Proceedings of Czech–Japanese Seminar in Applied Mathematics 2004
August 4-7, 2004, Czech Technical University in Prague
`http://geraldine.fjfi.cvut.cz`
pp. 57–62

INTERFACIAL PHENOMENA IN FLUID DYNAMICS: LINKING ATOMISTIC AND MACROSCOPIC PROPERTIES: CAN THEY EXPLAIN THE TRANSPORT ANOMALIES?

ROBERT F. HOLUB[1] , MICHAL BENEŠ[2] , AND BRUCE D. HONEYMAN[1]

Abstract. Many fields, including solid state physics, material and environmental sciences, are trying to introduce multiscale modeling of complex systems in order to obtain better agreement between theory and experiment and eventually to be able, for instance, to predict a failure in a given material, or transport of a contaminant in porous media. Using as an example transport of Rn through such media, and also of the so called "surface diffusion", in dependence on temperature, which involves both molecular diffusion (Fick's equation) and viscous flow (Navier-Stokes equation), we will attempt to show that the atoms of Rn behave in ways that cannot be described by a mere macroscopic continuum approach. We will show specifically the interplay of some quantum effects, surface structure and interface morphology. It is possible that even the intractable problem of "fingering", or too fast migration of "colloidal" Pu in Nevada test sites [1], [2], might be clarified by employing a microscopic approach based on the transport of what we call "geoaerosols". The biggest practical problem for experimentalists and engineers is to have models that "marry" mathematically the microscopic aspects to the macroscopic (continuum) ones. We think this is an opportunity for the applied mathematicians to help solve a problem that has been ignored for too long (due to its difficulty?), and which is of great practical importance in several fields.

Key words. Surface diffusion, anomalous transport, porous media

AMS subject classifications. 35K60, 35K65, 65N06, 68U10

1. Introduction. From the microscopic point of view, there are two main mechanisms that describe microscopically the transport on surfaces, namely the "surface diffusion" and "hopping". On typing these two topics into the Web of Science Citation Index, the former gives 4937 hits, the latter 12562, so clearly our preliminary paper cannot cover them all. The exception is our coverage of Rn transport (emanation) from solids, and especially of Rn transport via the so called surface diffusion, which we attempt to cover thoroughly in this paper. We hope that our treatment will apply to most other surface diffusion and hopping phenomena in other fields.

The notion of surface diffusion in Rn transport is invoked to describe the results of a well known method how to study surfaces, called Emanation Thermal Analysis (ETA), as described in a monograph by Balek and Tolgyessy [3], and its theory more recently by Beckman and Balek [4].

It should be pointed out that most fields agree on the need to link the microscopic to macroscopic properties; the problem is how to accomplish that because any microscopic calculations including more than 1000 atoms are prohibitively expensive and time consuming. While this is obviously true, we also feel the transport on surfaces (via surface diffusion and hopping) are plagued by inconsistencies and anomalies that have been ignored for too long [5], and which should be addressed. It is the main

---

[1] Department of Environmental Science and Engineering, Colorado School of Mines, Golden, CO 80401, USA

[2] Department of Mathematics, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Trojanova 13, 120 00 Prague, Czech Republic.

purpose of this paper to show that there is a need to include what we call long-range transport aspects of the microscopic phenomena and their unexpected ability to penetrate through porous media and high efficiency filters [1], [2], [6], [7], [8].

One group of authors called apparently similar attempts "non-local folklore" [9]. Unfortunately, they did not reference these attempts and a search on GOOGLE proved only partially successful. It seems by "non-local" some long-range stresses are meant. The closest we could find on this has been studied by Cushman et al. [10], using "fractional advection-dispersion equation", focusing on anomalous (i.e., non-Fickian) dispersion in natural geologic formations. The exact physical nature - as opposed to well worked-out mathematical procedures - appears not addressed in their papers. Vattulainen et al. [9] (incidentally, this paper has been quoted 25 times since 1997) solved the problem of too fast surface diffusion by invoking a "speed-up" distribution function $W(t)$, apparently ad hoc. Such speed-up occurs around a second-order phase transition at 710 K for oxygen on W(110) surface.

Toroczkai and Williams [11] measured the speed of surface diffusion of adatoms at room temperature and found speeds as high as $10^5 nm/s$, a mesoscopic length scale. It implies jumps over many millions of atoms per second.

Most treatments of both phenomena are based on some form of transition state theory, and the relationships are governed by a negative exponent term. It is our suggestion that, in view of the anomalies and discrepancies, a positive exponent term should be added in order to better explain the data. The contribution of the positive exponent relationship should be usually smaller than that of the negative exponent term. It should be mentioned, as Lagally [12] points out in a review article, that a big part of the great progress in measuring the surface diffusion and hopping is due to the discovery of scanning tunneling microscope (STM). The structural determinations were dominated in the early days by diffraction methods; STM enabled a transition to real-space imaging, making surface science visual and thus more accessible.

