations will exist that result in a concentration gradient varying from equilibrium values close to the interface to the pure phases as we move away from it (purple curve).

the velocity of the liquid front and the observed dynamic contact angle. Essentially, two different approaches exist: hydrodynamics and molecular kinetics<sup>13,15–18</sup>. Hydrodynamic treatments cannot elucidate the local wetting mechanisms and instead focus on conditions where the main source of dissipation is the viscosity in the bulk liquid drop. In systems with complete wetting, where a precursor film is present, the viscous dissipation in the film could be the main source of dissipation<sup>19</sup>. Molecular kinetic models concentrate on the local dissipation that occurs in the immediate vicinity of the triple line. In all cases, it is assumed that the capillary forces are the main forces driving the liquid towards a constant curvature shape, and the contact angle towards the one defined by the well-known Young's equation.

According to the hydrodynamic approach, the spreading behaviour of different liquids can be described in terms of a normalized relationship between the dynamic contact angle and the capillary number,  $Ca = v\eta/\gamma_{\text{lv}}$  ( $v$  is the velocity of the triple junction,  $\eta$  the liquid viscosity and  $\gamma_{\text{lv}}$  is the liquid surface tension). Cox and Voinov<sup>16,20,21</sup> proposed the following relationship:

$$Ca = \frac{1}{9\ln\left(\frac{L}{L_s}\right)} (\theta_D^3 - \theta_0^3) \quad (\theta_D \leq 135^\circ) \quad (1)$$

$$Ca = \frac{1}{9\ln\left(\frac{L}{L_s}\right)} \left[ \frac{9\pi}{4} \ln\left(\frac{1 - \cos\theta_D}{1 + \cos\theta_D}\right) + (\pi - \theta_D)^3 - \theta_0^3 \right] \quad (\theta_D \geq 135^\circ) \quad (2)$$

where  $\theta_0$  is the static, equilibrium contact angle,  $L$  is a characteristic capillary length, and  $L_s$  is the slip length;  $L_s$  corresponds to a thickness of the meniscus immediately adjacent to the solid wall over which the 'no-slip' boundary condition of classical hydrodynamics is relaxed to avoid a singularity at the triple junction. The parameters controlling the magnitude of the slip length are still largely unknown, but most hydrodynamic analysis of low-temperature data will result in a slip length of microscopic but measurable dimensions (typically between 1 and 100 nm)<sup>16,20,22</sup>.

Blake<sup>17</sup> developed a molecular-kinetic model that extends Eyring's theory of reaction rate processes<sup>23</sup> to spreading. It assumes that molecules of an advancing fluid displace the molecules of a receding one on adsorption sites on a solid surface. As a result, the following equation relating the capillary number and the dynamic contact angle can be written:

$$Ca = \frac{2\eta\lambda kT}{h\gamma_{\text{lv}}} e^{-\frac{\Delta G_w}{NkT}} \left[ \sinh\left(\frac{\lambda^2\gamma_{\text{lv}}}{2kT} (\cos\theta_0 - \cos\theta_D)\right) \right] \quad (3)$$

where  $\lambda$  is the average spacing between adsorption sites,  $k$  and  $h$  are the Boltzmann and Planck constants respectively, and  $\Delta G_w$  is a free energy for wetting that derives mainly from the solid–fluid interactions.

