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THE MOTIONS OF IRON PARTICLES ON GRAPHITE

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Small metal particles on a non-metallic substrate undergo complex motions reported in controlled-atmosphere electron microscope experiments by several groups. The interpretation of these motions is discussed. Simple Brownian motion and random diffusion are not adequate explanations for iron particles on graphite. Instead one must invoke forced diffusion, in which particle–particle forces are important, and the effects of inhomogeneity of the substrate. The analysis implies that the catalyst particles are liquid in the case discussed, and that catalytic behaviour can be modified by physical changes of the substrate alone.

1. Introduction

Small metal particles on a non-metallic substrate are the basis of many catalysts. It is often convenient to imagine the particles as static, unchanging and inert. Yet this is not so. Many experiments [1–11] have shown the particles can move at up to 1000 Å/s, and that they may show a range of most varied behaviour. Some features of this behaviour have been explained, qualitatively at least, in terms of known thermal behaviour, diffusion, and mutual interactions between the particles. This paper invokes these components, amongst others, to explain the remarkable correlated motions of iron particles on graphite [2]. Some of the motions have been described previously as Brownian motion. There is indeed an analogy but, as will be shown, it is quantitatively unacceptable. Instead, one can invoke a combination of elastic interactions between particles through their mutual distortion of the substrate, and the temperature dependence of the interfacial tensions which determine this interaction.

2. Uniform motions of catalyst particles

The experiments on iron particles on graphite in a controlled-atmosphere electron microscope show the particles moving at speeds of several hundred Ångströms per second. The motion only occurred in the correct atmosphere (in this case in CO rather than CO_2), and the metal particles appeared to be liquid, even though the substrate temperature was well below the particle melting temperature. The suggested explanation was that the electron beam produced different reaction products in CO than in CO_2, and that the particles were melted by heat generated by reactions of these products catalysed on the particles. This explanation is probably correct. For present purposes it is sufficient that a catalysed reaction occurs, that it depends on the atmosphere. The present results strongly support earlier comments that the particles are liquid.

Earlier workers have discussed the mechanism of motion in analogous cases, and the present analysis agrees in many respects. In essence, the particles move by driven diffusion. If D_p is the diffusion constant for the molten particle, their velocity v in response to an applied force F is given by

$$v = (D_p/kT)F\,, \tag{1}$$

where (D_p/kT) is, in effect, a mobility. The particle diffusion constant D_p is related to atomic transport processes within the particle. Roughly, if the particle moves by self-diffusion and has a radius (R/a) in units of the atomic radius a, then

$$D_p \simeq D_s(a/R)^4 \tag{2}$$

with D_s the self-diffusion constant. Eq. (2) is derived in different contexts in various ways [12,13]. Since it is independent of temperature, D_p and D_s should have the same activation energy. This is indeed observed: D_p has an activation energy 15.2 kcal/mole, whereas D_s for molten iron varies slightly with temperature from 12.2 to 15.7 kcal/mole [14]. The similarity of the two activation energies may be coincidental, however, since it is the substrate temperature and not the particle temperature which is measured. Further, it will become apparent that the particles need not all have the same temperature, nor need their temperatures remain constant in time.

One can combine the observed particle velocities with known values of D_s and R to deduce the magnitude of force F needed. The value of F turns out to be 10^{-6} to 10^{-5} dynes. This is precisely the range predicted [15] for elastic interactions, suggesting that driven diffusion is the main mechanism. There is a further piece of evidence, namely that the observed velocities [2] depend on particle radius. The data fit the expression $v(R) \approx R^{-2}$ approximately. If $D_p \approx R^{-4}$, from eq. (2), then the force F should vary as R^{+2} to explain $v(R)$. This dependence of F is predicted [15] for the elastic interaction[*] when particles of various radii interact with a given (R-independent) population of other particles. Finally, we note that the observed motions are consistent with the repulsive interactions between particles which one would expect from elastic distortion of the substrate. Electrostatic interactions seem unimportant. Net charges of $10^2|e|$ or more per particle would be needed for particles

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[*] There are several different dependences quoted in the literature. They appear to result from different assumptions about the precise forces the particle exerts on the substrate. The form used here should be appropriate for liquid particles on a solid substrate.

of 500 Å radius, and it is hard to see how such charges could persist given the conducting substrate, the possibility of field emission, and the fact that ions in the atmosphere strike the particle roughly every picosecond.