2. Why the positive exponent is needed. The surface diffusion, D, is traditionally described by means of Arrhenius form preceded by an entropic prefactor, D_0,

$$D = D_0 \cdot \exp\left(\frac{-\Delta H}{kT}\right), \tag{2.1}$$

where ΔH is the energy barrier, or activation energy, or the binding energy (of a particle).

The obvious interpretation of D_0 is that it is the diffusion coefficient when $\Delta H = 0$. However, it usually is used as what most might consider a fudge factor to get some limited agreement with the data.

For instance, Beckman and Balek [4], in order to fit their data, at temperatures used in a typical ETA range 800 to 1600 K, use $D_0 = 10^6 cm^2/s$ and the binding energy $\Delta H = 2.2$ to $4.4eV$. However, the well-known and well-measured values for Rn diffusion coefficient at room temperature in air (in which there is no measurable "barrier" preventing Rn atom from moving freely in air), $D = 0.12cm^2/s$. Note that D scales up as $T^{0.5}$. Equally well-known and measured value for the adsorption energy in charcoal, $\Delta H = 0.2eV$. It should be noted it is basically an upper limit, in view of the enormous specific surface area of charcoal, $\approx 1000m^2/g$, because such an atom of Rn is practically surrounded by charcoal surface atoms of carbon. Still, the measured value is at least 10 times lower.

In addition, the expression (2.1), differs from the measured values at room temperatures, as in most of the ETA theory expressions, by literally many orders of magnitude.

Hopping [13], similar to the surface diffusion, is also traditionally described using an exponential factor with a negative exponent,

$$k_T \approx \exp\left(-\beta x\right), \tag{2.2}$$

where k_T is transfer rate, β is a constant, x is the nearest neighbor distance.

It should be noted that even though the expression (2.1) differs from the expression (2.2) in the form of the exponent $\Delta H/kT$ versus βx, it amounts to the same type of distance dependence in both cases. In expression (2.1) in order to get further away from the original site, multiple jumps are needed and therefore the dependence on the distance becomes a compounded probability of successive jumps. Clearly it also decreases exponentially with distance.

Note that any real surface is full of ridges, valleys, dislocations and cracks. To hop, a particle has to be pushed out of its (shallow) potential well in order to end up in another potential well.

We claim there appears a need to include a term that increases the probability of a jump with the distance from its original potential well. The best choice appears an exponential increase in order to keep the symmetry with the conventional exponential decrease.

While the case for a major anomaly in Rn ETA analysis appears very strong, it is not so clear in the case of already mentioned fast Pu transport at Nevada Test Site. As pointed out in ref. [2], even though it is possible that Pu atoms attached to colloids of rather disparate sizes (15% to $> 1\mu m$, 40% to $50-1000nm$, and 40% to $7-50nm$) did travel the distance of 1.3 km in 29 years carried by the "inferred" groundwater flow [1], there is no direct proof. In addition, only a very small percentage of Pu can be expected to be attached to colloids; vast majority should be attached to all surfaces through which the groundwater has to travel. As a rule, the surfaces are the same material as the colloids [2]. So, it is possible that the ultrafast transport of Pu, a very closely watched substance, could also be transported by the mechanism suggested here. Before we get to the next section, it is useful to summarize:

1. Both surface diffusion and hopping are microscopic particle-like quantum phenomena.
2. Bulk properties are continuous (like Navier-Stokes) and describe most cases adequately - except at surfaces. For instance, Rn gas is often carried by viscous air flow through porous media, yet significant number of Rn atoms are stuck to surfaces.
3. Both approaches are needed and have to be "married", at varying proportions, in order to describe fully the often anomalous data.
4. The magnitude and nature of the anomalies is so vast that an addition of a positive exponent with distance to the usual negative ones appears a plausible step.

3. How to get a positive exponent into the microscopic expressions for transport. The basic ideas have been described previously [7, 8]. However, it is useful to recapitulate the key arguments here.

When stresses (thermal or mechanical) force a particle out of a 1-D potential well it reaches a state when $E \to 0$, and the solution is a discrete energy level, sin or cos

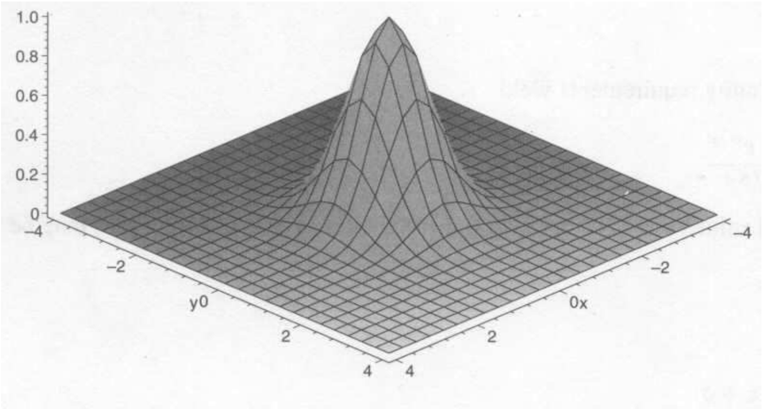

FIG. 3.1. $|\Psi|^2$ *in 2-D in the absence of a crack. It is meant only as a qualitative illustration and it is not to scale.*