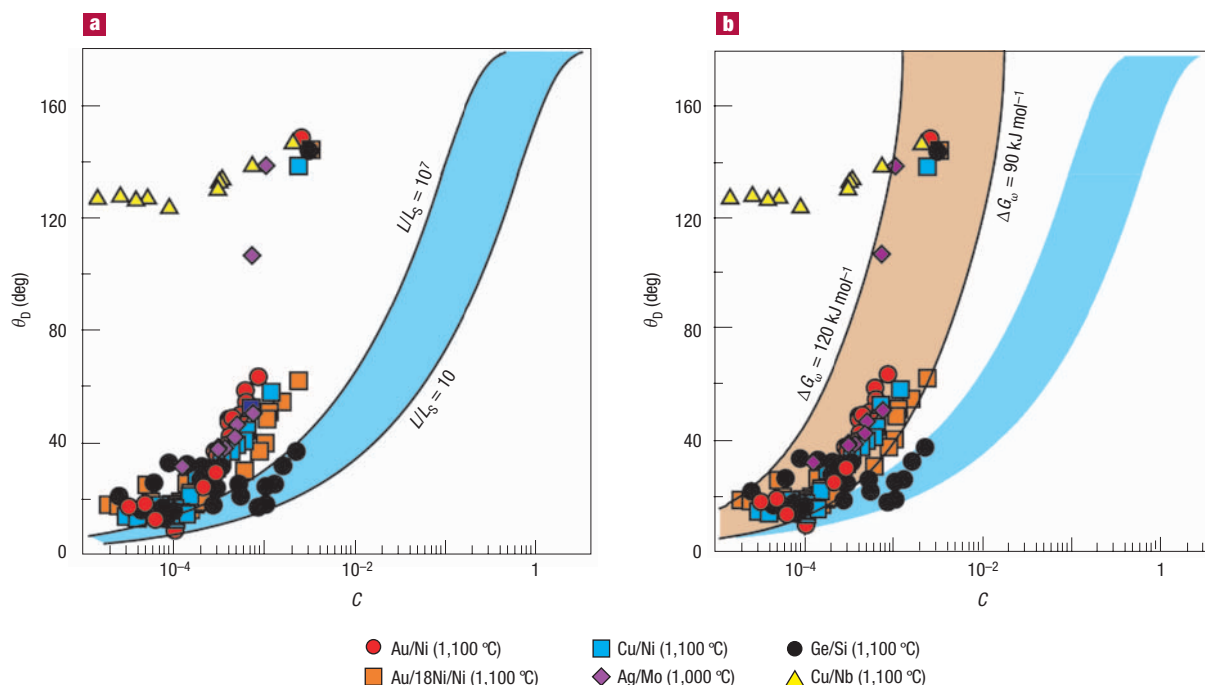
Both models have been developed for non-reactive liquids spreading on an ideally rigid and insoluble flat substrate. In order to extend their use to reactive systems, the instantaneous forces that drive the spreading of a reactive liquid should be defined in terms of a contact angle  $\theta_0$ . We propose that this could be done by defining, at a given instant of spreading, a set of "interfacial energies" that will correspond to the non-equilibrium interfaces present in the close vicinity of the triple junction.

In the case of two phases (A and B) with mutual solubility, a hypothetical experiment can be done in which the two pure phases are placed together without allowing interdiffusion and then separated without allowing mutual adsorption<sup>24–26</sup>. The necessary work, that of separation,  $W_{\text{sep}}$ , can be defined as:

$$W_{\text{sep}} = \gamma_A^0 + \gamma_B^0 - \gamma_{AB}^0 \quad (4)$$

where  $\gamma_A^0$ ,  $\gamma_B^0$  are the surface energies of clean A and B surfaces and  $\gamma_{AB}^0$  is a non-equilibrium interfacial energy that corresponds to the interface between the pure phases. If spreading is fast enough, such that there is no time for adsorption or interdiffusion close to the triple line, the driving force for spreading is determined by the  $\gamma^0$  values that can be used to calculate the corresponding  $\theta_0$  (Fig. 2). Intermediate situations are also possible, and as spreading decelerates, dissolution of the substrate can continuously change the liquid composition close to the triple junction, resulting in a variation of the driving force that should be taken into account when developing a detailed model. Additionally, the continuous dissolution of the substrate can change the composition of the liquid until it eventually solidifies, thereby 'freezing' the spreading front.

