Témoignage de P. Evesque

sur les politiques éditoriales de journaux

« scientifiques » à « comité de lecture a priori »

Sur quelques exemples de problèmes éditoriaux et d'articles refusés

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Conseil du laboratoire MSSMat, umr 8579 CNRS, 23 Juin 2011
Questions diverses

Avant propos et Résumé :

Il m'a fallu 10 années pour faire admettre la nécessité de ce témoignage aux intances du cnrs. J'espère que le moyen que j'inaugure sera repris par d'autres acteurs de la recherche scientifiqe.
Mon témoignage, comme toute mon action passée sur le problème des éditions, n'a pas pour but de dénigrer le moyen principal de communication scientifique mais plutôt de l'améliorer.
En effet, les dérapages que l'on peut voir ça et là sont plutôt liés à une politique de secret mal placée et engendrée par la nature « correspondance privée » de la communication entre auteur et journaux.
Il est cependant anormal que cette correspondance, parce qu'elle est de « nature privée », ne puisse pas être assujétie sérieusement et riogoureusement aux règles de la déontologie scientifique et qu'on ne puisse pas affirmer que cette déontologie est réellement respectée dans la pratique par les groupes de presse, les évaluateurs, les systèmes de gestion de la recherche. Il est en plus anormal à mon sens que les financeurs de la recherche ne puissent/doivent pas vérifier la qualité de ces échanges bien qu'ils soient les financeurs réels de l'édition scientifique, et qu'ils ont donc une responsabilité importante dans le maintien de la déontolgie. (Voir ce qu'en dit la commission européenne.)

De fait, on note une dérive alarmante (i) sur le nombre de publications redondantes ou fausses, (ii) sur l'utilisation d'argument faible ou fallacieux de la part de référees, et (iii) d'un lobbying actif contraire à une idée correcte du principe d'indépenndance si le système global n'est pas pensé dans son ensemble.
Ce dernier point est d'autant plus exact qu'on voit chaque jour paraître de nouveaux journaux, des mails d'éditeur proposant leur service… Tout ceci est mis à profit par les financeurs pour faire croîre à la qualité de la recherche qu'ils subventionnent.
Enfin ces financeurs n'hésitent pas à demander que les investissements soient partagés à plusieurs pour limiter probablement leur responsabilité et faire porter la responsabilité sur les lobbying actifs. Il n'empêche que sans financement ce lobbying serait inefficace, et donc nul. C'est donc du devoir des financeurs d'imposer ou de faire imposer une certaine transparence dans les services éditoriaux comme dans les services d'évaluation.

Pour que mon témoignage soit le plus impartial posible, j'ai décidé de décrire tous les cas pour lesquels j'ai essuyé un refus de publication. Ceci dit, j'intègre aussi à ce témoignage (i) d'une part une revendication sur la nécessité de transparance des évaluateurs et de la prise en compte de leur propre intérêt par les organismes financeurs, ou d'autre part (ii) des faits m'ayant pas lésé personnellement mais dont j'ai été témoin comme referee, qui ont pu léser d'autres (voir Affaire PRL Thomas-Squire), ou pour lesquels j'ai été témoin (en temps que lecteur) (voir affaire Makse , Nature) .

Comme je l'ai dit, pour moi la base principale de la communication entre scientifiques est l'article, car c'est un procédé relativement concis et précis de stockage de l'information. Le but d'un article de recherche scientifique n'est pas obligatoirement d'élucider complètement un point précis, mais plutôt bien souvent d'en donner quelques idées claires et/**ou prometteuses**. La rigueur du traitement scientifique nécessite cependant dans ce cas de montrer (i) les dangers du traitement ou du procédé, (ii) la limite de validité des raisonnements ou des analogies, et (iii) de tester les hypothèses et les résultats par rapport aux faits expérimentaux (dans le cadre des **sciences naturelles** cette dernière partie est effectivement une nécessité). On observe malheureusement que cette dernière obligation est trop souvent baclée pour laisser transparaître un lobbying de bon aloi… Un scientifique sérieux ne peut pas accepter cet état de fait. C'est pourquoi je me suis mis en marge des revues à comité de lecture classique, qui dérogent trop souvent à une volonté de confronter les points de vue.

Souvent l'avancée scientifique n'a lieu qu'après des débats ou des afrontements. Lorsque la divergence entre les tenants de différentes théories ou de pratiques et d'analyses est trop grande, il faut bien entendu des espaces de discussions et de confrontations. Ce sont les congrès. Bien trop souvent ceux-ci sont utilisés par les participants **pour parler**, pour se voir entre personnes se comprenant, mais peu restent aussi pour écouter les autres et réellement échanger. C'est pourtant un des points clés de la recherche pluridisciplinaire, mais c'est aussi le rôle du lobbying de combattre les autres lobbyies, ou de créer un autre lobby conjoint... C'est donc aussi aux managers de la recherche de gérer ces problèmes....

Dans ces conditions comment peut-on espérer que l'enseignement puisse s'améliorer, si les professionnels de l'enseignement et de la recherche n'arrivent pas à autogérer leur relations parce que le système managerial est inefficace, voir générateur de conflits d'intérêts mal placés. On ne montre là aussi qu'un système cacophonique, plus proche d'un « monothéisme » de bon aloi, qui change plus vite que les gouvernements... et qui ne posent pas les vrais problèmes.

Les systèmes étudiés par les scientifiques sont de plus en plus complexes et les phénomènes aussi ; de là on pourrait penser qu'il n'est plus possible de définir une vérité tangible. C'est possible dans beaucoup de cas, mais ces systèmes ne sont plus étudiables par les "sciences naturelles" ; ils doivent donc sortir du domaine scientifique expérimental: le but ultime du "scientifique naturaliste" est d'améliorer nos connaissances, jusqu'à pouvoir décider.

Le travail de chercheur est un travail compliqué qui ne pourra se maintenir que si l'on cherche à maintenir une déontologie certaine ; les dérives à court terme sont aisées et et engendrent des gains productifs, que l'on paie(ra) à long terme comme tout système basée sur la "cavalerie". Nos chefs d'entreprises sont redevenus maîtres récemment dans ce domaine, bien souvent à leur dépend, ou plutôt au dépend de leur société, de leurs salariés et de leurs actionnaires.
La déontologie scientifique a **toujours** été difficile à faire respecter; même lorsque l'on cherche réellement à l'appliquer, il n'est pas sûre que l'on n'y déroge pas ; mais en plus il est souvent beaucoup plus efficace de faire croire à la grandeur de l' « établissement[1] », plutôt qu'à celui du petit trouble-fête astucieux, ou à l' « imbécile » de génie. Du coup l' « établissement » scientifique a à se méfier de lui-même.
Pour faire respecter cette déontologie il faudra créer un code légal. Ce code n'existe plus à leur actuel: je ne vois plus les sociétés savantes menacer d'exclusion leurs membres ne respectant pas la déontologie. Bien au contraire, j'ai envoyé dans les années 2000 ma démission à la SFP pour manquement à faire respecter cette déontologie, personne ne s'en est ému.
Pour pouvoir établir un code, il faut établir certaines déficiences du système. C'est le but que je poursuis ici en détaillant certaines "affaires". Les principes de la déontologie scientifique a été décrite par de nombreuses sociétés savantes; elle transparaît aussi dans le code français[2], ou via les recommendations de la Commission Européenne[3].

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[1] J'utilise ici le mot « établissement » par référence aux grandeurs d'établissement de Pascal, cf. Poudres & Grains 11(1) 1-5 (2000), mot qui est proche de l'"establisment" anglais. Et voilà comment on trahit l'antériorité d'une citation! Et que l'on fait renaître B. Pascal au 21ème siècle!!

[2] voir le code de la recherche, Légifrance, en particulier à travers la mise en place des établissements de recherche scientifique tels que le CNRS.
http://www.legifrance.gouv.fr/affichCode.do?cidTexte=LEGITEXT000006071190&dateTexte=20110311

[3] Voir le texte "RECOMMANDATION DE LA COMMISSION du 11 mars 2005" concernant la charte europeenne du chercheur et un code de conduite pour le recrutement des chercheurs (Texte presentant **de** l'intérêt pour l'EEE , cote: 2005/251/CE)

Affaire éditoriale article B.Thomas-A.Squires (PRL 81.574 (1998))

Phys.Rev.Lett. (PRL) m'a demandé un rapport sur l'article joint. L'article est tout à fait valable à mon sens.
Le second référee a été de l'avis contraire et a surtout demandé que soit publié un grand nombre de photos démontrant l'effet. Celles ci ne pouvaient effectivement pas tenir dans la taille de l'article. Il a fait aussi d'autres critiques ; il a donc systématiquement et plusieurs fois cet article à la publication.

L'article a été jugé en appel par PG de Gênes ; aucune sanction ne semble avoir été requise envers ce « second » référee.

Pourquoi ?
Peut-on vérifier ?

Support for Faraday's View of Circulation in a Fine-Powder Chladni Heap

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Faraday, like Chladni, saw fine powder collect in a circular heap at an antinode of a vibrating plate. In each vibration cycle, the heap experiences a free-flight interval during which pressure gradients in the heap's interior drive powder centerward, as Faraday proposed. When heap-floor collision terminates flight, pressure gradients reverse direction; but passage of a compaction front has locked particles against further movement. Before a next flight interval, an increase in porosity will reverse the compaction that accompanied heap-floor collision. [S0031-9007(98)06672-1]

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Following Chladni's lead, Faraday [1] placed coarse or powdery matter upon a horizontal vibrating plate. He saw the matter migrate to form isolated "Chladni heaps," coarse matter accumulating at nodes, and fine matter at antinodes. Faraday attributed the difference in these behaviors to the absence or presence, respectively, of the influence of air currents created by development of a partial vacuum between plate and heap. In a fine-powder heap, seeing powder move down its conical surface and disappearing inward at its edge, he reasoned that air currents pull particles toward the heap's center and force them upward thereat. Using small bits of paper to deflect air flows, Faraday altered locations of his fine-powder heaps, in support of his argument. Observing the plate in a partially evacuated chamber, he saw them at their usual positions at 13 kPa; at one-half this pressure, powder migrated to nodes, like coarse matter.

Renewing their interest in vibration of granular matter, physicists have discovered nonlinear dynamical phenomena possibly relevant to areas of physics as remote as semiconductors, earthquakes, and clustering of galaxies [2–5]. As recent reviews [2,3] comment, however, the activity has cast doubt upon Faraday's view of the role of air currents in driving fine-powder Chladni heap circulation, several research groups [6–12] offering alternatives thereto.

When these came to our attention, we reviewed the large engineering literature on vibrated granular beds [13] expecting to identify evidence confirming Faraday's thought, but no one seems to have set out to prove Faraday right. From review of our own data [14–18] and their revisualization [19], we can now offer "proofs," by-products of effort directed toward understanding vibrated-bed heat transfer [20] and fashioning a microreactor disclosing the effect of axial gas dispersion upon heterogeneous reaction outcomes [21].

In a glass-walled vessel (25.4 mm × 162 mm in plan, 60 mm in height), we subjected "two-dimensional" granular beds to vertical sinusoidal vibration at 25 Hz [14]: $z = a_0 \sin \omega t$, where z = displacement, a_0 = maximum amplitude, $\omega = 2\pi f$, t = time, and f = frequency. Unless specified otherwise, all data herein are for alumina beads at 30-mm average bed depth, $a_0 = 1.59$ mm, $f = 25$ Hz, and $\Gamma = 4$ ($\Gamma = a_0\omega^2/g$, maximum acceleration over gravity) [22]. We can report phase angles to $\pm 1°$ [14]. Under strobe lighting, our setup permits ready viewing of heap-floor separation (lift-off) and what we call "Faraday circulation": slow powder movement centerward in the bed's interior, accompanied by rapid return flow from peak to sidewall, occurring in a relatively shallow, rarefied surface zone [14,23].

Although others [6,24–27] appreciated the importance of gas floor-pressure data for understanding vibrated-bed dynamics, we are the first, to our knowledge, to measure floor pressures at multiple locations for many types and sizes of particles [17,18]; we record data at 1° phase-angle increments. Qualitative capacitance data [26,28] suggested that beds expand at lift-off. Our pressure data permit us to confirm and quantify the effect. We have discovered that a bed does not lift when a net upward force first acts upon it: e.g., a bed of 177-μm alumina beads lifts at ~93°, while the first action of the net upward force upon the bed occurred ~78° earlier. During this lag, it imbibes a quantity of air that we can estimate from our pressure data, causing it to undergo an absolute porosity increase of ~0.8%.

This increase seems to be required to release particles from a compacted condition in which forces acting upon the particles are insufficient to initiate particle motion in shear: We report sighting a compaction front (inclined at ~28° to horizontal) traveling across the bed from the sidewall centerward during bed-floor collision. In cinematographs taken at 2500 frames per second (fps) and viewed at 25 fps, we can see the front in particles 177 μm and larger [29]. Cinematographs at 1250 fps reveal that powder circulates in start-stop fashion: Except in the surface layer, a particle moves only during bed flight.

