Why is diffusion in metals and on metal surfaces universal?

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Abstract
Recent experiments that determine mass diffusion D_s on the close packed surfaces of vacuum compatible metals are reviewed. The results turn out to be approximately universal when scaled to homologous temperatures T/T_m, with T_m the melting temperature. Similar behaviour for vacancy-driven diffusion in bulk metals has been recognized for decades. Remarkably, the uncertainty with which this scaling occurs is only $\sim$10%. Possible origins of the universality are discussed.

1. Introduction

My association with Marshall Stoneham began with shared ideas about polaron effects in the diffusion of ions through bulk materials. The relevant interaction of localized defects with the phonon system included, first, for light interstitials in metals, acoustic modes originating from misfit and consequent local strain, and second, optic mode displacements that arise from the electric polarization caused by charge misfit of defects in insulating solids. The main ideas remain the same in the two applications.

Nowadays research interest centres more on the diffusion of atoms across surfaces. This paper concerns new results for surface diffusion that echo back to unexplained past behaviour in the bulk diffusion of metals. The focus of enormous effort in research on the properties of surfaces has been justified in part by successes in the epitaxial growth of materials for both scientific and technical application. A typical vision for the future is of atoms of a mixed molecular beam, raining down on a pre-engineered substrate, where they are guided predictably, by tuned chemical potentials, to self-assemble into functional nanostructures (e.g. figure 1). In truth this image remains far removed from current capabilities.

Surface fluxes follow from the chemical potential μ and the Nernst–Einstein equation $F = -(D_s/k_B T A)\nabla\mu$ (for recent discussion see [1, 2]). Here, A is the surface area per atom and D_s is the surface mass diffusion coefficient, specifically the product of the hopping diffusion coefficient of the species, when mobile, and the fraction of the time it is not immobilized by incorporation into non-hopping environments. Current reality lies far
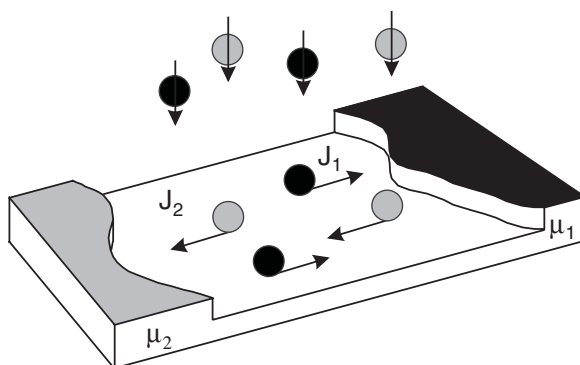
Figure 1. Sketch showing atoms from a mixed molecular beam, guided to self-assemble into nanostructures on a pre-engineered substrate. The point is that predictability of the process requires knowledge of both the surface mass diffusion coefficient D_s and the surface chemical potential differences (see text).

from the above vision because D_s is so difficult to measure that it has been determined for several surfaces only recently. While the hopping diffusion coefficients of single adatoms on terraces have been documented for many metals [3], the densities of thermal defects— adatoms or advacancies—that promote surface mass diffusion are scarcely known in any single case [4]. For surface defects the theory has not yet been developed to offer broad and reliable predictions [5]. Moreover, there is a similar paucity of information, both experimental and theoretical, about the chemical potentials at nanostructures [6]; these also are required to determine surface flow. Thus the precise rates at which specific, self-assembling configurations evolve remain unpredictable.

Pioneering experiments by Bartelt and Tromp [7] and Bartelt *et al* [8] have employed electron microscopy to observe the fluctuations of step edges on clean surfaces in ultrahigh vacuum. It turns out, under very general conditions, that the amplitudes of these capillary fluctuations yield the step stiffness, while their time correlations, under particular conditions, provide a direct determination of the surface mass diffusion coefficient [9, 1]. By these means, using low energy electron microscopy (LEEM) to image surface steps, values of D_s have been obtained over a temperature range above $0.5\,T_m$ for the close packed surfaces of a number of different metals [10]. Remarkably, the values turn out to be approximately universal when scaled to be functions of T/T_m [2]. A similar scaling has long been recognized for diffusion through the bulk of metals (see e.g. [11]). Section 2 of the present paper reviews the experiments and the values of D_s, with emphasis on the degree to which the results follow from a reliable base. Section 3 discusses the theory that underlies the behaviour. At the present time the bulk results have no persuasive explanation and, surprisingly, it is difficult to see any fundamental connection between the surface and bulk processes. Section 4 provides a brief summary.