Both models can reproduce the experimental data obtained in this work relatively well using a constant value of  $\theta_0$ . Final angles larger than  $0^\circ$  are reached in systems with limited solubility (Cu–Nb, Ag–Mo, Ag–W). These angles are similar to those obtained by fitting the data with equations (1–2) or (3). Furthermore, the final angles reached by pure silver on Mo and by saturated Ag–Mo liquids on Mo (the latter being in equilibrium) are very similar. These results suggest that in systems with limited mutual solubility, relatively small differences can be expected between  $\gamma^0$  and  $\gamma^{\text{eq}}$ . On the other hand, in systems with a large mutual solubility (for example, Au–Ni, Cu–Ni or Ge–Si), the final contact angles are close to  $0^\circ$  and the fitting of the spreading data typically results in  $\theta_0 < 0$  when using equation (1), or equivalently,  $\cos(\theta_0) > 1$  for the molecular kinetic model, equation (3). This is equal to a positive spreading coefficient ( $S = \gamma_{\text{sv}}^0 - \gamma_{\text{vl}}^0 - \gamma_{\text{sl}}^0$ ) and is consistent with a large driving force for spreading or a very low



**Figure 3** Comparison of the spreading kinetics of liquid metals to different models. **a**, Spreading kinetics for different metal–metal systems. Each curve represents the average of at least three experiments. It can be observed that the data (in particular the maximum recorded speeds) fall well off the expected region for fluid-flow controlled spreading (the fluid flow curves have been calculated using  $\theta_0 = 0^\circ$ ,  $L = 1$  mm and  $1 \text{ \AA} \leq L_s \leq 100 \text{ \mu m}$ ). **b**, Curves representing the expected molecular-dynamic controlled spreading (equation (3)) for a liquid with  $\gamma_v = 1 \text{ J m}^{-2}$ ,  $\lambda = 2 \text{ \AA}$ ,  $\theta_0 = 0^\circ$ , a temperature of 1,373 K and  $90 \leq \Delta G_w \leq 120 \text{ kJ mol}^{-1}$  are plotted for comparison. Corrections due to the different liquid surface energies and small variation of  $\lambda$  will only slightly alter the curve in the logarithmic scale. However, the curve is extremely sensitive to the wetting activation energy. Freezing of the liquid due to substrate dissolution or ridge-like events at the triple junction can lead to an abrupt stop of spreading when the angles approach the stationary value and the velocity of the liquid front decelerates. For the Ag–Mo or Ag–W systems, there is not an appreciable dissolution of the substrate. It should be pointed out that, even at the lower angles, in most cases the experimental data lies above the fluid-flow band.

solid–liquid interfacial energy. Computer calculations of solid–solid interfaces, for which even negative interfacial energies are obtained in fully miscible systems, show similar trends<sup>26</sup>. Reasonable fittings can be obtained using a constant  $\theta_0$ , which reinforces the hypothesis that spreading is fast when compared with dissolution, and that the triple junction consists of pure liquid moving on a flat substrate during most of the process.

It has already been observed in many low-temperature systems that both the hydrodynamic and molecular-kinetic models can adequately fit the experimental data. Therefore, the best way to determine the validity of each model is to analyse the physical implications of the fitting parameters. The hydrodynamic fitting results in a value of  $L_s \approx 0$ . The recorded spreading speeds are orders of magnitude slower than expected for finite values of  $L_s$  (Fig. 3).  $L_s \approx 0$  implies that other sources of energy dissipation within the three-phase region are controlling the spreading kinetics<sup>27,28</sup>. On the other hand, if the distance between adsorption sites is set to be of the order of interatomic distances ( $\sim 1\text{--}3 \text{ \AA}$ ), a good fitting of the data can be obtained using equation (3) and the wetting activation energies are of the order of  $10^2 \text{ kJ mol}^{-1}$  (Fig. 3). The activation energies are two to three orders of magnitude higher than activation energies reported for viscous flow in metals ( $\sim 1\text{--}10 \text{ kJ mol}^{-1}$ )<sup>23</sup>, and lower than reported desorption energies for metal–metal systems ( $300\text{--}900 \text{ kJ mol}^{-1}$ )<sup>29</sup>. However, they are of the order of activation energies for surface diffusion in metal–metal systems<sup>29</sup>. These wetting activation energies are approximately one order of magnitude higher than those reported for low-temperature liquids, but the effect on the equilibrium frequencies