3. Brownian motion of metal particles

The conclusion of the last section was that the mobile iron particles move in response to elastic interactions between the particles. On this picture, one would expect apparently random motions in which particles tended to avoid each other. This is an important part of what is observed. Two significant omissions remain. One is a result of steps on the substrate surface, or possibly subsurface structure. These can pin the particles completely, or may simply constrain particle motion to a particular path. The second is seen most clearly in groups of particles thus constrained to a straight trajectory on the surface. An example is given in fig. 1, taken from reference [2]. Here the group undergoes a coupled motion whose direction changes every few tenths of a second. One simple way to interpret the motion would be to say that particle A is moved by some agency to be identified, and particles B, C and D follow in response because of their interactions with A, with each other, and with more distant particles. We shall return to the question of agency later. The immediate step is to see to what extent the motion can be called "Brownian".

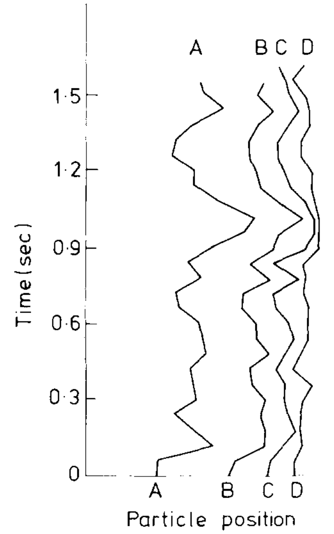

Fig. 1. Motions of four catalyst particles (Fe on graphite) observed by Baker et al. Roughly speaking, the displacements correspond to particle A driving the others through mutual repulsive interactions. The motions are essentially one-dimensional, presumably because of a ledge on the substrate surface.

The important parameters of the motion are these. First, the average diameter of the particles was 380 Å, and the measurements were made at 775°C. The trajectories were constructed from a cine-film taken at 20 frames/s, so that really rapid motions are not seen. However, it is reasonably certain that major changes in direction occur every 0.1–0.5 s. The scale of the displacements is not given, so one can only note that the mean velocities must be around 0.1–1μ/s. The particle diffusion constant, D_{p}, is around 5×10^{-14} cm^2/s.

In the classical theory of Brownian motion [16], there are just two time constants. We now show that both time-constants must be vastly too short to be the source of these reversals of motion. The first time-constant, τ_D (usually written $1/\beta$), represents the damping of the particle motion; when the forces acting on the particle are switched off, the particle velocity falls to zero as $\exp(-t/\tau_D)$. The theory of Brownian motion relates τ_D to the particle diffusion constant:

$$\tau_D = 2MD_{\mathrm{p}}/kT\,, \tag{3}$$

where M is the particle mass. In the present case, τ_D is around 10^{-16} s, with a slight dependence on the shape assumed in estimating M. A second estimate of τ_D can be obtained by assuming the damping results from a viscous layer of thickness λ and viscosity η between the bulk of the particle and the substrate. This gives an expression:

$$\tau'_D = M\lambda/\pi R^2\eta\,. \tag{4}$$

For the present case $\tau'_D \approx 1.5 \times 10^{-13}$ s (λ in Å/η in cgs units). For standard gases and liquids η lies in the range 10^{-4} to 1. Since λ will surely be less than 10^2 Å, it is clear this prescription leads to a τ'_D less than around 10^{-7} s, and possibly much smaller. Both models show the motion is very heavily damped.

The second time constant in classical Brownian motion characterises the atomic collisions from the atmosphere surrounding the particles. This time constant, τ_{c}, does not appear in the expressions for Brownian motion, since a time-average of a correlation function alone is needed. However, it is worth noting that kinetic theory gives τ_{c} around 10^{-12} s, and that collision-induced displacements would be extremely small.

The only time-constants in Brownian motion are thus at least six orders of magnitude (perhaps ten or more) faster than the time scale for abrupt changes in motion of the particles*. An explanation is needed of both the persistence of the motion for up to 0.1 to 0.5 s and of the reasons for the abrupt change. The persistence is presumably a consequence of the persistence of the forces driving the diffusion. In the next section one possible explanation of the abrupt changes is proposed.

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* One might well ask what it is which is seen in conventional undergraduate experiments on Brownian motion. Turbulence from the heating by the light source and vibration from neighbouring students seem likely contributors.

4. Model for the abrupt changes in motion

The discussion in the previous sections suggests that the abrupt changes in motion correspond to changes in the forces driving the particles. Since these forces are primarily due to particle–particle interactions by elastic distortion of the substrate, presumably the interaction of at least one particle with the substrate changes significantly and in a time rapid compared with the observed cine record. In fig. 1, one can understand the motions if only particle A is affected, though this may not be typical.