2. Experimental determination of D_s using LEEM

Here we briefly review the experiments, the basic concepts, and the results of recent diffusion studies of metal surfaces.

The LEEM employed in the work (for experimental details see e.g. [10]) operated at TV rates of 30 frames s^{-1}, and had resolution of $\delta \sim 7$ nm; motions of step profiles were tracked to about $\delta/5$ by intensity fitting over neighbouring pixels during the digitization of step profiles
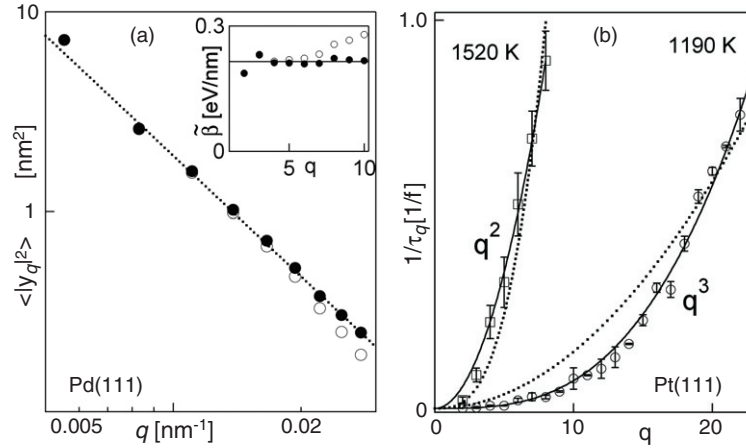
Figure 2. (a) Mean square amplitude of fluctuation, shown on a logarithmic scale, as a function of wavevector q for Pd(111) at 1090 K. The raw data (open circles), and the results corrected for temporal and spatial resolution of the LEEM (full circles), conform well to the q^{-2} prediction for capillary waves (after [10]). Inset are values of $\tilde{\beta}$ derived from amplitudes for different q. (b) Measured relaxation rates of fluctuation modes for step edges on Pt(111) at 1190 K. The results conform well to the q^3 variation (solid line fit) predicted for capillary waves relaxing by surface diffusion (equation (2)). A crossover to q^2 from bulk diffusion (solid line fit) occurs at high T (see [10]). The dotted lines indicate fits to the reversed exponents.

from video images. These characteristics confine the research roughly to relaxation times $\tau_q > 30$ ms, wavelengths $2\pi/q > 20$ nm, and fluctuation amplitudes $y_q > 1$ nm. For the given step edge energies these conditions are fulfilled on metal surfaces between 0.5 T_{m} and 0.7 T_{m}, owing to the universality of concern in section 3. For the given parameters, atomic details are not apparent, and the step motions appear entirely smooth and capillary.

The LEEM could operate at temperatures up to 1700 K with base pressures in the 10^{-11} Torr range, thereby offering reproducible results on clean surfaces of vacuum compatible metals. We chose to explore close packed surfaces, and have completed experiments on Pt(111), Pd(111), Ni(111), Au(111), Ag(111), Mo(011), and Nb(011), of which only the latter could not be fully cleaned, owing to chemisorbed O. Ag(111) and Mo(011) results are not yet fully analysed.

Data documenting step profile fluctuations, taken from sequences of LEEM frames, conform convincingly to theoretical expectations for superposed capillary modes. This requires mean square amplitudes of thermal fluctuation that are inversely proportional to a step stiffness $\tilde{\beta}$, and vary as q^{-2} with wavevector q. The step stiffness measures the added step free energy caused by curvature according to $\tilde{\beta}(\theta) = \beta(\theta) + \partial^2\beta/\partial\theta^2$, with $\beta(\theta)$ the free energy per unit length of a straight step oriented along azimuth θ. Figure 2(a) shows [10] for Pd(111) how the data agree with the predicted q dependence for a sample at sufficiently low temperatures that many modes, q, have $\tau_q > 30$ ms.