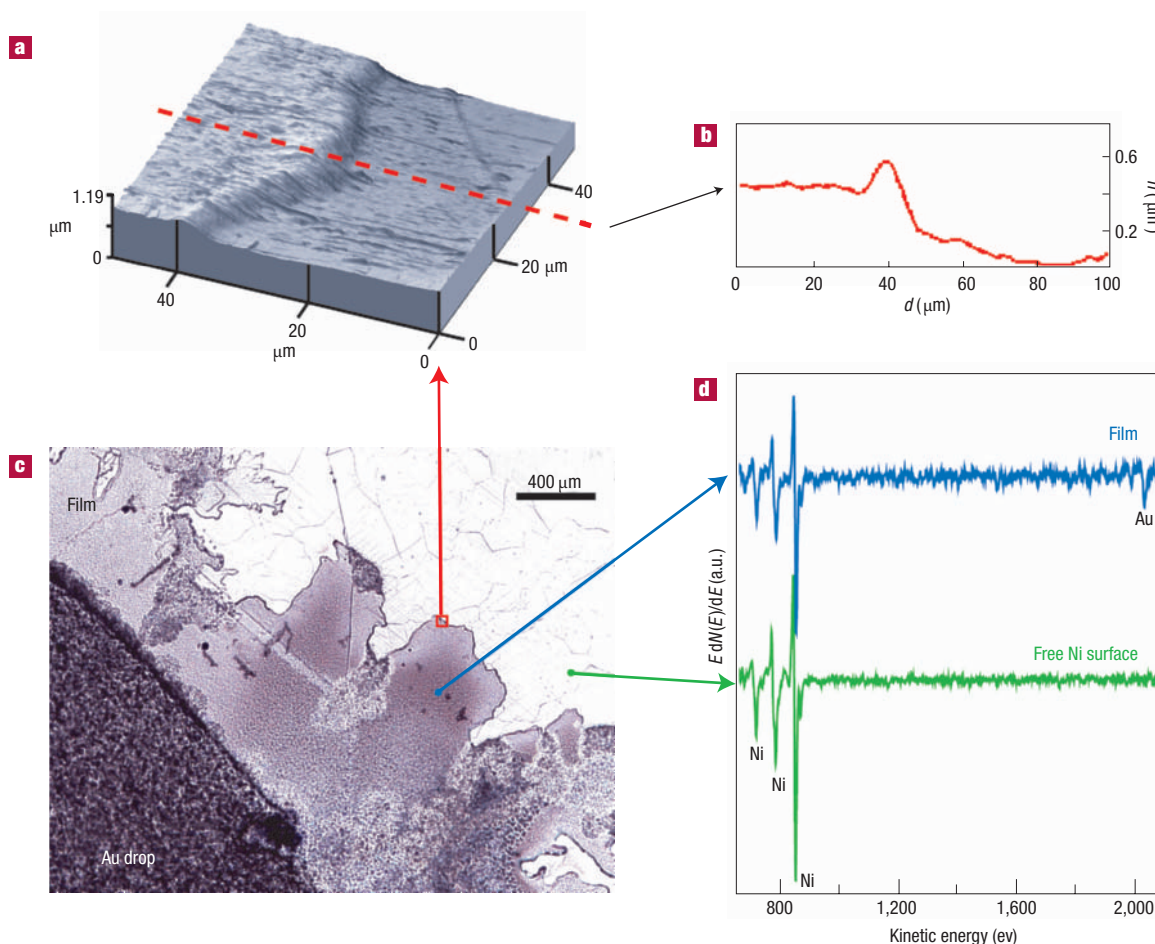
$$K_w^0 = \frac{kT}{h} e^{-\frac{\Delta G_w}{NkT}} \quad (5)$$

is not so large due to the differences in experimental temperature<sup>17</sup>. The calculated frequencies for high-temperature systems are only slightly higher than those measured in experiments performed at room temperature.