Figure 1 gives the status of a center-high 177-μm alumina bed (a Chladni heap truncated by side walls) at two phase angles during flight. Shortly after lift-off, at 105°, downward drag per unit bed weight is greater near the wall than at the center. The discrepancy has two effects, each contributing to maintenance of the heap. First, downward drag works against the "throw" the bed

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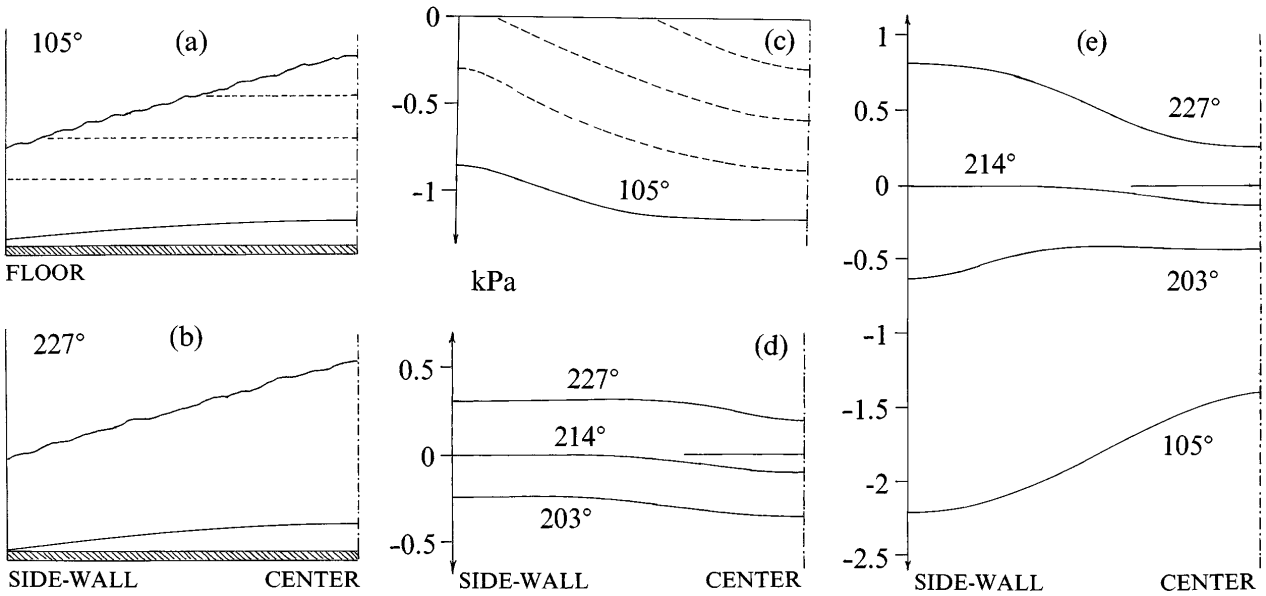

FIG. 1. Status of "two-dimensional" center-high vibrated bed (a slice of a truncated Chladni heap) at selected sinusoidal phase angles during free flight. Bed = 177-μm "Master Beads" (crude alumina, nearly spherical), 25.4 mm $\times$ 162 mm in plan, 30 mm in average depth; vibration at 25 Hz; vibrational intensity $\Gamma = 4$ (maximum acceleration divided by gravity). Diagrams represent left one-half of the bed. Curves of gas pressure (departure from atmospheric in kilopascals) are drawn to pass through three measured values (at wall, center, and halfway in between) and to display horizontal tangents at wall and center (no gas can flow across these boundaries). For reference in (c), dashed horizontal lines in (a) are drawn at $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ distance from peak to bottom of bed at its center. (a) and (b) give bed profiles at designated phase angles: (a) early in gap formation; (b) bed-floor collision just commencing (gap just closed at side wall). In (c) and (d), solid curves: floor pressure; in (c), broken curves: pressure profiles along dashed horizontal lines in (a). (e) plots a dimensionless ratio, vertical drag divided by bed weight (drag is downward if negative).

receives from the floor; eventual gap height is less at wall than at center. Second, some gas entering the developing gap near the wall must flow horizontally centerward within the gap. A horizontal pressure gradient at the floor drives this flow, as Faraday hypothesized. For the bed of Fig. 1, when floor pressures are negative, gas compressibility effects upon a vertical pressure profile are negligibly small [24]. To obtain a pressure within the bed along such a profile, linear interpolation between pressures at floor and bed surface provides a good approximation. Using such interpolation, we have derived the broken curves in Fig. 1(c), which correspond to horizontal dashed lines in Fig. 1(a). Horizontal pressure gradients within the bed easily move the "flying" alumina beads centerward. Floor pressures become positive shortly after 214°. Thereupon, as Fig. 1(e) illustrates, an upward drag cushions the bed-floor collision, which just commences at ~227°.

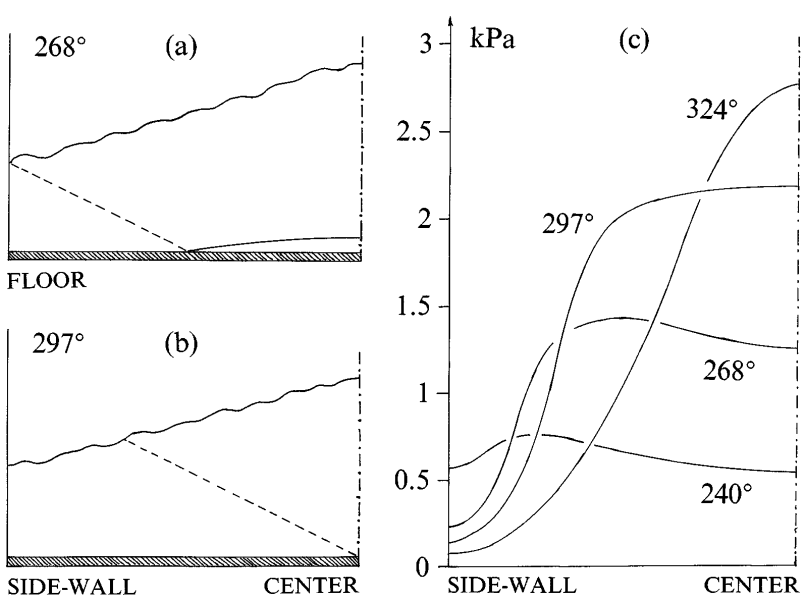

FIG. 2. Status of center-high vibrated bed at phase angles during gap closure. (See Fig. 1 caption for bed description and vibration parameters.) (a) and (b) Show bed profiles at two phase angles: gap closed halfway to center and gap just closed at center, respectively. Dashed lines indicate positions of compaction front. (c) Gives approximate floor pressure profiles at designated phase angles.

Figure 2 illustrates the bed status during bed-floor collision. At a given point along the floor, the compaction front's arrival is simultaneous with gap closure. Ahead of the front, gradient in floor pressure is centerward. Behind, the gradient reverses direction, but a concomitant gas flow cannot cause the compacted particles to move. At a given point, floor pressure peaks later than gap closure: The lag is 13° at the wall, 29° midway between wall and center, and 27° at center. These delays can be understood: Because the compaction front is inclined toward the sidewall, the front arrives earlier at a given point along the floor than at an elevation within the bed above the given floor point. Compaction of particles at the higher elevation drives gas downward as well as toward bed surface; eventually, gas driven downward reaches the surface, horizontal pressure gradients behind the compaction front having first driven this gas laterally, toward the wall.

While adding particulars, Figs. 1 and 2 confirm Faraday's basic ideas: that circulation in a fine-powder Chladni heap is aerodynamically driven, primarily while floor pressures are negative (between 93° and ~214° in our example).

Hypothesizing an inclined "condensation front" analogous to our compaction front, Laroche *et al.* [6] suggested particles move centerward by an "internal avalanche flow" [7] sliding downward along the hypothesized front. We see no such avalanche in high-speed cinematographs. *From the onset of free flight,* long before a compaction front appears, we see particles moving with largely horizontal components of velocity centerward. Afterward, behind the front, particles are stationary. Cinematographic evidence also rules out the suggestion [12] that heaping arises from positive pressure effects accompanying gap closure.

The discussion so far has focused upon 177-μm alumina beads. We deal briefly with beads of smaller and larger size.

At 30-mm average depth, although no gap forms beneath 88-μm beads, they form a heap displaying Faraday circulation during a "weightless" interval. Floor pressure data [30] confirm the presence of the driving gradients and reveal cyclic variation in porosity (an absolute ~2% rise and fall). Pressure data even disclose passage of the "compaction front" that we do not see in a cinematograph.

Before lift-off, 707-μm beads undergo an absolute porosity increase of ~0.13%; they exhibit a horizontal compaction front originating at floor and traveling upward. In 272-μm beads, the front is inclined at ~14° to horizontal. Fronts seen cinematographically may be traveling passive failure planes: Between $\Gamma = 3$ and 5, their angles are constant, each a fundamental property, apparently, of particle and orientation of principal stresses. Although Faraday circulation is not evident in coarse matter, nevertheless, it will form a heap slowly: 505-μm alumina beads require 3 min at $\Gamma = 2$. In all granular solids, heap slopes approach a dynamic angle of repose as Γ approaches one from above [6,12,17].

Withdrawing gas (air, helium, or propane) from closed chambers housing vibrated beds, Pak *et al.* [12] saw sharp declines in heap slope. Calling attention to the nonlinear partial differential equation for pressure in one-dimensional vibrated-bed theory, they suggested that the declines occur when a term (with pressure in the denominator) can no longer be safely ignored when the equation is linearized [26,31]. Mean-free-path calculations disclose another possibility. In each experiment, upon progressive reduction in pressure, a decline in slope coincides with departure from viscous flow [32], first, to slip flow with progressive reduction in viscous drag, and, finally, to molecular streaming and zero drag. Slopes must decline when within-bed gas flow loses its power to shape and maintain a heap and to cushion bed-floor impact.

All particulates that we studied (10 to 707 μm) experience zero drag at 8 Pa. All behave just the same. There is no heaping. All display a gap. All exhibit a friction-driven circulation characteristic of coarse powders at all pressure levels [33]. All are noisy: We hear the sharp crack of each uncushioned bed-floor collision.

Some researchers [9–11] reported upon nonsymmetrical, wall-high heaps. Evesque [11] pointed out the practical impossibility of establishing strictly vertical vibration, unbiased by horizontal velocity components. If such components are large, formation of a symmetrical, center-high heap may become an impossibility. In our work we succeeded in reducing the effect of horizontal velocity components to a degree allowing useful study of center-high heaps. An "indicator" glass duct [21] displaying substantially uniform distribution of powder in the "coherent-expanded" state [15] provides an acutely sensitive indication that bias in the vibration is sufficiently small such that symmetrical, center-high heaping can be reliably achieved.

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[22] Although $\Gamma = 4$ is a modest value from an engineering standpoint, period doubling at high Γ can complicate heaping studies [7,17,18]. Important results, however, have arisen from work at Γ near 1.0 (e.g., [6,12,15]).
[23] Photographs [14] of 177-μm glass beads at selected phase angles under stroboscopic top lighting show how this zone's existence depends upon a sharp upward rush of air across bed surface during heap-floor collision. Lateral surficial flow varies along with expanded zone thickness, each reaching a maximum just after the collision. The zone then shrinks twofold to threefold before its renewal in the following cycle.
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[29] We will provide experimental details: M. O. Mason, B. Thomas, R. T. Chan, and A. M. Squires (to be published). A viewer best perceives the front when situated well away from the projected image. Although efforts to use frame-by-frame analysis, both by eye and with the aid of an image analyzer, failed to find the front, its sighting is not a subjective matter. A number of observers (including persons unfamiliar with our research and its objectives) speak up simultaneously when the front appears. Their visual response may reflect the sudden fixing-in-place of particles behind the front, these particles having just earlier been in motion. The front angle can be estimated if one observer holds a rod up to the image at about the right angle, while another across the room gives instructions for correcting the angle during successive passages of the front.
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Affaire éditorial Nature (1997) /Article Makse et al. (Nature386,379,(1997))

Cet article présente un certain nombre d'effets sur la ségrégation comme s'ils étaient inconnus du scientifique, et donne une explication du phénomène.
Malheureusement, Ces fait sont connus depuis longtemps. Je demandais ici que l'erreur éditoriale soit reconnue.
Cela n'a pas été le cas.
J'ai réécrit plusieurs lettres cette année (2010-2011) pour demander la permission de mettre cette correspondance sur le Web. Nature n'a rien répondu.

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Objet : our correspondence EX7099 ; 22/July/1997, and related

Dear Editor,

I confirm my e-mail on 24/2/2011. I would like to put on the web few editing problems I encountered, or that others have encountered.
I am interested in the reproduction of our correspondence EX7099 22/July/1997, and related.
Do you see a downside.
From the human point of view, time has done its work, and concerns that can not be scientific.

Thank you in advance for your favorable response.

cordially

Pierre Evesque

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Voir le rapport CNRS de Pierre Evesque 2011, Annexe 10, p. 69-72

Autre problème rencontré avec Nature:

Je pourrais aussi traiter du cas de l'article: G. Metcalfe, Tr. Shinbrot, J. J. McCarthy & J. M. Ottino; Nature 374, 39-41 (2 March 1995); Avalanche mixing of granular solids, qui traite d'un problème de ségrégation grnulaire dans un système (bidimensionnel) cylindrique et générant des avalanches.
Une petite phrase m'était apparue incompréhensible, et ai demandé l'explication aux auteurs, ou à leur collaborateur (Khakhar?).
En quatre lignes ils m'ont expliqué, preuves à l'appui à partir de l'équation de Navier-Stokes 2d et de son analogie hamiltonienne, qu'un système 2d à écoulement continu ne pouvait pas générer un mélangeage car les lignes du courant ne peuvent pas se croiser en 2d, et que ce système ne générait donc que de la ségrégation irréversible ; en d'autres termes, il fallait introduire de l'intermittence (d'où les avalanches) pour que le mélangeage soit efficace.
C'est ainsi que j'ai compris la vraie raison de leur propos, l'intérêt réel de leur article; et ils m'ont démontré qu'ils connaissaient bien mieux le problème que ce qu'ils en disaient dans l'article.

À leur décharge, cet article n'aurait probablement pas pu paraître dans *Nature* sans cette présentation. **À croire que Nature veuille devenir le spécialiste de la "désinformation scientifique"**.

Pas d'autre information

Ceci termine l'exposé des quelques problèmes litigieux dans le principe de sélection des articles par les revues.

Pour en faire une revue détaillée, mieux vaudrait demander l'expertise des évaluateurs professionnels, des revues et des personnes ayant eu à souffrir de ces pratiques. J'expliquerai par exemple un cas d'expertise où la déontologie n'a pas été respecter par le sevice évaluateur: le CNES et l'affaire dynagran. Encore que là je n'insisterais pas sur certaines pratiques très mauvaises permettant aux managers de dénigrer les meneurs de projet qu'ils sont sensés défendre, et qui permettent ainsi aux partenaires/concurrents internationaux des mêmes meneurs nationaux d'emporter les positions.
La France semble très friante de cette pratique permettant de faire croire au fairplay de la hiérarchie française quand celle-ci est peu impliquée dans le projet, ou lorsque cele-ci connait moins bien le projet que les leaders qu'elle est sensée appuyer et que les autres hiérarchie en fasse d'elle.

Problèmes éditoriaux personnels rencontrés

par P. Evesque

Transition d'Anderson : essai J. de Phys. France (1983) #3.0082

Cet article sur la localisation d'Anderson a été écrit en 1983 pendant ma thèse d'État. Il rappelle un article publié par PG de Gênes en 1959, pour qui montre que la localisation d'Anderson se caractérise par une percolation dans certains cas où le désordre est non diagonal. Art qui était passé sous le silence dans la littérature.
Après une étude de ces rapports assez extensive et après discussion avec Shlomo Alexander, nous avons conclu que les deux rapports étaient contradictoires, l'un disant que l'article était juste, mais le résultat connu, donc l'article est non publiable car connu; l'autre disant au contraire que les conclusions de l'article étaient fausses, ce qui est bien connu, donc l'article est aussi non publiable car basé sur des idées fausses.