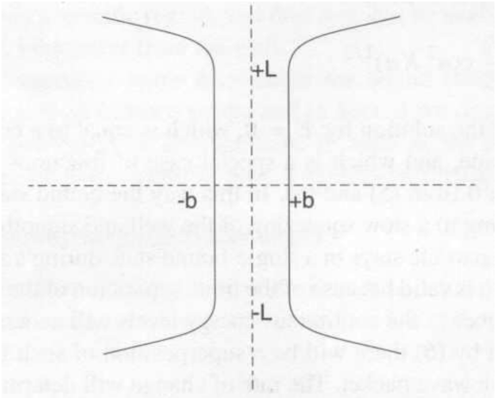

FIG. 3.2. *The simplified geometry of the crack, length* $= 2L$ *and the width* $= 2b$.

inside the well, and $\exp(-kx)$ outside (k is a wave number). When $E = 0$ the solution outside the well is constant. Solutions for $E > 0$ are again sin or cos except they are no longer discrete, in fact there is an infinite number of levels. Instead of a single wave function there will be a superposition of such functions with k distributed over an interval, resulting in a wave packet. The rate of squeezing will determine the width of the packet, slower deformation leading to a greater width, and vice versa. As it is shown in detail in ref. [8], the bound states may rise toward zero energy owing to squeezing of the well and then smoothly enter, passing through the $E = 0$ stage, the positive energy region. When in 2-D (or in 3-D, in fact the sufficient condition is that it is in more than 1-D), the Schrodinger equation for $E = 0$ reduces to the Laplace equation

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} = 0, \tag{3.1}$$

and the solution is as shown in Figure 3.1. Note that the highest probability of finding the particle is around the original location of the potential well.

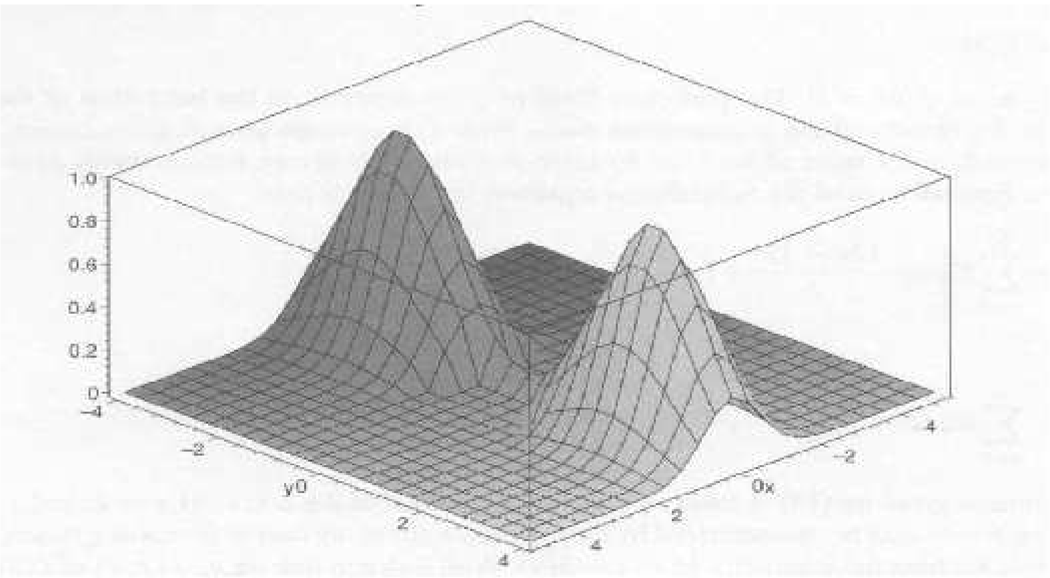

FIG. 3.3. $|\Psi|^2$ *in 2-D when a crack is present. It is meant only as a qualitative illustration and it is not to scale. The crack of width* $2b$ *and length* $2L$ *is located between the peaks along the y-axis*

When the boundary conditions are such that the potential well is located in a finite length crack (Figure 3.2) with impermeable walls (supplied by employing the Pauli Exclusion Principle) surrounding it in one dimension, the solution looks like shown in Figure 3.3. Note that there are peaks of the highest probability of finding the particle on the outside of the crack.