These results are a radical departure from the generally accepted trend in low-temperature systems, where there is a myriad of phenomena for which the velocity of a triple junction escalates with the liquid viscosity. Perhaps the most striking example is the normalization of a large number of room-temperature spreading data with the capillary number<sup>16</sup>. Our results clearly show that during the spreading of liquid-metal drops, the main source of dissipation is the local dissipation at the triple line, not the viscous dissipation in the drop. Consequently, spreading kinetics is controlled by the friction of the triple junction in a way that can be described using molecular-kinetic models. The wetting activation energies for liquid-metal spreading are orders of magnitude larger than the fluid flow activation energies, and these systems provide a unique example of a situation where atomic dynamics at the triple junction control the spontaneous spreading of small drops.

A fundamental question remains, however. Why are most of the reported times for the spontaneous spreading of liquid metals orders of magnitude larger than those observed here? High-temperature wetting experiments are generally performed using a conventional sessile drop configuration in which it is





**Figure 4** Images and chemical analysis of the Marangoni film in the Au-Ni system. **a**, Atomic force microscopy (AFM) image of the film edge. **b**, Corresponding AFM profile. **c**, Optical micrograph showing a continuous film extending hundreds of microns ahead of the drop. **d**, Auger electron microscopy spectra taken inside and outside of the film. No Au was detected on the free surface of the Ni ahead of the film using scanning electron microscopy with associated energy dispersive spectroscopy (SEM-EDS) or Auger spectroscopy.

difficult both to separate the basic spreading process from additional effects (such as melting, equilibration with the atmosphere, oxide skin removal and so on) and to accurately record the spreading kinetics. Our drop-transfer setup provides a unique opportunity to systematically analyse isothermal spreading and avoid all these complications. Additionally, at high temperatures some local diffusion or solution precipitation can occur and the substrate can no longer be considered as ideally rigid and insoluble. As a result, triple line ridges can form at the solid-liquid-vapour junction in order to equilibrate the vertical component of the surface tension. The formation of triple line ridges has been pointed out as one of the reasons for the abnormally slow spreading kinetics and large wetting hysteresis often recorded in high-temperature systems<sup>5</sup>. If the front remains attached to the ridge, spreading kinetics will be dictated by ridge movement. The spreading velocity of a liquid front attached to a ridge evolving under interfacial diffusion will escalate as:

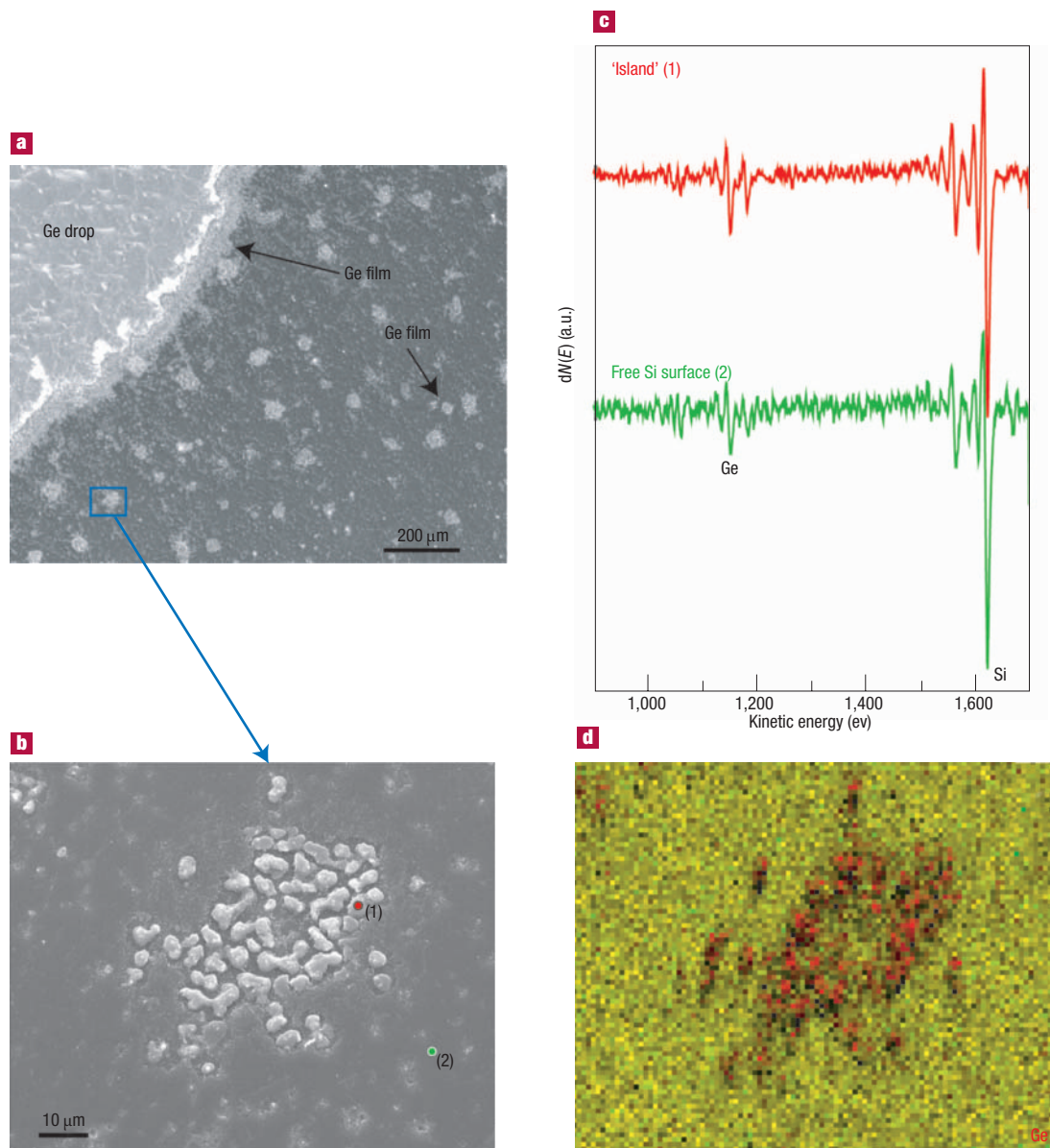
$$v \propto \frac{\omega D \gamma_i \Omega}{kT} \frac{1}{h_0^3} \quad (6)$$

with  $\omega D$  being the width-diffusivity product for the specific interface,  $\gamma_i$  its interfacial energy,  $\Omega$ , the atomic volume and  $h_0$  the ridge height<sup>5</sup>. However, in our systems, the expected velocities when the ridge is a few nanometres high are orders of magnitude slower than

what we recorded<sup>5</sup>. Furthermore, the spreading speeds recorded in metal-metal systems with different interfacial diffusion coefficients and dissolution rates are similar, reinforcing the hypothesis of a liquid front moving on a flat substrate. Either the liquid front moves too fast for the ridge to nucleate or the geometry is such that a ridge cannot pin the triple junction<sup>5</sup>. It is important to note that in the Cu-Nb case, the final contact angles are much larger than those recorded in other metal-metal systems. This could be due to saturation of the liquid Cu with Nb or to the fast formation of a triple line ridge that pins the triple junction. The movement of the ridge will be so slow compared with our experimental times that spreading will effectively stop as soon as the ridge forms. This hypothesis is supported by recent experiments with advancing and receding Cu drops on Nb that show a very large wetting hysteresis: the difference in the final contact angles reached by the advancing and receding fronts is larger than 50° (E. Saiz and A. P. Tomsia, unpublished results).