The interaction with the substrate depends on two main factors: the interfacial tension γ, and the contact radius R, together with any other geometric factors which may be needed to describe the region of contact. Thus abrupt changes in forces should correspond to abrupt changes in γ or in contact geometry. In both cases the picture is this:

(i) The particles melt and become mobile.

(ii) The particles move under a combination of repulsion between catalyst particles and any interactions with substrate defects. The motion tends to take the particles to a new equilibrium geometry.

(iii) As this new geometry is approached, the contact region changes in geometry and/or in interfacial tension, so that the new net forces tend to restore the original particle configuration.

Obviously one can conceive further possible models, including those which involve the gas-particle interface, rather than the substrate-particle interface discussed so far. Analogies might be drawn with systems like sodium or camphor on water, where the precise local shape affects a reaction rate and leads to momentum transfer. Whilst such mechanisms seem unlikely, they can be covered by modest changes in the arguments of the present section. These can be compared usefully with previous work on catalyst particle motion [20]. In the earlier work the basic diffusive motion only occurred during transient local heating by the catalytic reaction. Here the reaction gives sufficient heat for continuous motion, and the (different) transient changes lead to a change in velocity.

The simplest mechanism to understand is that in contact geometry, where the detailed substrate surface structure is the important factor. The other mechanism is less obvious, but may also involve the detailed surface structure. The important point is that surface tensions and interfacial tensions vary with temperature: γ falls as T rises. Several empirical forms exist [17], e.g. $\gamma(T)/\gamma(0) = (1 - T/T_c)^{1+R}$ with $R \approx \frac{2}{9}$, or a simple linear form $\gamma(T) = \gamma(0)(1 - \beta T)$. In all cases for which data exists, it is agreed that γ falls by a significant fraction between the metal's melting and boiling points. Thus the forces will vary significantly as the temperature changes between these limits.

Two factors control the particle temperature: heat input from reactions catalysed on it, and heat losses to the substrate. The heat input is hard to estimate, since it depends on the precise role the substrate plays, and on the residence time τ_R of the rate-determining reactant on the surface. If there are N suitable surface sites per unit area of particle, and each reaction contributes energy Q to the particle, the heating rate is $H \equiv NQ/\tau_R$ per unit area. The temperature reached in the steady state for a disc-like particle of thickness d [18] is $\theta = H/(\frac{3}{2}\,\Gamma\, v\, c_s)$, with Γ the transmission coefficient, v the velocity of sound, and c_s the specific heat per unit volume per phonon branch. If the heating is removed, the cooling is characterised by a time $(2d/v\Gamma)$. With reasonable magnitudes θ can be large, e.g. 1000°, and the cooling time is very short, always μs or less. Now the transmission coefficient can vary enormously. For perfect surfaces, Γ is determined by acoustic mismatch, and normally lies in the range 0.05 to 0.2 for catalytic systems. Yet, in other cases, Γ may fall below this acoustic mismatch figure by even two orders of magnitude [19]. Clearly, Γ needs to vary rather modestly during the particle motion for the heat loss, and hence γ and the forces, to change significantly. Such changes are probably significant during the abrupt reversals of motion, since the steady motion shows thermal activation for a temperature close to that of the substrate.

The two mechanisms, geometric and in interfacial tension, are thus related. In one case the inhomogeneity of the substrate affects the contact shape, in the other the transmission coefficient. On might ask whether changing the heating rate (e.g. by small changes in the atmosphere) could judge the relative importance of the two components. This is not simple, for whilst the forces fall with temperature, so other factors like the viscosity change, and the mix is hard to unravel.

Finally, we note that the period of the motions seen, of order 0.1 s, is determined by the scale D over which the substrate-particle interface changes significantly and by the particle velocity, which is itself given by eq. (1). An important conclusion is that the physical form and operating temperature of the catalyst particles can be controlled by the precise topography of an inert substrate. The topography can influence both the precise shape of a particle (and hence numbers of critical sites, if such exist) and the extent of aggregation of catalyst particles.

5. Conclusion

The main point of this article is to demonstrate that the complex movements of catalyst particles need explanation, and to argue that fairly simple models invoking substrate inhomogeneity appear to describe well what is seen.

The model has two obvious implications. First, even when the substrate is kept at constant temperature, the catalyst itself may vary greatly in temperature. Consequently it is hard to make unambiguous analyses of thermal effects. Secondly, the detailed physical shape of the catalyst probably changes in its motion. It need not have constant area, nor need the numbers of "critical" catalytic sites be constant. Control of the physical features of the substrate can affect catalyst behaviour, even when the substrate is chemically inert.

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