La conclusion de l'éditeur était donc que cet article ne pouvait pas être publié.

Je regrette cette position éditoriale qui est visiblement néfaste à un vrai dialogue scientifique correct. Ceci dit, j'ai accepté le verdict, et ne pas pousser plus loin la volonté de publier : « les vrais chercheurs professionnels doivent être au courant des informations disponibles ».

Par ailleurs, j'ai discuté de cet article avec A. Blumen ; d'après mes souvenirs, il en a fait une simulation numérique, avec G. Zumofen, pour démontrer les effets que je calcule dans cet article qu'ils ont publié.

Lettres au Journal de Physique
manuscrit n° 3.00 82
reçu le

A DIFFERENT APPROACH TO THE ANDERSON TRANSITION IN THE EXCITED STATES OF DOPED CRYSTALS

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Résumé

Les états excités des systèmes expérimentaux où la transition d'Anderson est généralement recherchée, peuvent être décrits par le modèle de l'alliage binaire. Après avoir rappelé que ce modèle peut conduire à une coïncidence en énergie des états délocalisés et localisés, on décrit un système expérimental ne présentant pas cet inconvénient et une expérience propre à tester la longueur de cohérence des états électroniques.

Abstract

The binary alloy model is generally appropriate to describe the experimental systems where the Anderson transition in the excited states is searched for. It is recalled that, in this model, delocalized and localized states can stand at the same energy. We describe another system which does not display such coïncidences. Moreover, an experiment which tests the coherence length of the states is described.

PACS Nb : 71.55.J , 71.35

Since the Anderson pioneering work /1/ has demonstrated the existence of delocalized states for sufficiently small disorder in random lattices, a lot of experiments have been attempted in order to detect such a transition for the excited states of impurities in either organic /2/ or inorganic /3/ crystals. This research field has been stimulated by R. ORBACH /4/ who predicted a pure exponential desexcitation behaviour for the delocalized states in the presence of supertraps which should be different from the laws expected for small migration /5/.

However, LORING et al theories /6/ predicted also such an exponential behaviour for sufficiently fast incoherent energy migration between donors states. Consequently, it should be difficult to demonstrate which theory has to be applied when an exponential behaviour is observed.

Moreover, in the case of a coherent motion, as a lot of delocalized states can only be excited, actually a sum of exponentials should be expected which can finally exhibit a non exponential behaviour. Another more important problem arises when extended and localized states stand at the same energy : the delocalized states cannot be any more excited selectively and the exponential desexcitation criterium cannot be checked any more.

As it will be proved in the first part, this last difficulty is to be expected for the generally studied system which is similar to the binary alloy model. Then, it will be argued that a system corresponding more accurately to the Anderson one, can be realized using a set of different isotopes.

The last part of this paper will be devoted to the description of an experiment which is designed in order to provide a good test for the delocalization and the extension of the wavefunctions.

First, we will recall the definition of the Anderson transition problem. This one is based on an hamiltonian which can be written as :

$$\mathcal{H} = \sum_i \varepsilon_i \, |\psi_i\rangle\langle\psi_i| + \sum_{i,j} V_{ij} \, |\psi_i\rangle\langle\psi_j| \qquad (1)$$

where $|\psi_i\rangle$ stands for the electronic wavefunction of the site labelled i, at energy ε_i ; this energy can be distributed randomly and this distribution leads to the so-called diagonal disorder. V_{ij} is the coupling strength between site i and site j and can be either short or long range. A disorder on this V_{ij} is called an off-diagonal disorder.

For sake of simplicity we will limit the discussion here to the case of short range interactions such as exchange ones and of crystals made by a mixture of different isotopes. This last point will cancel out the off-diagonal disorder because the V_{ij} will be unchanged through the exchange of the isotope components.

In a perfect lattice with only one kind of isotope the ε_i will be equal ; but the random substitution of one isotope by another one will lead to a random distribution of the ε_i and then to a diagonal disorder. These ε_i will change from site to site depending only on the

isotope laying on the considered site. Thus assuming a continuous diagonal disorder distribution as in Fig. 1b, will lead to the real Anderson problem where delocalized states will stand at the center of the band and localized ones on the wings, for an appropriate disorder bandwidth.

I - THE "IDEAL" ANDERSON SYSTEM

The continuous diagonal disorder can only be achieved if the crystal is made up by a large number of different isotopes, the energy of which laying very near in V_{ij} unity. Thus it is rather different from the usual approach of the "Anderson transition in the excited states" of which has been to dope the host with only one isotope or impurity and to study what was happening to the electronic wavefunctions of this isotope or impurity when concentrating it in the crystal ; moreover the energy mismatch between the host levels and the impurity ones has been chosen very large compared to V_{ij}. Then the original Anderson problem has been turned into another one because :

i) the ε_i distribution of the hamiltonian instead of being a continuous one turns out to be discontinuous and is the sum of two Dirac functions the weight of which being equal to the concentration in each isotope (Fig. 1).

ii) Since the Anderson delocalized states can only happen for sufficiently narrow distribution /7/, the total hamiltonian cannot lead to an Anderson transition : if the delocalized states exist they will mostly pertain to one isotope or to the other one, but not to the both at a first order approximation.

These features tend generally to distort the initial problem of Anderson by forgetting the host and studying only the traps, which is equivalent to introduce an off-diagonal disorder in the coupling strengths V'_{ij} between these traps : these V'_{ij} will be calculated from the V_{ij} and the V'_{ij} statistical distribution will depend on the statistical distribution of the ij distances. Actually, from a theoretical point of view, the off-diagonal disorder seems to reduce the coherence length of the wavefunction /7/ : for instance, in a 2 dimensional system any off-diagonal disorder leads to a complete localization /7,8/.

Moreover, if delocalized states still exist, they can stand at the same energy as localized ones ; such a doped crystal is actually nearly identical to the model treated by P. G. de Gennes et al /9/ who assumed an infinite energy mismatch between the host and the impurity levels. They have found that, in such a system, delocalized states only exist for concentrations larger than the percolation threshold and pertain to the infinite cluster ; the finite clusters always lead to localized states. As the finite and infinite clusters energy levels are centered on the same energy, some coincidence in energy is expected for between localized and delocalized states.

1 ph.

Therefore clearer experimental results should be expected in systems where such a coincidence would not be expected and for which the percolation phenomenum is not the leading process for delocalization. In other words, the ideal Anderson system can be achieved by the association of the two essential features previously discussed. These requirements are a continuous diagonal disorder and a small off-diagonal disorder. This can then be achieved, as mentioned previously, by mixing a lot of different isotopes (Fig. 2). Moreover, a three dimensional

lattice structure is also required in order to minimize the influence of the off-diagonal disorder /7/.

Thus, choosing an organic molecule which has a sufficiently large number of isotopes and blending these isotopes together in appropriate proportion should give the ideal Anderson system after crystallization. Changing the relative concentration in each isotope will allow to go through the Anderson transition and study the appearance of delocalized states.

II - EXPERIMENTAL APPROACH OF THE ANDERSON TRANSITION

The basic idea underlaying the following experiment comes directly from the observation of the absence of any hyperfine structure in the EPR experiments on triplet states of pure organic crystals /10/. It consists in studying the transition line width between the states of two bands which are approximately driven by the same Anderson hamiltonian.

If these two hamiltonians were strictly equal, there would be a complete one to one correspondance between every state of the first band and every state of the second band : both states of every pair will have the same wavefunction coefficients. The transition will only occur between the states of each pair. As the energy mismatch between the states of these pairs is equal to the mismatch between the two band centers, it will be independent of the pair and the transition will be very narrow.

However if the two hamiltonians are slightly different and if their difference is equivalent to an additional diagonal disorder, without any correlation with the first one, one may consider the

previous eigen states as still valid if this additional disorder is very small. In this case, the transitions will still only happen between the pairs of states mentioned previously. If the states are extended, the extension will average the additional disorder and most of these states will lay at the energy they had without this additional diagonal disorder. The line width of the transition between such delocalized states must be very narrow. On the contrary, if the states are strictly localized, no averaging of the additional diagonal disorder will be achieved and the energy of the states will be changed randomly. The transition linewidth of the strictly localized states will then be equal to the additional diagonal disorder width.

This feature should be expected for the triplet states of organic systems as described in part I. For sake of demonstration we will limit ourselves to the case of one molecule per unit cell and to the case of non zero coupling strengths V_{ij} for only adjacent molecule i and j. Then V_{ij} will also be assumed to be independent of the electronic and nuclear spins. The hamiltonian $\mathcal{H}$ of any triplet state in a magnetic field B is given by :

$$\mathcal{H} = \sum_i (\varepsilon_i + g\mu_B B\, S_{zi} + I_i\, S_{zi})\, |i, m_i\rangle \langle i, m_i| + \sum_{i,j} V_{ij} |i, m_i\rangle \langle j, m_j|\, \delta m_i\, m_j \qquad (2)$$

where $g\mu_B B\, S_{zi}$ and $I_i S_{zi}$ stand for the Zeeman and hyperfine hamiltonian. m_i and I_i are the eigen values of the electronic and nuclear spins. The energies ε_i are distributed at random. The I_i will be assumed to vary from site to site randomly but to be time independent.

Forgetting first the hyperfine structure, any eigen states of the hamiltonian /2/ can be written as :

$$|\Psi_m^k> = \sum_i a_i^k \, |i, m>$$

$$\text{with} \qquad \sum_i a_i^k \, a_i^{k'*} = \delta_{kk'} \tag{3}$$

These k eigen states will be localised if only a few of the a_i^k will be different from zero. In the opposite case, they would be extended. In this last case the a_i should be some random variable. However the a_i^k do not depend on m and the EPR transition can only occur between the eigen states $|\Psi_m^k>$ and $|\Psi_{m\pm1}^k>$ which have the same k. According to the hamiltonian property, the energy mismatch between these two states is independent of k. Thus an EPR experiment on such states will lead to an infinitely narrow linewidth.

If the disorder introduced by the hyperfine coupling is very small compared to the ε_i one and as far as one studies a system sufficiently far away from the Anderson threshold, one can consider that the electronic eigen states will be not significantly changed and that the a_i^k will be stil independent of m_i. Thus an EPR transition will only occur between the same previously mentioned states, which will be displaced in energy by δE :

$$\delta E_{k,m} = \sum_i a_i^k \, a_i^{*k} \, I_i \, m \tag{4}$$

For a k state delocalised on N sites, one should expect a mean energy displacement :

$$<\delta_{E_{k,m}}^2>^{1/2} = \frac{1}{\sqrt{N}} <|I_i|> |m| \tag{5}$$

because $a_i^k \sim \frac{1}{\sqrt{N}} e^{i\varphi_i}$ and I_i is some random variable independent of a_i.

When studying systems made up of two molecules per unit cell which have not the same orientation, some attention has to be paid in order to preserve the property of this hamiltonian (2) : Peculiarly, it is necessary to deal with a sufficiently large magnetic field in proper directions in order to act in the same way on both molecules.

CONCLUSION

By measuring directly the coherence length of the wavefunction, this method should bring a real evidence of the Anderson delocalized states : for instance, if no relaxation processes exist between the eigen states of the bands one can determine the Anderson edge by using a laser selective excitation technique associated with this experiment. Moreover, even if there are some relaxation processes, one can, in principle, determine the ratio of "delocalized" to localized states by comparing the width of the EPR line to the width of the natural hyperfine structure. An important feature relevant to paragraph I, is that this last determination can even be done in a random binary alloy where delocalized and localized states can stand at the same energy.

It should be compared to the time resolved experiments which detect together coherent and incoherent processes without distinguishing between them. Moreover, these last experiments can be disturbed by some stray effects as biexcitonic fusion and up conversion which lead to non exponential behaviours. The analysis of the hyperfine structure which gives information more directly and at shorter characteristic times, must allow a much more accurate determination of the Anderson transition.

Till now, most of the approaches to the "Anderson transition in the excited states of doped crystals" have been to dope a crystal

with an impurity and to consider the properties of the energy migration inside the energy levels of this impurity to determine the Anderson threshold. This paper is aimed at suggesting to reverse the problem : starting with a pure crystal where the states are delocalized and distorting it sufficiently largely should allow to study the localization. The randomnization which is needed in this problem can conveniently be achieved by using isotopic substitution.

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FIGURE CAPTIONS

Fig. 1 - Energy distribution of the density of states D(E) of a mixed crystal as generally studied (a), of the real Anderson problem (b). The energy scale is in V_{ij} unity.