## MARANGONI FILMS

The formation of Marangoni films in low-temperature liquids is well documented. When the evaporation of a volatile component or gradients in temperature cause gradients in the liquid surface tension,



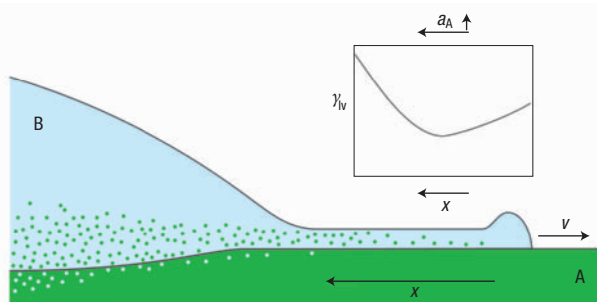
**Figure 5** Images and chemical analysis of the Marangoni film Ge-Si system. **a-c**, In the SEM-EDS analysis a continuous film is visible, and isolated Ge-islands can be observed further ahead. The islands suggest the formation of a germanium film that dewetted during cooling. **d**, Ge was found by Auger spectroscopy in the area between islands.

the corresponding Marangoni stresses drive the formation of liquid films ahead of the main liquid front<sup>8–11</sup>. Reported thicknesses<sup>9–11</sup> of Marangoni films are of the order of 0.1 to 1 μm. The films usually develop a hump at the end because the contact line cannot move as fast as the fluid being driven in by the Marangoni stresses. Although amply documented in low-temperature systems, these films have never before been observed for liquid metals, or in any other high-temperature systems.

We have found that in the Au-Ni (Fig. 4) and Ge-Si (Fig. 5) systems there is clear evidence of the existence of a liquid film extending a few hundred micrometres ahead of the macroscopic drop. In all the other systems, there are no films and a sharp triple junction could be observed after cooling. In the Au-Ni system, the film is continuous and its thickness (100–400 nm) and shape after cooling (with a hump at the edge) clearly exhibit the features of Marangoni-driven films. In the Ge-Si system, isolated islands

containing germanium can be observed on the silicon surface suggesting that the film broke up during cooling.

In high-temperature systems with large mutual solubility, compositional and temperature gradients can arise due to the simultaneous spreading and dissolution. These can result in gradients in the surface tension that can drive the formation of Marangoni films. A possible scenario is depicted in Fig. 6. In order for the film to grow, the surface-tension gradient should be such that surface tension is higher at the edge of the film. We have observed films only in fully miscible systems in which there is a minimum in the liquidus temperature in the binary phase diagram. We propose that this minimum is accompanied by a minimum in the surface energy of the corresponding liquid<sup>30</sup>. Our sessile drop measurements of the liquid surface tension of Au (1.10 J m<sup>-2</sup>) and Au18Ni (82:18 wt% of the composition of the liquidus minimum, 0.96 J m<sup>-2</sup>) suggest this is so. As a consequence, a continuous increase in the concentration



**Figure 6** Schematic showing the formation of a Marangoni film in systems with large mutual solubility. If the surface energy of the liquid does not change monotonically with liquid composition, and there is a minimum at some concentration of the solid atoms as represented by the curve, then a negative gradient of  $\gamma_w$  can develop due to simultaneous spreading and interdiffusion, as required for the development of a Marangoni film.

of substrate material in the liquid film, as we move away from the film edge towards the drop, will result in a minimum in  $\gamma_w$  at some distance from the triple junction (Fig. 6), and the required negative gradient in surface tension will form. As an added factor, the existence of a minimum liquidus temperature in the phase diagram also results in increased solubility of the substrate material in the liquid. This will help the film to advance longer before the liquid saturates with the substrate atoms and solidifies.