A curved step has a local chemical potential determined by the Gibbs–Thompson equation, proportional to the profile curvature and step stiffness. This drives currents over the terraces by surface diffusion that allows fluctuations to relax. Surface diffusion affords a specific signature, with relaxation rates given [1] by

$$\tau_q^{-1} = (2\tilde{\beta}A/k_{\mathrm{B}}T)D_s q^3. \tag{1}$$

Here, A is the surface area per atom. Equation (1) is a robust prediction that is independent of mechanism and presumes only linear response to the weakly perturbing chemical potential;
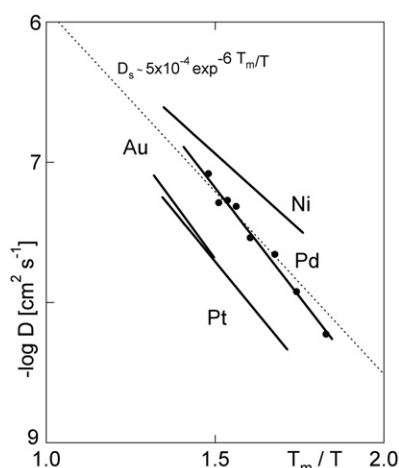
Figure 3. The measured surface mass diffusion coefficient shown as a function of T_m/T for some close packed metal surfaces, after [12]. The results fall close to $5 \times 10^{-4} \exp(-6T_m/T) \, \mathrm{cm}^2 \, \mathrm{s}^{-1}$, as suggested in [2].

also, it is insensitive to perturbations at the step from Ehlich–Schwoebel barriers. Figure 2(b) shows [10] for the case of Pt, at relatively low temperatures, how experiments conform accurately to the predicted q dependence. Above $0.6 \, T_m$ there is a change of mechanism to bulk flow, and the rates then vary approximately as q^2 (see figure 2(b) for data at 1520 K). As part of the universality discussed in section 3, similar behaviour is expected of other metals.

As the stiffness $\tilde{\beta}$ enters the determination of D_s, it may be mentioned as a further point of verification that the values determined by the present methods are weakly temperature dependent and have anisotropies with step orientation that differ widely from one surface to the next. The anisotropies are confirmed by independent results. In the case of Au(111), for example, the extremes of anisotropy differ by a factor of five, and the observed dependence on orientation θ from step fluctuations accurately predicts the equilibrium shapes of small islands, also observed by LEEM [12].

The main point at which this paper aims is revealed when the values of D_s thus determined for several different surfaces are displayed as a function of T_m/T (as befits an activated process). Figure 3 is a graph of this type [13] for Au(111), Ni(111), Pd(111), and Pt(111). When displayed in this way the results are approximately universal, with values within a factor of three of an average behaviour earlier speculated [2] to be $D_s = 5 \times 10^{-4} \exp(-6T_m/T) \, \mathrm{cm}^2 \, \mathrm{s}^{-1}$ (see dotted line). Results for Ag(111) and Mo(011), although as yet incompletely analysed, appear to conform well to the same pattern of behaviour.

In summary of the experiments it may be stated that, although surface mass diffusion is difficult to measure, the values obtained by step fluctuation spectroscopy have a strong theoretical underpinning in which experiment agrees well with explicit predictions for the relaxation of capillary waves by surface diffusion. The universality is manifested by values of D_s so determined that are within a factor of three of a common variation, when displayed as a function of T/T_m.