Fig. 2 - Energy distribution of the density of states D(E), in V_{ij} unity, for the Anderson's problem (———), for a real problem simulating the Anderson's problem (- - -)

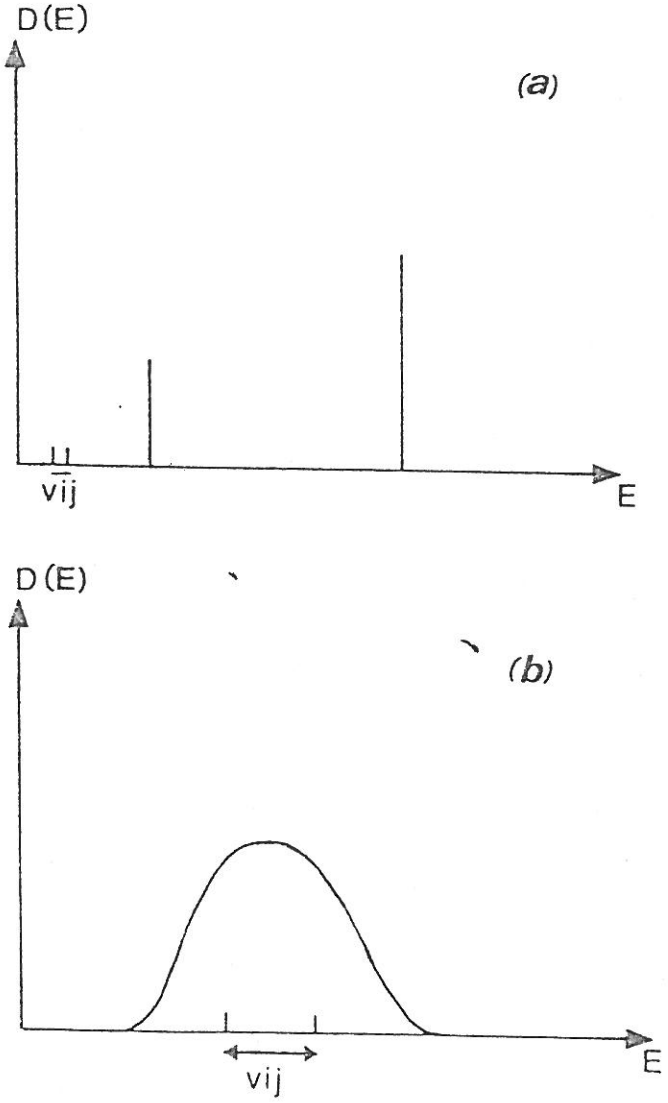

fig 1

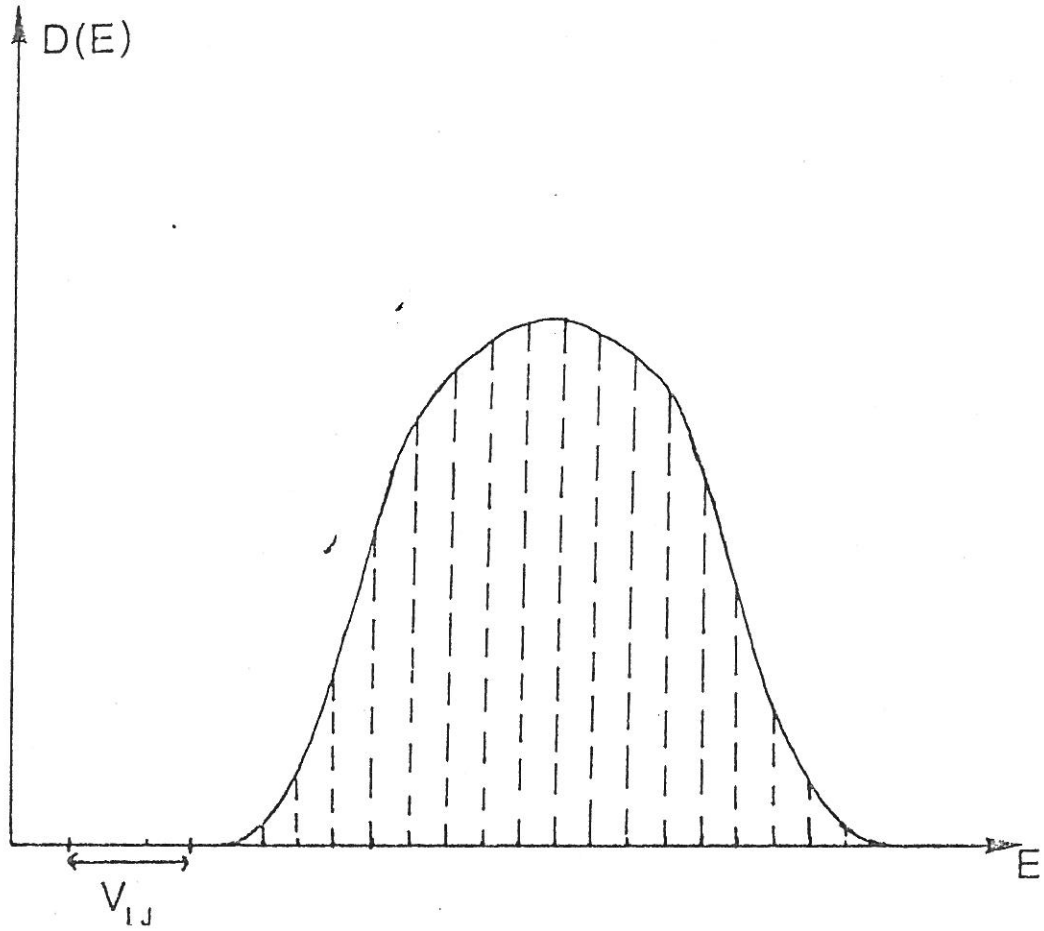

Fig 2

Société Française de Physique / Centre National de la Recherche Scientifique

Commission des Publications Françaises de Physique

Secrétariat : Bâtiment 510, Université Paris-XI, F 91405 Orsay

941.69.32 [illegible]3) et 928.71.69

11 juillet 1983

Monsieur P. Evesque
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n/réf. 3-0082

Monsieur,

Nous avons le regret de ne pouvoir accepter pour publication au Journal de Physique-Lettres votre article intitulé

"A different approach to the Anderson transition in the excited states of doped crystals"

Nous vous renvoyons ci-joint votre manuscrit, accompagné d'une copie des rapports rédigés par des physiciens spécialistes de la question choisis par la Commission des Publications Françaises de Physique.

Compte tenu des rapports ci-joints, nous ne pouvons envisager de publier votre Lettre. Si toutefois vous pouvez réécrire un article qui réponde aux nombreuses questions et critiques des rapporteurs, nous pourrions aussi évidemment reconsidérer notre position.

Nous vous prions de croire, Monsieur, à l'assurance de nos sentiments dévoués.

J. des Cloizeaux
(en l'absence de J. Zinn-Justin)

p.j.

Secrétariat de la Commission des Publications Françaises de Physique

Bâtiment 510, Université Paris-Sud, F 91405 Orsay Cedex

Manuscrit proposé pour *Journal de Physique - Lettres* n/réf. 3-0082

Auteur (s) : P. Evesque

Titre : A different approach to the Anderson transition in the excited states of doped crystals

RAPPORT

L'article "a different approach to the Anderson transition in the excited states of doped crystals" est dans la suite d'une proposition faite par R. Orbach en 1974 d'étudier la transition de localisation d'Anderson en considérant la largeur de raie des transitions optiques.

Dans la première partie, le modèle de l'alliage binaire, où le potentiel de site ne peut prendre au hasard que deux valeurs, est abordé. L'auteur affirme la possibilité qu'il existe, pour une même énergie, des états localisés et étendus. Cette affirmation va à l'encontre de l'opinion communément admise, quoique la question reste ouverte. Mais la référence citée, pour supporter cette affirmation, date d'une époque (1959) où il y avait quelques confusions entre le problème de la localisation et celui de la percolation. Elle ne suffit donc pas.

La deuxième partie décrit, sans précision suffisante, le lien entre la largeur des raies et l'extension spatiale des états propres. L'auteur conclut, sans plus de détail, que cette méthode donne accès à la longueur de cohérence des états, sans la définir préalablement. On entend d'habitude par longueur de cohérence la longueur de cohérence de phase qui reste finie, aussi bien pour les états étendus que pour les états localisés. Son étude ne saurait donc mettre en évidence la présence d'états étendus. La longueur d'intérêt dans la transition d'Anderson est la longueur de localisation, caractéristique de la décroissance spatiale exponentielle de l'amplitude des états localisés, qui devient infinie pour les états étendus.

Cet article, qui reste au niveau d'une discussion trop qualitative, non exempt d'ambiguïté (longueur de cohérence), ne me semble pas contenir assez de résultats nouveaux pour être publié comme lettre au Journal de Physique.

Secrétariat de la Commission des Publications Françaises de Physique
Bâtiment 510, Université Paris-Sud, F 91405 Orsay Cedex

Manuscript submitted for publication in *Journal de Physique · Lettres* our ref. 3-0082

Author (s) P. Evesque

Title A Different Approach to the Anderson Transition in the Excited States of Doped Crystals

REFEREE'S REPORT

Dans la première partie de cet article l'auteur critique l'emploi de systèmes de type alliage binaire dans la recherche de la transition d'Anderson. Il pourrait condenser cette partie et en venir plus rapidement au but de ce travail.
Dans la deuxième partie l'auteur propose un nouveau système (un cristal organique) qui se rapproche beaucoup plus du système d'Anderson idéal. Ici, les détails manquent aux non spécialistes de ce type de système. Par exemple, la raison du caractère aléatoire des ε_i (équation (2)) n'est pas évidente. Doit-on comprendre que l'on propose d'étudier l'effet des I_i aléatoires superposé à celui des ε_i déjà aléatoires eux-mêmes? Enfin, et surtout, on s'attendrait à une estimation des ordres de grandeur qui interviennent dans l'expérience proposée. En vue des remarques précédentes et du fait que pour l'instant il n'y a ni de proposition concrète d'expérience ni de résultats nouveaux, nous concluons qu'il serait prématuré de publier cette discussion. Etant donné, d'autre part, que l'idée nous semble originale, nous imaginerions très bien la publication d'une version mieux rédigée et tenant compte des critiques et des questions formulées ci-dessus.

Problème éditorial : article refusé (J.Chem. Phys (1984)):

Cet article porte sur mon travail de thèse d'état. Il voulait amender les résultats que nous avions publiés auparavant dans ce journal.
Les référées y ont considéré les modifications peu importantes et ont refusé l'article.
Nous avions autre chose à faire, d'autant que j'étais aux USA pour 1 an en stage post-doctoral.

No comment.

….

PACS Numbers : 66.30 LW, 71.55 JV

Rb. J. Chem. Phys
May 84

COMMENT ON : "TIME RESOLVED STUDIES OF NAPHTHALENE MIXED CRYSTALS. FRACTAL AND EUCLIDIAN BEHAVIORS OF THE MIGRATION"

P. Evesque and J. Duran

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Recently,[1] we proposed an analysis of the time dependence of the singlet intensity (I_S) created by the fusion of triplet excitations in binary molecular crystals of naphthalene. Briefly stated, at short time, the kinetics of the system is governed by a percolation of the bonds connecting the traps (naphthalene H_8), according to the following equation :[1,2]

$$I_S \sim t^{-\alpha}$$

A set of experimental α values are reported in table I (1) which shows that α depends on temperature and naphthalene H_8 concentration. In this comment we want to introduce a more realistic interpretation of the α dependence.

A) Concentration dependence of the percolation threshold

In paper [1] and [2] we assumed that the percolation is induced by the steep dependence of the transfer times versus distance between two impurities. In this case, the cut-off length which is introduced in our model depends on the real trap concentration. This approximation implies that :

i) the time dependence of the delayed luminescence I_S should decay according to the $(t/\tau)^{-\alpha}$ law, α being independent of concentration ;

ii) this percolation kinetics should be detected at times shorter than a time T_o ; in turn, this T_o time should depend on the real trap concentration as shown in Table I ;

iii) τ and T_o should be roughly proportional. The proportionality constant describes the mean number of visited sites during the time range of the fractal kinetics and is nearly independent of the trap concentration ;

iv) T_o is then the proper parameter which describes the euclidian regime. Consequently it turns out that the supertrapping time should be proportional to T_o and to the supertrap concentration.

As a matter of fact this last remark is in agreement with both the results of Ahlgren and Kopelman [3] and our own experiments : from Table I, one can predict that an 8% sample doped with 10^{-3} betamethylnaphthalene should exhibit the same normalized supertrap luminescence as a 12% sample doped with 10^{-4} betamethylnaphthalene.

Actually, a more complete analysis of the experimental value of the α parameter requiresthat we take into account the laser repetition rate as explained in the following.

B) Influence of the laser repetition rate

The experimental results reported in [1] have been obtained by exciting the samples with a dye laser providing repetitive pulses every $T = 0.2$ s. So that it appears from Table I that the characteristic time T_o of the low concentrated samples is larger than T. We propose a semi quantitative analysis of the influence of this effect on the experimental values of the α exponent.

In order to analyse this process, we firstly consider the situation of the excitations after the first laser pulse. At short time (during the fractal time range), the excitations are moving inside clusters which are completely disconnected from each other. As the time goes on, the smallest clusters are fully explored and the fusion will only occur among large clusters. Obviously this process which favorizes the smallest clusters will induce a non random distribution of the excitations at the end of the fractal time range (T_o). After T_o, new bonds appear between clusters, which will restore the random distribution of the excitations.

Therefore, it is easily understood that the time T of the second pulse excitation turns out to be a crucial parameter in the experimental estimate.

If time T is smaller than T_o, we will superimposed two excitations distributions ; one being provided by the first pulse will be non random, whereas the second one will follow a regular statistical law. As explained above, the final distribution will be in favor of the excitations of the smallest clusters. Then according to the percolation theory, this can be taken into account by increasing the ε exponent previously defined in [1] and [2]. As in a percolation model below the threshold, the α exponent is

$$\alpha = 1 - \bar{d}(1 - \varepsilon) / 2$$

it turns out that the α value should be larger than in the regular case, when the time T is much larger than T_o which corresponds to a pure random distribution of the excitations immediately after any pulse.

Table I shows that this feature is readily observed from our experiments : α is seen to increase when T_o increases and becomes larger than T. We observe also that the limit value of α is obtained for the largest concentrations and, within experimental error bars, correspond exactly to the predicted value for a 2 D percolation model (α = 0.37). This space dimensionality is in good agreement with the well known 2-dimensional character of the triplet states interactions in naphthalene.

Unfortunately, the quantitative derivation of the real α value versus the laser repetition rate turns out to be excessively intricate since the pulse energy of the laser should probably be included in the calculation.

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* Equipe de Recherche associée au CNRS n° 133

1 P. Evesque and J. Duran, J. Chem. Phys. 80, 3016 (1984)

2 P. Evesque, J. de Physique (Paris) 44, 1217 (1983)

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Table Caption

Table I : Experimental values of the α exponent and of the time T_o during which the singlet decay follows the $t^{-\alpha}$ law versus naphthalene H_8 concentration C and temperature of the samples (cf. Fig. 6 and Table I in [1]).

TABLE I

c (%)	Temperature (K)	$\alpha : I_S \sim t^{-\alpha}$	T_o (ms)
12	1.7	0.38	20
10	1.7	0.37	70
8	4.2	0.40	100
8	1.7	0.43	200
5	4.2	0.43	$T_o > 200$
5	1.7	0.47	$T_o > 200$

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FILE NO. Ct4.05.004

Comment on time resolved studies of naphthalene mixed crystals. Fractal and euclidian behavior of the migration

P. Evesque and J. Duran

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FRANCE

Dear Dr. Evesque:

Your above Comment has now been returned by the second referee who was asked to look at it. A copy of his comments is enclosed.

As you can see from the comments, he does not feel the manuscript should be published in its present form. However, the suggestion he makes for additional work to settle the issue appears sensible. If, for some reason you cannot follow his suggestion and still wish to have the Comment published, please return it to me with an explanation.

If the additional work requires a longer manuscript, it may, of course, be submitted ase a regular Article.