In general, what appears best to describe the situation of anomalous fluxes would have the following form:

$$FLUX(x,y) \approx \exp(-y) + \epsilon\exp(+y), \tag{3.2}$$

where usually $\epsilon \ll 1$ and it indicates that such condition occurs in the real world only rarely; however, at phase transitions when thermal stresses are large, it can happen that $\epsilon \gg 1$. The first term is the conventional surface diffusion (hopping) term; the second is the one described – in an exact form for a square well in 2-D – in Holub and Smrz [8].

4. Discussion. Common to all these unexpected phenomena we are faced in surface diffusion and hopping is penetration of certain number of particles (not only *Rn*) over large distances through tortuous media, without apparently exchanging energy between the particles and the surfaces, which is the gist of the action of the Pauli Exclusion Principle at low momentum transfer regimes. In classical physics, when gaseous particles are penetrating through filters, or penetrating through porous media, they interact with walls of the pores. It is true that *Rn* atoms rarely get stuck, but they are exchanging (small amounts) of energy nevertheless with the porous medium. It can be diffusion, or advective flow, which both are quite slow. The acting force is usually the short-ranged van der Waals force. Yet, as it is put forth in this paper, there exists a long-range transport that quickly penetrates through porous media. There is only one mechanism that can explain this anomaly - the avoidance of obstacles without exchanging energy - and it is the Pauli Exclusion Principle. As said in Holub and Smrz [8], "...the crack does not have to be necessarily straight or in a vacuum for the effect to take place". In other words, a bound particle, similar to bound electrons in an atom, "knows" where not to go since there already is another particle (an orbital electron), regardless whether it is impermeable wall or a molecule of air. It should be noted there is a Coulomb interaction between electrons in atoms, just like there is a short-ranged van der Waals interaction between the particles in a situation within a crack; yet it has no effect on the avoidance mechanism.

5. Conclusion. Experimentalists have accumulated enough data to show that the continuum (bulk) approaches do not describe the transport data fully. Furthermore, the nature of the anomalies is such that, in the transport equations, a positive exponent with the distance, should be included in order to better reconcile the theory with the data. As we showed on the example of Rn transport through porous media, the discrepancies are literally many orders of magnitude if the measured values are used in the formula they use (eq. (2.1)). In our suggested approach to "surface diffusion" and "hopping", via Schrodinger equation for $E = 0$, for a particle originally located in a shallow potential well, and in a finite length crack, seems a plausible approach to bring such a positive exponent into the theory, as sketched in eq. (3.2). Then it becomes similar to a wave guide problem. The probability of localization of the particle increases with the distance from its original location. Together with the conventional microscopic and the bulk approach, the addition of the positive exponent may remove the anomalies. Experimentalists and engineers are rarely capable of coming up with equations that could handle the problem of "marrying" the disparate bulk and microscopic - increasing with distance - approaches. The help of applied mathematicians therefore appears essential.

Acknowledgements. The first and second authors were partly supported by the project "Applied Mathematics in Technology and Physics" MSM 6840770010 of the Ministry of Education of the Czech Republic. Participation in this seminar was possible due to the support of the Internal Grant of the Czech Technical University in Prague, No. 0415314.

REFERENCES

[1] A.B.Kersting, D.W.Efurd, D.L.Finnegan, D.J.Rokop, D.K.Smith, J.L.Thompson, *Nature 397, 56* (1999)

[2] B.D.Honeyman, *Nature 397, 23* (1999)

[3] V.Balek and J.Tolgyessy,*Emanation Thermal Analysis*, Akademiai Kiado, Budapest (1986)

[4] I.N.Beckman and V.Balek, *J.Thermal Anal.Calorimetry 67*, 49 (2002)

[5] A. Lightman and O.Gingerich, *Science 255, 690* (1991)

[6] M.Ito and D.Shooter,*Atm.Env. 38, 899* (2004)

[7] R.F.Holub, M.G.Reimer, B.D.Honeyman and P.K.Smrz,*J.Radioanal.Nucl.Chem. 249, 239* (2001)

[8] R.F.Holub and P.K.Smrz,*Can.J.Phys. 80, 755* (2002)

[9] I.Vattulainen, J.Merikoski, T.Ala-Nisila and S.C.Ying,*Phys.Rev.Lett. 79, 257* (1997)

[10] J.H.Cushman and T.R.Ginn,*Water Res.Research 36, 3763* (2000)

[11] Z.Toroczkai and E.D.Williams, *Phys. Today, 24*, December 1999

[12] M.G.Lagally, J. Vac. Sci. Technol. A, *Vacuum, Surfaces, and Films, 21, S54* (2003)

[13] M.Bixon, B.Giese, S.Wessely, T.Langenbacher, M.E.Michel-Beyerle and J.Jortner, *Proc.Nat.Acad.Sci. 96, 11713* (1999)