3. Universality in diffusion

A recent discussion analyses [2] the homologous behaviour (scaled to T_m), documented above, for surface diffusion on close packed surfaces. The diffusion is attributed generally to adatom

hopping over surface terraces, and the universality revealed by diffusion experiments derives from a similar universality of the adatom creation and hopping energies. It requires mention that a similar universality of bulk diffusion in metals has been recognized for several decades (see e.g. [11]). Bulk diffusion also may be described in terms of defect formation and hopping energies, but in the case of bulk diffusion the mobile defects are bulk vacancies. The author is not aware of any fundamental treatment of this remarkable scaling, or even an identification of the fundamental behaviour that is regular. The topic has worthwhile content, discussed here, starting with the simpler bulk case.

Diffusion in metals follows

$$D = 0.3 \exp(-17 T_m/T) \text{ cm}^2 \text{ s}^{-1} \tag{2}$$

at high temperatures, typically within an order of magnitude. Since actual values of the prefactor typically lie within an order of magnitude of $0.3 \text{ cm}^2 \text{ s}^{-1}$, this means that the values of the activation energies observed in experiments track $17 k_B T_m$ with impressive accuracy of $\sim 10\%$ see e.g. [11]. Very few many-body properties conform to so simple a prediction with this precision.

What does this mean in physical terms? To within a correlation factor near unity

$$D = ca^2 w, \tag{3}$$

for bulk diffusion, with c the vacancy concentration, a the lattice parameter, and w the defect jump rate per jump path [11]. A treatment using classical methods [14] (which should serve well here) yields

$$w = \nu \exp[-(\hat{G} - G_1)/k_B T]; \qquad c = \exp[-(G_1 - G_0)/k_B T], \tag{4}$$

in which G_1 cancels from D, and, for a system of N particles,

$$\exp(-G/k_B T) = \int d^{3N} \mathbf{x} \exp[-V(\mathbf{x})/k_B T], \tag{5}$$

with the integral extending over all coordinate space, in I_0 for the perfect system without a vacancy, and for the same system but with one vacancy, and with the jumping atom confined to the saddle surface, in $\hat{I}$. In equation (5), $V(\mathbf{x})$ is the full many-body energy of the system with N atoms at $3N$ coordinates specified by $\mathbf{x}$, and ν in equation (4) may be taken as the Debye frequency for the crystal (a corresponding term in the $3N$th dimension must be introduced into V for the saddle surface to remove this arbitrary choice [11]). Apart from a correction for return jumps, which observed values for the isotope effect establish [15] as unimportant here, equation (5) is exact in classical physics, and the discussion below is accordingly well based.

For the factor νa^2 it is not possible to estimate values for metals far from $10^{-2} \text{ cm}^2 \text{ s}^{-1}$, since Debye temperatures are hundreds of K and lattice parameters are 3–4 Å. This differs significantly from the observed diffusion prefactor $\sim 0.3 \text{ cm}^2 \text{ s}^{-1}$, and it has been suggested [11] that the difference arises from anharmonicity that is neglected by quasiharmonic treatments. The combined results thus indicate that

$$\hat{G} - G_0 \approx (17 T_m - 4T)k_B. \tag{6}$$

A variability of D by an order of magnitude near T_m places an uncertainty only of order $\pm 2 k_B T_m$ on this value. Consequently, the observed 10% deviations of the diffusion activation energy from the mean value $17 k_B T_m$ do represent a realistic assessment of the precision with which the homologous behaviour exists in the configurational integrals themselves.

No persuasive explanation is currently available for the homologous behaviour. It seems reasonable to predict that the result must recur in calculations using model forces that create close packed crystal structures. The result is remarkable both for its reliable accuracy and

its validity for all metals. To place it in context suppose, as seems reasonable, that the main difference between the two configurational integrals arises from the immediate neighbourhood of the atom that jumps. Note that the entropy of melting is $\sim k_B$ per atom (Trouton's rule), so that the difference of free energy between the liquid and solid for one atom and ~ 12 neighbours, at temperatures T close to T_m, is

$$\Delta G \approx (13T_m - 13T)k_B. \tag{7}$$

By comparison with equation (6), this suggests the analogy that the saddle surface for the jumping atom and 12 neighbours may be liquid-like, but only the internal energy difference of $13\,k_B T_m$ (not the entropy contribution $13\,k_B T$) enters the difference of configurational integrals near T_m. This analogy is also consistent with the fact that the 13 atoms relevant to the saddle-surface configuration include one vacant site and thus extend over 14 lattice cells, comparable with the typical volume difference of 5–10% between liquid and solid. It must be stated that this analogy offers the breadth but not the precision of the experimentally observed universality.