Sincerely yours,

J.C. Light
D.H. Levy

JCL:mj
enclosures

P.S. Your Comment now has 902 words, well under the 1200 word limit for Letters to the Editor.

I have reviewed the Comment by Evesque and Duran (your file number Ct4.05.004) as you requested. As discussed below, I do not think that it is suitable for publication.

The original paper (J. Chem. Phys. 80, 3016 (1984), submitted July 22, 1983) was one of the first to use concepts of fractal geometry to analyze excitation energy transfer in disordered molecular crystals. Other papers by Klymko and Kopelman (J. Phys. Chem. 87, 4565 (1983), submitted August 29, 1983) and Jortner et. al. (Phys. Rev. Letters 52, 2164 (1984), submitted March 23, 1984) now have been been published. It was my view that the Evesque and Duran paper merited immediate publication, even though it contained some questionable points, because it was at the leading edge of a new thrust in understanding energy transfer processes in solids. The problem now is how best to deal with these points.

One of the questionable points was the use of a three dimensional energy transport topology in the analysis of the experimental data. The excitation transfer interactions in naphthalene are known to be anisotropic, so the original analysis of the data implied that the disorder makes the effective topology more isotropic. The Comment now offers an alternative explanation that is consistent with a two dimensional topology. No new evidence is presented, however, to substantiate the revised point of view even though the new explanation is subject to a simple experimental test.

The point being addressed is why alpha in Table I of the Comment and also in Table I of the original paper depends on the naphthalene concentration. The explanation given in the Comment is that this dependence results from the fact that the time T_o (see Table I in the Comment) for the least concentrated samples is comparable to the time between laser excitation pulses. If the explanation is correct, then all the alpha values will approach 0.37 when the time between laser pulses is lengthened. Rather than simply publishing alternative explanations of an observation, we should require experimental evidence to substantiate one point of view over another.

I therefore recommend that the authors repeat the experiment using a lower laser pulse repetition rate and include the results in the Comment or better in a short paper or Note. In addition, the validity of the theory for the concentrations used should be discussed, and reference citations to previous work that has established the 2 dimensional topology for naphthalene should be given.

Article n° 7-1075 , refusé à J. de Physique France (1987)

Cet article « **Rotational relaxation of azobenzene in porous Vycor glass**.", M.T. Portella, P. Montelmacher, A. Bourdon, P. Evesque & J. Duran a finalement été publié dans *J. of Phys. C: Condensed Matter* **1**, 981, (1989).

Je crois que c'est presque le seul article que j'ai cherché à publier en présentant à un autre journal, pour ne pas priver d'un les étudiants de leur travail à cause d'une instance évaluatrice qui ne fait pas son travail correctement, ce qui est somme toute **inadmissible** !

Mais dans cette partie de mon travail, portant sur l'utilisation des fractals pour interpréter les propriétés optiques des matériaux, j'ai introduit l'idée elle-même (cf. fractal et Naphthalène H8), mais j'ai surtout eu à lutter contre son utilisation (trop) intensive/abusive du concept (cf. mes articles avec M.A.E. El Sayed).

L'exemple suivant (P. Evesque & D. Sornette, A dynamical system theory of large deformations and patterns in non cohesive solids, Phys. Lett. A 173, 305-10, (1993)) a été rejeté par phys Rev Let.

Le troisième cas est légèrement different: c'est celui des 3 articles suivants :

- P. Evesque, *Phys. Rev.* **A 43** , 2720, (1991), Analysis of processes governing sandpile avalanches using soil mechanics results and concepts
- P. Evesque, *J. de Physique France* **51**, 2515-2520, (1990), Granta gravel model of sandpile avalanches: towards critical fluctuations?
- P. Evesque, *Europhys. Lett.* **14**, 427-432, (1991), Analysis of processes governing sandpile avalanches using triaxial test results and "critical state" of soil mechanics.

J'avais soumis les deux derniers à PRL, qui ne m'a donné son accord que pour publier un article plus complet (i.e. le premier). Compte tenu de ceci, j'ai ressoumis ces deux articles à Journal de Pphysique et à Euro physics Lett. Avant de soumettre à PR A le 1er dans la foulée.

J'ai été surpris de voir paraître dans Phys Rev. A « communication rapide » un article par Nagel et al. Expliquant les effets de taille fini, ce que j'expliquais aussi dans le 3ème article.
J'ai essayé de publier un comment avec P. Porion. Ce qui m'a été crefusé par PHys Rev A.
(voir Comment)

Secrétariat de la Commission des Publications Françaises de Physique
Bâtiment 510, Université Paris-Sud, F 91405 Orsay Cedex

Manuscript submitted for publication in *Journal de Physique* - ~~Brèves Communications~~ our ref. 7-1075

Author (s) M.T. Portella, P. Montelmacher, A. Bourdon, P. Evesque, J. Duran

Title Rotational Relaxation of Azobenzene in Porous Vycor Glass

REFEREE'S REPORT

This paper deals with a very interesting problem: rotational relaxation in a porous material. It is however somewhat problematic:

1. Although the authors used the transient grating technique, which had been applied in Ref. 6 for a similar system, they did not prepare their system in a way which would minimize the surface sticking effects - they did not derivatize the surface. Ref. 6 gives specific instructions on how to overcome surface sticking. Without derivatizing the surface it is difficult to relate the problem to concepts like pore tortuosity. A recent work by IBM group in Phys. Rev. Lett. demonstrates that the derivatization is really effective.
2. The picture of PVG as a system of packed glass spheres has to be confirmed. How does one connect leached spinodal decomposition to the sphere case?
3. I agree with the authors that the results of Ref. 5 do not prove the fractalness of PVG. Ref. 8, however, does not disprove it.
4. The current paper addresses a very different issue than the one in Ref. 6. The authors have used a different excitation and let their azobenzene adsorb.
5. The long time dependence is not clear at all. The results do not depend on the fringe spacings and so no conclusion can be drawn.
6. There is no data analysis in the paper. What is the time evolution of the relaxation? What is the role of a distribution of surface sticking times?
7. As stated in the conclusions the microscopic-macroscopic relationship can be applied for the case of unstuck molecules. It seems that the present paper misses this possibility.

The authors should address the above points before the paper is reviewed again for publication.

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Answer to questions asked by the Referee

Réf. n° 7-1075

Answer to question 1

We have prepared Vycor samples according to the specific instruction given in Ref. 6. This has been clearly explained in our manuscript. Thus we could expect that our sample preparation would minimize the surface sticking effect as it is proclaimed in Ref. 6. Question 1 is meaningless since our purpose was to determine wether or not there were sticking effects with samples prepared according to Ref. 6 procedure. This question should have probably been asked to authors of Ref. 6. Moreover and contrarily to what referee's saying, no experimental evidence of the absence of sticking effect is given in Ref. 6.

Answer to question 2

We have never proclaimed that the compact packing of sphere has not be confirmed, but what to say of the fractal nature of PVG : According to "fractal authors" one measures by one method a fractal dimension $\vec{d} = 1.75$ between 50 and 90 Å, by an other method $\vec{d} = 2.5$ between 15 Å and 50 Å ; is that a dilation symmetry ? Moreover by transient grating experiments, one does not measure any fractal or fracton dimension or any ratio of the two, since the length scale probed is much too large ; for this last experiment one only assumes such a fractal space. Is that a scientific demonstration of the fractal nature of PVG ?

Moreover spinodal decomposition has been related to the sphere packing by author of Ref. 3. In the same way, the glass sphere packing agrees with the porosity value $\Phi = 0.28$, with the small fluctuation of the pore diameter, with the values of this pore diameter compared to the sphere radius measured by the electromicroscopic study, with the pictures taken using this technique. It also agrees with experimental results on superfluid helium films in PVG obtained either in UCLA or in Boston (Ref. 4). This packing seems also to be consistent with the dipole-dipole energy transfer results which had previously been interpreted

using fractals. It also agrees with the small amount of scattered light. Before proclaiming that PVG is fractal, one has first to explain the complete set of phenomena we have pointed out.

Finally, we would like to emphasize that it seems to us of a pure figure of speech to ask questions and to want experimental proofs on the first paragraph of a paper. This paragraph is generally written in order to settle the problem. So it is obvious that any packing has to be confirmed.

Answer to question 3

We also agree with Referee that Ref. 5 does not prove the fractalness of PVG, that Ref. 8 does not disprove it (see also answer to question 2). We would like however to emphasize that the three first questions of the referee only concern the introduction of the paper and the possibility of the existence of a fractal shape for Vycor. It seems to us that such a passion for detending the fractal shape of Vycor is real proof of the total absence of experimental evidence for this fractal shape.

Moreover we want to emphasize that ideas explained in question 3 are also expressed in our paper.

Answer to question 4

It seems to us that question 4 is voluntarily dodged : **we have not let azobenzene adsorb on PVG** ; we have used the same procedure as Ref. 6 one in order to **minimize** any sticking effect. Contrarily to Ref. 6 which is proclaiming that they "took much care in order to avoid any sticking effect" (without giving any experimental evidence of such a fact), our experiments unambiguously prove the presence of sticking.

Moreover Ref. 6 experiments cannot determine if azobenzene molecules are stuck or not ; this is partly why we have performed this experiment.

Answer to question 5

This question is quite clearly asked in our paper : it is one of its conclusion to say that the interpretation of the long time behavior is not clear. However the experimental result is quite clear since the signal goes to zero for a long enough time. The life time of this excitation is also given.

It seems then to us that question 5 has no meaning except to lead editor to reject the paper.

Answer to question 6

What does this question mean ?

We have given in this paper the excitation decays of a transient grating experiment on azobenzene embedded or not in PVG. We have been able to measure the rotation relaxation time of this molecule, to give the life times of the different excited states. Can the Referee say that there is no data analysis ? We cannot extract more details of the time behavior due to our experimental uncertainty. Obviously it is impossible to demonstrate from our experimental results the existence of a distribution of sticking times. Such distribution will lead to a non-exponential decay.

Contrarily to what is said in this question, the rotational relaxation has been fitted to a one-exponential process of life time 450 ps in the case of vycor glass. It seems to us that the Referee has read the manuscript with not enough care.

Answer to question 7

One of the aim of this paper was to determine experimentally wether or not the azobenzene molecule are stuck in PVG. As we could prove that azobenzene is adsorbed, we have reached our goal ; this obviously casts a serious doubt on the fractal interpretation of Ref. 6. We want also to emphasize that our experimental data are not in contradiction with those of Ref. 6, but only with a Ref. 6 assumption which was not proved.

An other aim of this paper was to emphasize the analogy between rotation and translation diffusions. This should enable to check a fractal space at different length scales.

We think that this paper does not miss its goals since it gives a new experimental methodology to prove through a diffusion study that a structure is fractal or not, since it also proves that azobenzene is adsorbed by PVG, and since it studies both the rotation relaxation of azobenzene and the relaxation of the excited states. This has been clearly explained in the introduction and in the conclusion and we do not undestand how the Referee could have missed these points.

Secrétariat de la Commission des Publications Françaises de Physique
Bâtiment 510, Université Paris-Sud, F 91405 Orsay Cedex

Manuscrit proposé pour *Journal de Physique* · ~~Letters & Communications~~ n/réf. 7-1075

Auteur (s) : M.T. Portella, P. Montelmacher, A. Bourdon, P. Evesque, J. Duran

Titre : Rotational Relaxation of Azobenzene in Porous Vycor Glass

RAPPORT

I am sorry to say that the manuscript by M.T. Portella et al. is not of sufficient quality, in its present form, to be published in the Journal de Physique.

It would be too easy to pin-point many errors in the use of the English language. These mistakes make the text difficult to read. My objections are more serious because in several instances the text gives the impression that the physics has not always been correctly digested.

1° The discussion on the fractal behavior of Porous Vycor Glass (P.V.G.) is so sketchy that it is unreadable. There is not enough clarity between geometrical (Haussdorf) fractal exponents and dynamical ones. About fractal structures, the expression "dilation symmetry" is unclear. One should rather talk of self-similarity.

2° The description p. 10 of azobenzene in terms of a spherical molecule of geometrical radius 4.5 Å (hydrodynamic radius 6.5 Å) is dubious if one takes the time to build a molecular model. Azobenzene is actually a rod.

3° Although I am willing to admit that azobenzene is adsorbed onto glass, I cannot take that "azobenzene prefer to lay in P.V.G. because its energy is less in P.V.G. than in bulk fluid" (p. 7). This is really non-scientific. Similarly on p. 9, the assumption of a concentration gradient of the dye, normal to the interface, is so speculative that it has to be proven experimentally. Otherwise this is science-fiction.

4° The presentation on Transient Grating Spectroscopy on page 9 is too general to be useful. There exists good reviews which can be cited. That would leave more space to explain the actual experiments performed by the authors. One has to wait until p. 11 to understand that polarization effects have been used. There is no mention of possible optical Kerr effects. What is the linear dichroïsm of azobenzene ? The magic angle (last lines of p. 9) stays "magic" to me until the end.

The main reported experimental fact is that azobenzene molecules stick to glass walls under certain conditions to be specified accurately and that this adsorption affects the re-orientational time. This finding may perhaps be published as a short note but certainly not as a full article in the Journal de Physique.

On the whole, and having carefully the manuscript, I have the impression that the authors are knowledgeable about picosecond spectroscopy but are rather naïve concerning the system investigated. They should try to learn more on the physisorption of small dye molecules. For instance, there are ways to prevent adsorption on silica surfaces through selected preparations. Similarly the optical properties of azobenzene have not been investigated sufficiently in bulk to allow a good understanding when they are incorporated in P.V.G.. One should bear in mind that adsorption will be different, depending on the nature of the excited state.

When this ground work is done, I think that the experiments are worth repeating but at one condition (which is underlined in the conclusion) : perform translational and rotational diffusion on the same sample. To-date the relevance to Dozier's work is very weak.

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Answer to questions asked in the referee's rapport

Ref. n° 7-1075

Answer to question 1

The discussion on the fractal behavior of porous Vycor glass is obviously very short since it appears mostly in the introduction of our paper in order to introduce our goal in performing such experiments and to introduce our experimental methodology. In this introduction many references of papers are given in which one can get extensive discussion of this interpretation. This discussion also appears in page 12 of our manuscript where it has been clearly distinguished between the fractal and the spectral dimensions.

In most meeting on fractals, physicists generally accept as difinition of fractal spaces as well a space which exhibits dilation symmetry as a space which is self-similar ; moreover both definitions have the same meaning so that I do not understand this part of the question.