In summary, the analysis of liquid-metal spreading has uncovered a regime in which the liquid front is moving on a flat unreacted substrate at faster speeds than organic liquids of similar viscosity. Owing to the physical characteristics of liquid metals (their low viscosity and relatively large desorption energies), viscous impedance in the bulk liquid is not the main source of dissipation, and the fluid-flow analysis typically applied to organic liquids cannot be used. The data presented in this paper are better described by a molecular-kinetic approach for which the wetting activation energies are of the order of  $10^2$  kJ mol<sup>-1</sup>, suggesting that the rate-controlling step is akin to surface diffusion. Such analysis requires the definition of non-equilibrium interfacial energies. Our results suggest that in highly miscible systems, the non-equilibrium solid-liquid energy between the pure phases can be very low. However, if these non-equilibrium energies are non-definable, a fundamentally new approach will be needed. Finally, the existence of Marangoni liquid films in high-temperature systems has been observed for the first time. These films are driven by liquid surface-energy gradients that are a consequence of the varying liquid composition that results from the simultaneous spreading and dissolution.

## METHODS

The spreading of metallic drops was analysed using a drop-transfer setup combined with high-speed photography. The experiments were performed inside an induction furnace with a tungsten heating element in Ar + 5% H<sub>2</sub> flowing at  $\sim 2 \times 10^{-5}$  m<sup>3</sup> s<sup>-1</sup> ( $p(\text{Ar})$  10<sup>5</sup> Pa). The oxygen content of the gas leaving the furnace was measured using a ZrO<sub>2</sub> sensor (Centorr, model 2D). For all the experiments, the oxygen content in the gas was kept lower than  $1 \times 10^{-15}$  ppm [ $p(\text{O}_2) < 10^{-21}$  atm]. Before the experiments, the polycrystalline metal substrates (round plates,  $\sim 10$  mm diameter, 3 mm height) were polished with 0.3  $\mu\text{m}$  Al<sub>2</sub>O<sub>3</sub> particles. The metallic pieces and the substrates were cleaned with acetone and ethanol in an ultrasonic bath and dried with an air gun.

Drop-transfer spreading experiments were performed using the following procedure. A small piece of metal ( $\sim 0.1$ – $0.2$  g) was placed on an inert ceramic substrate (single-crystal alumina or zirconia) inside the furnace. The metallic substrates were placed on a molybdenum holder situated  $\sim 5$ – $10$  mm above the metal. Subsequently, the furnace was evacuated to a pressure of  $\sim 6 \times 10^{-4}$  Pa and refilled

with gas (Ar + 5% H<sub>2</sub>). The gas was flown for  $\sim 2$  hours before heating to assure that the required  $p(\text{O}_2)$  was reached. The assembly was heated at 25 °C per min to the required temperature. Afterwards, the metallic substrate was lowered slowly until it just touched the drop surface and the liquid spread on it, transferring from the Al<sub>2</sub>O<sub>3</sub> plate to the alloy. Spreading was recorded using a high-speed motion analysis system (Kodak, series SR) with a digital camera able to take up to 2,000 frames per second providing a time resolution of  $\pm 0.5$  ms.

After the experiments, the samples were analysed using optical and scanning electron microscopy (ISI, DS130-C) with associated energy dispersive chemical analysis (EDAX, DX-4), as well as atomic force microscopy (Park Scientific, M5) and Auger electron spectroscopy (Physical Electronics, PHI 660 SAM).

Received 23 April 2004; 24 September 2004; published 14 November 2004.

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## Acknowledgements

This paper benefited from discussions with M. Ruehle and R. M. Cannon and was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Correspondence and requests for materials should be addressed to E. S.

## Competing interests statement

The authors declare that they have no competing financial interests.