Turning briefly to the universal characteristics of available surface diffusion results (section 2) we see similarities and differences. The two problems can be articulated in identical terms, which require the comparison of two configurational integrals, one on a saddle surface and the other without a defect. Both cases lack significant complication from correlated jumps or quantum mechanics, and in both processes the important differences between the configurational integrals must be localized near the moving atom. On the other hand, the bulk process concerns a vacancy defect and the surface process an adatom—the surface equivalent of an interstitial—and systematic similarities are then surprising. Certainly, the motion of one adatom on a flat terrace has nothing obviously in common with the liquid-like configurations that provide some useful analogy for the bulk behaviour.

One connection between surface and bulk diffusion concerns the observed prefactors. The anharmonic factor of ~ 30 identified above for bulk diffusion with activation energy $17\,k_B T_m$ scales to a factor ~ 3 for the surface with activation energy $6\,k_B T_m$, and this must be reflected in the prefactor for surface diffusion. A further reduction by a factor ~ 10 in ν for adatom vibrations parallel to a smooth surface then reduces the bulk prefactor of 0.3 cm^2 s^{-1} to 3×10^{-3} cm^2 s^{-1} for the surface, which differs not unreasonably from the values experimentally observed. This offers some hope that the factors that enter the diffusion processes are at last becoming understood, even though the principles underlying the observed approximate universality still remain obscure.

4. Summary

Recent results for surface mass diffusion on the close packed surfaces of vacuum compatible metals are reviewed. Like long-documented bulk diffusion results for metals, the surface data fall close to universal values when scaled to homologous temperatures T/T_m. Few complex many-body behaviours conform to so simple a result with such precision. For example, even the Dulong–Petit law that the specific heat is $3N\,k_B$, as explained readily by normal modes, fails by $\sim 10\%$ at T_m, owing to anharmonicity; this is the same magnitude of characteristic uncertainty that occurs in the universality of diffusion discussed here. It is as if some underlying principle determined the diffusive behaviour. There is at present no useful hint of an explanation for the observed regularity.

References

[1] Flynn C P 2002 *Phys. Rev.* B **66** 155405
[2] Flynn C P 2005 *Phys. Rev.* B **71** 085422
[3] Kellogg G L 1994 *Surf. Sci. Rep.* **21** 1
[4] Tromp R M and Mankos M 1998 *Phys. Rev. Lett.* **81** 1050
[5] Pimpinelli A and Villain J 1998 *Physics of Crystal Growth* (Cambridge: Cambridge University Press)
[6] Thayer G E, Hannon J B and Tromp R M 2004 *Nat. Mater.* **3** 95–8
[7] Bartelt N C and Tromp R M 1996 *Phys. Rev.* B **54** 11731
[8] Bartelt N C, Goldberg J L, Einstein T L, Williams E D, Hayraud J C and Metois J J 1993 *Phys. Rev.* B **48** 15453
[9] Jeong H C and Williams E D 1999 *Surf. Sci. Rep.* **34** 171
[10] Ondrejcek M, Rajappan M, Sweich W and Flynn C P 2006 *Phys. Rev.* B **73** 035418
[11] Flynn C P 1972 *Point Defects and Diffusion* (Oxford: Pergamon)
[12] Ondrejcek M, Rajappan M, Sweich W and Flynn C P 2005 *Surf. Sci.* **574** 111
[13] Ondrejcek M, Rajappan M, Sweich W and Flynn C P 2006 *Phil. Mag.* at press
[14] Vineyard G H 1957 *J. Phys. Chem. Solids* **3** 121
[15] Marchese M, DeLorenzi G, Jacucci G and Flynn C P 1986 *Phys. Rev. Lett.* **57** 3280