Answer to question 2

It is clear that the hydrodynamic shape of azobenzene molecule is not spherical. We agree then completely with this referee's remark. However we think that such a distinction has not to appear in more details in this paper, since we have already mentioned that this shape was an approximation : it has only been used in order to give an estimation of the molecule size and to compare it to the diameter of the pores ; it has also been used to extract, from our experimental data, the characteristic time of the rotational relaxation of the molecule since our experimental accuracy is too poor to determine precisely more than one relaxation time of the rotation.

Moreover is it true that azobenzene is a rod ?

Answer to question 3

We do not understand the first remark of question 3 : it is generally admitted that a local increase of concentration is either due to an increase of the number of states which can be occupied by a molecule or due to an increase of the interaction strength. The first hypothesis is not valid in the case of a porous material for which the number of states or the accessible volume is reduced proportionally to the porosity of the medium. It is then generally well admitted that it exists an interaction strength between the molecule embedded in the porous medium and the pore surface. This corresponds to an additional energy which is mentioned in our text ; this additional energy is wether negative or positive, so that the concentration of the molecule is larger or smaller inside the porous medium than outside this medium.

It seems also to us that the second remark appearing in this question and concerning the concentration gradient mentioned on page 9 of our manuscript is not well come since we have only made this assumption in order to enligthen the experimental result and to discuss it in more details ; it was then purely speculative, and this was cleraly said in the text, so that we cannot and have not to prove this assumption experimentally. We would like to keep it in the course of the paper since such an assumption is most likely true : it is expected that for any rather intricate surface-volume geometry, a simple uniform distribution of stuck-unstuck molecules is really doubtfull so that one has to introduce a more complexe distribution.

Answer to question 4

Transient grating technique is now well known and we think that references 11 and 14 are enough. It can be found in these references a quite good definition of the magic angle which seems to us also well known so that it only needs the half page recall.

We have taken into account the referee's remark concerning the experiment principle ; we have introduced a sentence telling that polarization effects have been used in the abstracts and in page 3 of the manuscript.

Answer to general questions

We agree that one of the main experimental result is that azobenzene molecules stick to glass walls. However the other major aim of this paper is to demonstrate that rotational and translational diffusion can be tested using the same transient grating experiment, so that one can test the diffusion behavior over a length scale varying on more than 3 orders of magnitude ; this last point requires also proper condition and adequate molecules.

We give also the experimental rotational relaxation of azobenzene in Vycor and the dynamics of relaxation of the excited states of azobenzene. We prove that this relaxation occurs through the excitation of a long life time intermediate state. We also demonstrate that picosecond excitation and millisecond excitation do not excite same states.

The aim of this paper **was not to prevent adsorption on surfaces but to test adsorption** ; we took similar conditions as those already published [6] and shows that our experimental methodology could detect any sticking effect even when these ones could not have been detected using other methods.

It is really doubtful that analysing the optical absorption spectrum of such a broad band can allow to determine the distribution of molecules in P.V.G.

We completely agree with the referee's remark "one should bear in mind that adsorption will be different, depending on the nature of the excited states". This is why we do not really conclude that our experiment definitively prove the non fractal behavior of porous vycor glass (since our experiments do not deal with the same state than this one of Ref. 6). However this remark can be made also to Ref. 6 : this is not because Ref. 6 have checked that molecules do not stick to the wall in their ground state, that the isomeric form also does not stick !!

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ROTATIONAL RELAXATION OF AZOBENZENE IN POROUS VYCOR GLASS

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Abstract

Picosecond transient grating experiments on azobenzene molecules doping a 4.3 molar solution of methanol in toluene demonstrate that rotational relaxation is much faster in the bulk fluid than in the fluid embedded in the Corning 7930 vycor glass. As rotational and translational Brownian motions are related to each other, this proves a drastic change of the diffusion coefficients even at a microscopic length scale, which is in contradiction with a previously suggested fractal model. We interprete this feature in terms of sticking effects on porous walls. Since macroscopic and microscopic diffusion coefficients can be determined using the same transient grating experiment by looking respectively at the long and the short time scale behaviors, it is suggested to associate these two techniques in order to investigate the influence of pore tortuosity and connectivity on the diffusion properties.

Résumé

La relaxation rotationnelle de l'azobenzène, mesurée par la technique du réseau transitoire, dans une solution 4,3 molaire de méthanol dans du toluène est plus lente lorsque ce fluide est inclus dans un poreux, tel que le vycor 7930 de Corning Glass, que lorsque ce liquide est libre. La différence entre les coefficients de diffusion de cette molécule à l'échelle locale, observée dans ces deux milieux, est en contradiction avec un modèle publié antérieurement et qui faisait appel à une géométrie fractale. L'accroissement du temps de relaxation rotationnelle est interprété par une adsorption temporaire de la molécule d'azobenzène sur les parois du poreux. En conclusion, nous suggérons d'utiliser la technique du réseau transitoire en temps résolu pour déterminer l'influence de la porosité et de la tortuosité d'un milieux poreux sur les caractéristiques du mouvement brownien : l'étude aux temps courts permet de mesurer le mouvement brownien local à l'échelle submicronique via les rotations et celle aux temps longs (> 1ms), le mouvement brownien macroscopique ($\ell > 1\mu$).

1. Introduction

Nowadays a great interest has been devoted to the study of porous materials and recent works [1] on rocks structures seems to indicate that the geometry of some pore spaces is fractal [2] (structures with a dilation symmetry). On the other hand, one of the most intensively studied porous materials is the Corning vycor glass (PVG), (7930), the structure of which seems to be well represented through a compact packing of glass spheres of about 200 Å diameter so that the pore radius is about 20 Å and the porosity about 28% [3] ; this is confirmed by electron microscope photographs [3]. In the same way, this description quite agrees with recent results on superfluid helium embedded in this porous material [4].

However different authors have tentatively suggested a fractal structure for PVG in view of their recent results concerning one-step energy transfer [5] and diffusion of excited molecules [6] in this porous material. For instance, the time and concentration dependences of the energy transfer occuring between an excited donor molecule (the rhodamine B) and a distribution of acceptor (malachite green) have been determined by Even et al. [5] who have interpreted their results in the light of the Blumen and Klafter theory [7] of a one-step trapping process due to a dipole-dipole interaction occuring on a fractal space of $\bar{d}$ dimension. They have concluded to a 1.75 fractal dimension of the pore structure. However Yang et al. [8] have demonstrated that such a transfer strongly depends on the variations of the local environment at a typical length scale so that this experimental set-up is unable to test a real dilation symmetry and the fractal character of the space.

Moreover, they [8] have theoretically derived the main features of the experimental results assuming only the previously mentioned structure made of a compact packing of spheres, which makes really doubtfull the fractal interpretation.

Dozier et al. [6] have performed transient grating experiments on a solution of a dye molecule (azobenzene) which undergoes a photoisomerization. After much care has been taken in order to try to avoid any sticking of the azobenzene on the surface of the pores and after an index matching of the liquid embedding the vycor, they could measure the diffusion coefficient in both the bulk solution and the solution in PVG and have found these two diffusion coefficients to differ from each other. They have interpreted this result by assuming a large tortuosity of the paths connecting the pores and a small connectivity of the pores at a small length scale compared to the interfringe of the gratings. Assuming that these geometrical features can be mapped on a fractal or a percolation model, the diffusion coefficient can be calculated [9] ; it does not only depend on the fractal dimension but also on the spectral one [10] so that a whole class of different fractal spaces with different fractal dimension is possible [6] without taking into account any sticking effect.

This paper is aimed at detecting any sticking anomaly on these diffusion coefficients by performing transient grating experiments on a picosecond time scale and measuring typical reorientation times of the molecule. The basic idea underlying this work can be summarized as follows : since the works of lord Rayleigh, Einstein,

Langevin and Perrin on Brownian motion, it is well established that rotational and translational diffusions are related to each other. So, assuming that the translational diffusion coefficient measured by the transient grating method is not disturbed by sticking effects implies also that the rotational relaxation time of the molecule is independent of the fact that the liquid is or is not embedded in PVG. On the contrary, if we find two different rotational relaxation times for the molecule in the bulk solution and in the liquid embedded in PVG, this will be induced by a very local change of the translational and rotational diffusion properties (i.e. at a much smaller length scale than the 40 Å diameter of the pore size since the hydrodynamic radius of azobenzene is about 6.5 Å). In turn, this will probably mean that the molecule sticks on the wall of the pores.

It is this last phenomenon which has been detected with this study. It is corroborated with optical density measurements which definitely prove that the equilibrium concentration of azobenzene in the bulk liquid is smaller than the one in the liquid embedded in the pores. This finally means either that azobenzene sticks spontaneously on the vycor glass or that chemical properties of the liquid inside and outside the vycor are drastically different, which is an other possibility since this liquid spontaneously wet the porous materials and due to the large surface area of this solid material.

2. Experimental set-up and detection

The transient grating set-up is schematically reported in Fig.1. A 1.06 μ infrared beam of an acoustooptically mode-locked and Q-switched Nd:Yag laser is frequency doubled through a CD*A

crystal. This 532 nm beam is then divided into two equal parts which are focused at the same point of the studied sample. Changing the focal length of this lens allowed to vary the angle θ between the two excitation beams (wave vector $\vec{k}_1$ and $\vec{k}_2$) and then the interfringe of the gratings.

A probe beam of wave vector $\vec{k}_3$ obeying the Bragg condition has been focused on the excited region of the sample. Analyzing the time dependence of the signal diffracted along the direction $\vec{k}_4 = \vec{k}_3 - \vec{k}_2 + \vec{k}_1$ has allowed to determine the evolution of the grating contrast. The 532 nm excitation beam is made of a repetitive series of some 40 pulses of 100 ps width and separated by 6 ns. These series are emitted at a repetition rate equal to or less than 500 Hz (the Q-switch frequency). So, two time scales have been investigated by this method which are the 0.1ns - 6ns range and the 0.3 μs - 2 ms one. Last range has been investigated using a 0.1 mW CW He-Ne laser ; the diffracted signal has been detected using a photomultiplier and averaged on a Le Croy 9400 digital oscilloscope. In the shorter (0.1-6ns) range case, 20% of the excitation beam intensity has been optically delayed and used as a probe beam ; varying the delay has allowed to determine the time dependence of the grating contrast. In order to increase the signal to noise ratio, a mechanical chopper running at half the Q-switch frequency switched off the probe beam intensity every two emission. The diffracted signal has been detected using a Schottkybarrier photodiode and a lock-in amplifier, then stored in a microcomputer which has also been used to drive the optical delay time τ_D.

2.1. Sample preparation :

Industrial porous vycor glass (PVG) is made by phase separation of boron in borosilicate glass. The phase-separated boron which is removed by HF acid leaching, forms a connected path which produces the pore space. Its pore size diameter is sharply peaked at 42 Å ± 2 Å which is large compared to the typical hydrodynamic radius of azobenzene molecule in ordinary fluid (6.5 Å) [6].

It is well known that in porous materials much care has to be taken in order to get reproducible results so that we have used the well defined and studied experimental conditions determined by Dozier et al. [6]. For instance, the binary solution of azobenzene has been chosen as a mixture of 4.3 moles of methanol in toluene which leads to a perfect index matching with PVG. Two different concentrations of azobenzene (8 mM and 48 mM) has been used to study the azobenzene properties in the bulk fluid, but only the smaller concentrated solution has been embedded in PVG, the second one leading to a too large optical density in PVG for transient grating experiments.

According to Dozier et al. [6], the experimental procedure for preparing the PVG sample was the following : PVG has been firstly immersed in methanol during three days : the methanol has then been evaporated. The same procedure has then been repeated with the binary solvant alone (without azobenzene) (imbibition and evaporation). Finally, PVG has been embedded in the azobenzene solution during three days. Both, the PVG and bulk fluid samples were 4 mm thick ; they have been set in a rotating mount in order to minimize the chemical destruction of the molecules.

2.2. Optical density measurements :

Index matching between PVG and binary fluid has been obtained and scattering of light has then been avoided. Moreover we have checked that the ratio of the optical densities of two different samples is nearly independent of the wavelength and can be used to determine the concentration of the samples. At 532 nm, the optical densities of the bulk fluid doped at 8 mM with azobenzene and of the PVG sample are respectively $d_B = 0.5$ and $d_p = 2.31$, so that the c_p/c_B of the azobenzene really contained in a pore of PVG (c_p) to this one in the bulk fluid c_B is given by :

$$c_p/c_B = d_p / (\varphi d_B) = 16.5$$

where φ is the PVG porosity ($\varphi = 0.28$).

Each of these two samples is in equilibrium with the other one, since they have been prepared from the same solution, so that the 16.5 c_p/C_B ratio clearly indicate that azobenzene much prefer to lay in PVG than to stay in the bulk fluid or, in other words, that its energy is less in PVG than in this bulk fluid. Different models can be set up to explain this result.

The first simplest one is to consider that the fluid in the pore has the same azobenzene concentration than in the bulk fluid but that the average concentration of azobenzene in PVG is increased due to sticking effects on the walls of the pores. Labelling c_W the azobenzene concentration on the walls and according to $c_p = c_W + c_B$, 94% of the azobenzene contained in PVG are sticking on the walls, which enables us to compute the coverage ratio of the pore surface by azobenzene molecules :

If we label R the radius of a glass sphere ($R \sim 200$ Å) and according to a cubic face-centred compact packing model which

can explain the value of φ, the total surface area S of the spheres in a volume V is $S = \pi V/(\sqrt{2}R) \sim 2\ V/R$ which is about $10^5 m^2/\ell$. Taking account of the typical radius R_0 of the azobenzene molecule ($R_0 \sim 4.5$ Å) and of the concentration of the stuck azobenzene, the surface coverage of pore walls in PVG samples is $\pi R_0^2 N_A \varphi c_W$. ($N_A$ is the Avogadro number). This leads to an experimental estimate of the surface coverage ratio of order 1 which indicates a strong azobenzene-glass interaction.

This model obviously is based on crude approximations and one should introduce other parameters : for instance since the fluid spontaneously wets PVG and due to the large surface area of PVG, it is highly probable that chemical properties (and then the real concentration of azobenzene inside and outside the porous material are different.

Moreover it is possible that instead of azobenzene molecules stuck or unstuck on the walls of the pores there could exist a concentration gradient of azobenzene along the perpendicular to the surface of the walls. The surface itself could also be made of a distribution of sites with different sticking probabilities especially near the contact point between two glass spheres. Finally, instead of covering the walls by a monolayer of azobenzene,there might exist in some locations a distribution of superimposed two or three layers, which will change drastically the time behavior of the sticking-unsticking phenomenon.

3. Results and discussion

When two coherent light beams of wavelength λ_0 are time coincident, and are polarized along the same axis and cross each

other at an angle θ' in a sample, their electric fields interfere. In some cases these interferences can be printed in the sample so that one gets a spatially modulated gratings of interfringe Λ $\left(\Lambda = \lambda_0/(2 \sin(\theta'/2))\right)$ during a given time. These gratings can then be read out during this time using the diffracted signal coming from a third incident beam. This is the transient grating technique.

In an absorbing medium this intensity modulation generates a spatial modulation of the electronic excited and ground state populations so that the complex index of refraction turns also to be spatially modulated during a characteristic time equal to the lifetime of the excited states. This light modulation can also produce a local heating or an electrostriction effect which induces phonon generation which, in turn, is dissipated through either a coherent propagation or an incoherent diffusion process [11] ; this dissipation occurs within a characteristic time which depends on the interfringe, on the sound velocity or on the diffusion coefficient. Moreover, when the excited states are mobile (i.e. when the sample is made of absorbing molecules in solution), migration of electronic states (or molecules) can occur and lead to processes of modulation fading similar to the coherent or incoherent migrations which occurs in the phonon case ; its also leads to a new phenomenon : due to optical selection rules, the molecules which are excited by the two excitation beams have a preferential orientation so that the intensity of the diffracted signal depends on the probe beam polarization. After excitation, molecular orientational relaxation occurs. It can be proved that the diffracted signal is independent of these reorientation processes when the probe beam polarization is oriented at the magic angle orientation $\theta'_m = 54°7$. So that the behavior of the diffracted beam reflects the pure time dependence $I_e(t)$ of the average excited

and ground state populations. It can also be shown [12] that the time dependence of molecular reorientation r(t) can be obtained from the experimental dependences of the intensity $I_{//}(t)$ and $I_{\perp}(t)$ of the diffracted signals arising from probe beams polarized respectively parallely and perpendicularly to the excitation beams. According to Tao [12]

$$r(t) = \left(I_{//}(t) - I_{\perp}(t)\right) / \left(I_{//}(t) + 2\, I_{\perp}(t)\right).$$

In the most general case r(t) is the sum of three exponential decays since the three principal axes of a molecule are not equivalent and correspond to three different coefficients of rotational diffusion [13]. However in the case of a spherical molecule of hydrodynamic volume V_H in a liquid of viscosity η, r(t) turns out to be a pure exponential of time constant $\tau_r = V_H \eta/(kT)$ (where T is the temperature and k the Boltzman constant).

Accordingly, we have performed transient grating experiments on the three samples under three different probe beam polarizations (parallel, perpendicular and oriented at the magic angle), with different interfringes Λ varying from 4 to 13μm and with different excitation power ranging from 5 MW/cm^2 to 50 MW/cm^2.

We could not detect any difference between the behaviors of the 8 mM solution of azobenzene and of the 48 mM one, in either the short or the long time range, so that we only report here the experimental result concerning the 8 mM solution of azobenzene as a bulk fluid or in PVG.

3.1. Short time behavior (Fig.2)

We report on Fig. 2a the first 6 ns of the time dependence of the diffracted signal arising from the 8 mM solution of azobenzene

using a probe beam polarized parallely to the excitation beam polarization. It consists in a rather constant signal superimposed to a sharp peak of 100 ps width which is the coherence spike [14].This is confirmed since polarizing the probe beam perpendicularly to the excitation leads to cancel the peak intensity. Moreover as the constant signal intensity does not depend on the probe beam polarization, one is led to conclude that azobenzene rotational relaxation occurs in a time shorter than 100 ps (the width of the coherence spike) and that the excited state of azobenzene has a life time much larger than 6 ns.

Figure 2b reports the short time dependence of the signal diffracted from the PVG sample with different probe beam polarizations (at magic angle, parallely and perpendicularly to the excitation polarization). These time behaviors are complex and have been interpreted using the rotational relaxation model previously described. The experimental result obtained at the magic angle provides a 2.2 ns lifetime for the excited state of azobenzene. Combining the results concerning the two other excitation polarizations allows to compute the time dependence r(t) of the rotational relaxation. Assuming then a spherical hydrodynamic shape for azobenzene leads to the evaluation of the rotational relaxation time τ_R to be 450 ps.

This result together with the fast rotational time of azobenzene in the bulk fluid can be crudely interpreted in two different ways :either the large increase of the rotational time is induced by a large increase of the fluid viscosity when it is embedded in the pores or, and, more likely, this change is induced by the existence of an equilibrium between the azobenzene molecules which are

stuck to the walls of the pores and those which are free in the fluid ; in this last case the 450 ps time which has been measured here has the simple interpretation of a mean time during which the molecules are stuck to the walls.

Within our experimental accuracy, it has only been possible to conclude that the average rotational relaxation time of azobenzene is much faster in the bulk solution than in PVG. This result together with the optical density behavior and with the fact that rotational and translational diffusion coefficients are related to each other lead to conclude that the microscopic (and macroscopic) translational diffusion coefficient of azobenzene in a solution embedded in PVG should be much smaller than that of the bulk solution, this feature being induced by the very local property of the azobenzene to stick spontaneously on the glass sphere surface.

This experimental fact has been actually found by Dozier et al. [6] who have measured the macroscopic diffusion coefficients (D_B in the bulk solution and D in PVG). They obtained $D_B = 2.4 \times 10^{-6}$ cm^2/s and $D = 3.6 \times 10^{-8}$ cm^2/s. However their interpretation is rather different from ours since they have attributed this change to a large increase of the path tortuosity together with a lack of connectivity of the pores. In order to compute the scale between which this material seems to be disordered they mapped the diffusion problem and the path structure on a fractal space, characterized by its fractal and spectral dimensions $\bar{d}$ and $\bar{\bar{d}}$ [10], on a length scale larger than the pore size (ℓ_1 = 30 Å) but smaller than a typical length ($\ell_2 > \ell_1$). According to the transient grating theory on a fractal space [6,9] the ratio between the macroscopic and the

microscopic diffusion coefficients can be expressed as

$$D/D_B = (\ell_1/\ell_2)^{2(\bar{d}-\bar{z})/\bar{z}}$$

It exists an infinity of different fractal spaces for which the experimental results are satisfied. For instance, Dozier et al. | 6 | have obtained ℓ_2 = 300 Å and ℓ_1 = 30 Å when assuming a percolation network.

It seems to us that our result casts a serious doubt on this interpretation | 6 |. However it is well known that porous media lead to unreproductive experimental results which are induced by the great sensitivity of these experimental results on the conditions of the sample preparation. Moreover it is worth noticing that our excitation conditions are different from theirs so that the excited states and molecules which are studied here are probably not the isomeric form the diffusion properties of which have been already investigated by Dozier et al. | 6 |. We have then investigated the long time behavior of the diffracted signal intensity in order to prove this feature.

3.2. Long time behavior (Fig.3)

The long time behavior of the diffracted signals which are reported on Fig.3 neither depends on the probe beam polarization nor on the interfringe. These datas clearly establish that the gratings decay much faster in PVG than in the bulk solution and the two respective decay times are 5 and 50 s. As they are both several order of magnitude shorter than the cis-to-trans azobenzene relaxation time | 6 |, these lifetimes must concern the triplet ground state of the trans-azobenzene. It definitely proves that our experiments deal with different states from the isomeric form studied by Dozier et al. ones. This is in agreement with the well

known result that an efficient photoisomerization is only performed when using light pulses longer than 1 μs.

The relaxation times which have been measured are much shorter for the azobenzene in PVG than for this molecule in the bulk fluid. This may come from an enhancement of non-radiative desexcitation processes which is probably induced by repetitive collisions of azobenzene on the porous walls ; in other words this is related to repetitive sticking-unsticking processes on the PVG surface.

4. CONCLUSION

Optical density measurements on azobenzene in a 4.3 molar solution of methanol in toluene have clearly demonstrated that the azobenzene concentration in the bulk fluid is 16 times smaller than that of the fluid embedded in a porous vycor glass. This result together with the large change of the rotational relaxation time measured by picosecond transient grating experiment is consistent with an interpretation assuming a sticking mechanism of azobenzene on the walls of the pores ; in this case the average sticking time would be equal to the measured rotational relaxation time (450 ps).

These results seem to be in contradiction with the hypothesis relating the large decrease of the macroscopic diffusion coefficient of the cis-azobenzene to the existence of a pore tortuosity and to a fractal structure of the pore space [6]. Our results, on the contrary indicate that most of the observed features should come from a sticking effect of molecules on the pore surface.

However since our experiment, performed at a time scale longer than 1μs, measures an excited state lifetime which is much

smaller than that determined by Dozier et al. [6], it definitely proves that our experimental se-tup does not test exactly the same diffusion problem. Moreover as it is well known that an experimental measurment performed on porous materials is drastically depending on the preparation condition of the sample it might happen that our results and theirs are not concerned with identical samples.

In any case as far as transient grating experiment can be performed on both picosecond and second time scales, this technique can bring information on both the rotational relaxation and the macroscopic diffusion characteristics of molecules. However, when these molecules do not stick on the porous surface and since the rotational relaxation is related to the microscopic diffusion properties, this technique is quite appropriate to determine the exact effect of the pore structure on the macroscopic diffusion problem and the fractal nature of the pore space. On the contrary, when a large amount of molecules are sticking to the walls of the pore, the rotational reorientation time corresponds to the average time during which the molecules stay stuck on a wall, (since rotation and migration are unlikely to occur when a molecule is stuck) ; under these circumstances, the rotational relaxation time can no more be related to the microscopic diffusion coefficient. Then, determining the average ratio of the stuck to unstuck molecules and assuming that the microscopic diffusion coefficient of the molecule in the fluid embedded in the pore is equal to that of the molecule in the bulk fluid, allow in principle to compute the macroscopic diffusion coefficient in porous material. Under these circumstances, the calculated diffusion coefficient will only concern

a material which does not present any tortuosity or lack of connectivity. So, the ratio of these computed and measured macroscopic diffusion coefficient will determine, at least in principle, the tortuosity of the paths and the fractal nature of the pore spaces.

It seems then to us that transient grating experiment can be an efficient tool in investigating diffusion properties of disordered materials. This will be as much true as one can perform such an experiment over a quite large range of time scales. This last condition is unfortunately difficult to achieve experimentally, but it is realized when dealing with a photoisomerization process.

Acknowledgments

One of us M.T. Portella would like to acknowledge the CNP_q and FAPESP (Brazil) and the CNRS (France) for financial support.

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Figure captions

Figure 1 :

The experimental set-up. Beams 1 and 2 are the excitation beams of a Qswitched mode locked Yag laser which has been frequency doubled. Beam 3 is either a CW He-Ne laser for long time scale experiments (1μs - 2ms) or a part of the frequency doubled Yag laser excitation beam for short time scale experiments (0.1 - 6ns).

Figure 2 :

Short time response of a transient grating experiment.

a) for a 8mM azobenzene bulk solution

b) for a 8mM azobenzene solution in a porous vycor glass at three different probe beam polarizations

(—) polarization parallel to the excitation beam polarization

(····) " perpendicular " " " "

(– – –) " at the magic angle (see text).

Figure 3 :

Long time behavior of the transient grating response

(····) on bulk solution doped with 8mM of azobenzene

(– – –) on a 8 mM azobenzene solution in porous vycor glass.

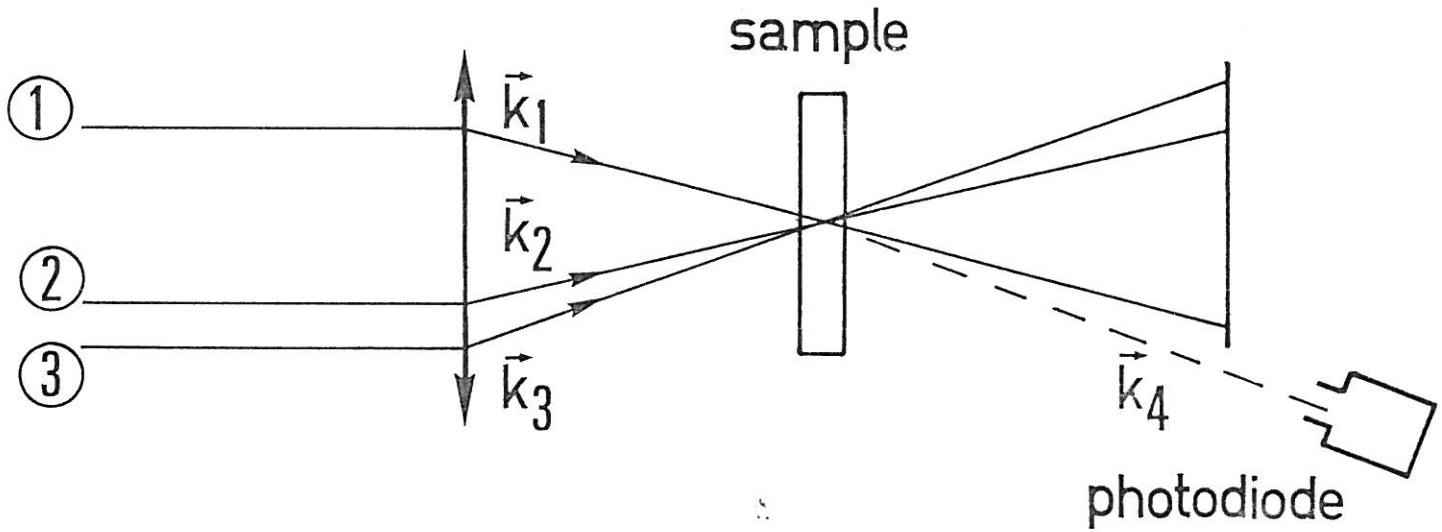

Fig 1

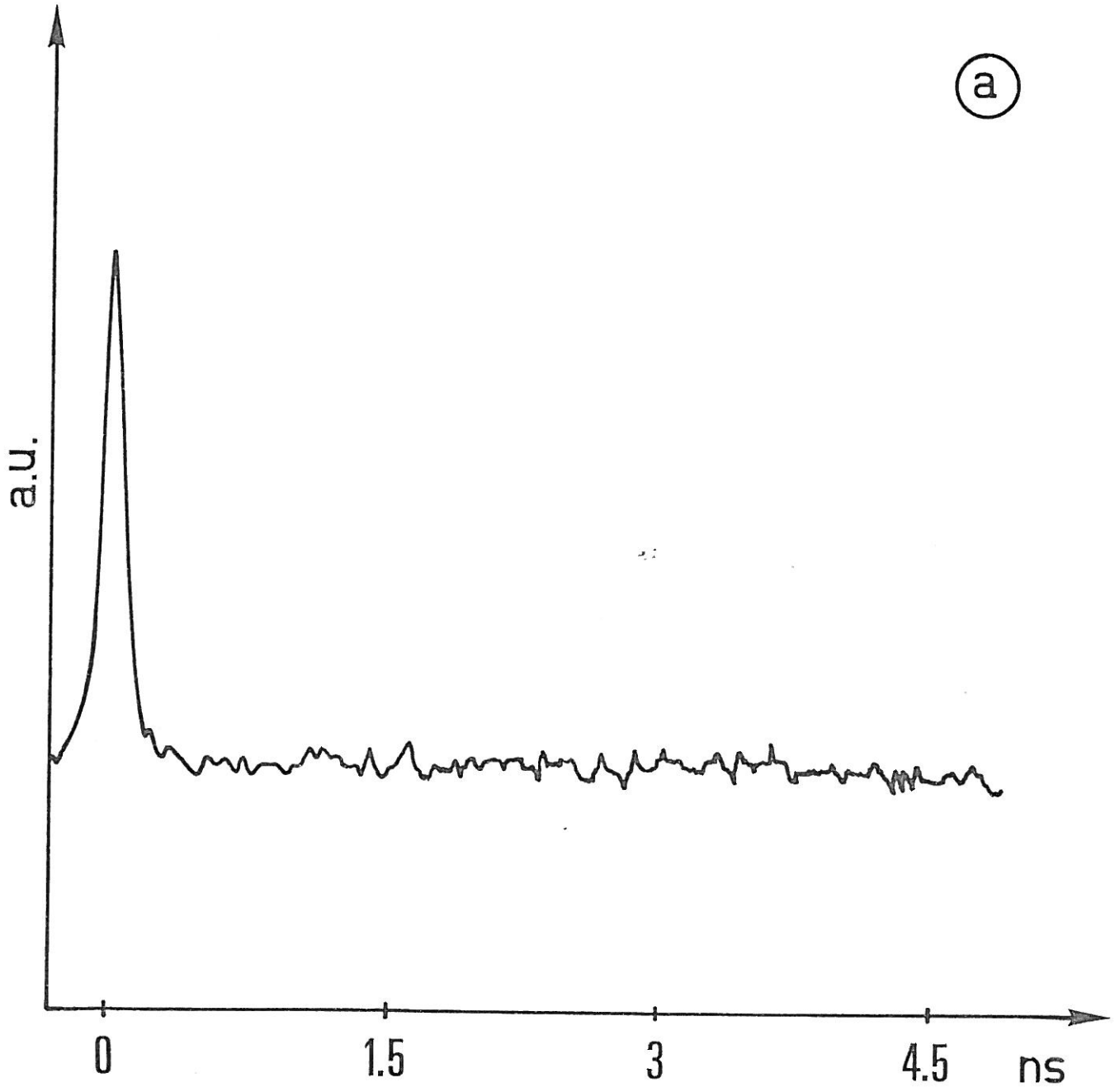

Fig 8a

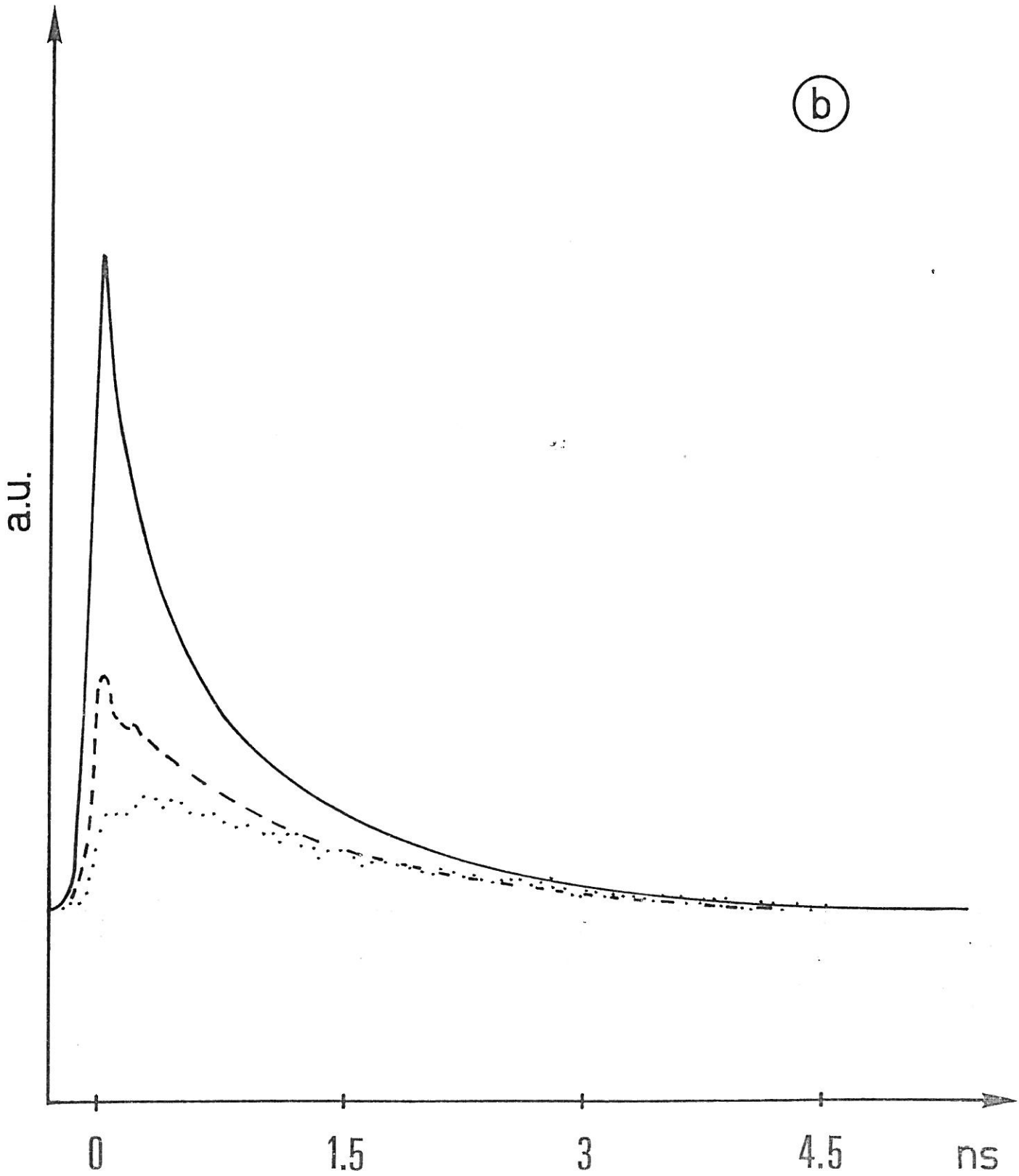

Fig 2b

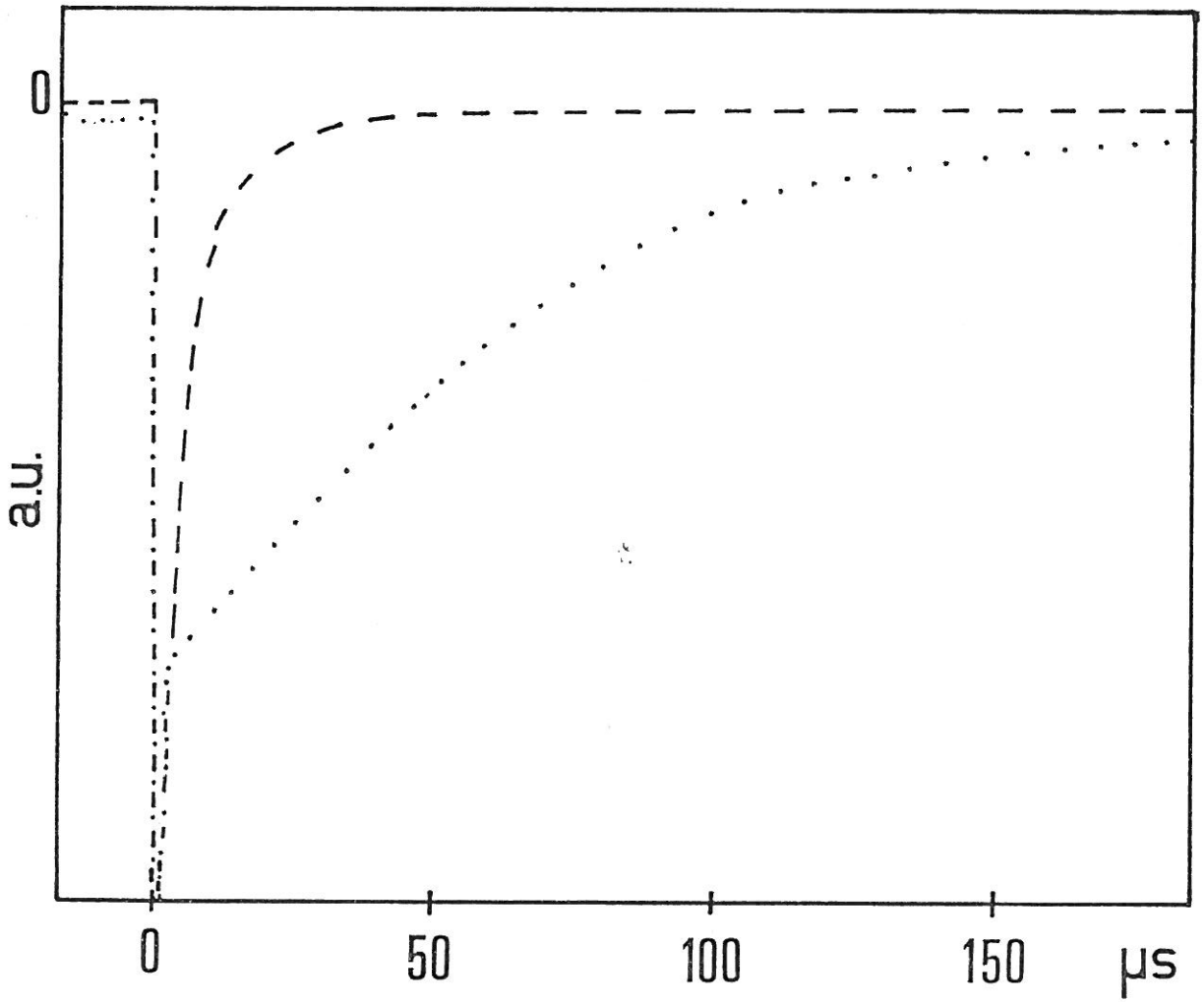

Fig 3

Problème du modèle BCCW, rejet d'article surla théorie BCCW :
cf. Poudres & Grains n°7, 1-18, (1999)

J'ai déjà relaté dans ma notice de Titres et Travaux 2001 et dans mon rapport cnrs 2011 le rejet de cet article par le Journal de Physique.
L'expérience que je propose a été montée avec l'accord de JP Bouchaud. Cette expérience a été exposée au congrès de Powders & Grains 2007, puis au KITP de Santa Barbara, USA, pendant un mois, sans réellement qu'elle soit discutée par les physiciens présents.
Je ne pense pas que les critiques des référees soient correctes

Il est malheureux qu'aucune interprétation théorique pour expliquer le résultat n'ai été réellement propposée par les contradicteurs de cet article, voir aussi le rapport de M. Cates.

cf: Titres et Travaux de P.Evesque 2001 (puis suivant) et dans rapport cnrs 2011 de P.Evesque

Refus (1992) par PhysRev A du Comment by P.Evesque & P.Porion on C.H.Liu, H.M. Jaeger, S.Nagel, Phys. Rev. A 43, 7091(1991)

Comme je l'ai dit, ce troisième cas est légèrement different: c'est celui des 3 articles suivants :

P. Evesque, *Phys. Rev.* **A 43** , 2720, (1991), Analysis of processes governing sandpile avalanches using soil mechanics results and concepts

P. Evesque, *J. de Physique France* **51**, 2515-2520, (1990), Granta gravel model of sandpile avalanches: towards critical fluctuations?

P. Evesque, *Europhys. Lett.* **14**, 427-432, (1991), Analysis of processes governing sandpile avalanches using triaxial test results and "critical state" of soil mechanics.

J'avais soumis les deux derniers à PRL, qui ne m'a donné son accord que pour publier un article plus complet (i.e. le premier). Compte tenu de ceci, j'ai ressoumis ces deux articles à Journal de Pphysique et à Euro physics Lett. Avant de soumettre à PR A le 1er dans la foulée.

J'ai été surpris de voir paraître dans Phys Rev. A « communication rapide » un article par Nagel et al. Expliquant les effets de taille fini, ce que j'expliquais aussi dans le 3ème article.
J'ai essayé de publier un comment avec P. Porion. Ce qui m'a été crefusé par PHys Rev A.
(voir Comment on1992)

Article refusé: P. Evesque D. Sornette: A dynamical system theory of large deformations and patterns in non cohesive solids; Phys. Rev. Lett (1991), accepté dans Phys. Lett.

L'exemple suivant (P. Evesque & D. Sornette, A dynamical system theory of large deformations and patterns in non cohesive solids, Phys. Lett. A 173, 305-10, (1993)) a été rejeté par phys Rev Let. (voir les rapports).

Cet article a été renvoyé à Phys. Lett. A, où il a été accepté.

THE PHYSICAL REVIEW

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21 August 1991

Dr. Pierre Evesque
Lab. Mecanique: Sols, Struc. Mat.
Ecole Centrale Paris
F-92295 Chatenay Malabry, FRANCE

Re: Dynamical system theory of large deformations and patterns in noncohesive solids

By: Pierre Evesque and Didier Sornette LE4574

Dear Dr. Evesque:

Our recent referral for the above manuscript has not produced a report. New referrals are being made. We regret this unexpected delay and hope for reports soon.

Yours sincerely,

George Basbas
Editor
Physical Review Letters

Referee A:

COPY

Review of "A Dynamical System Theory of Large Deformations and Patterns in Non-Cohesive Solids," by P. Evesque and D. Sornette, LE4574.

I must admit at the outset that I am not an expert at all in powder mechanics, but hope that I can nonetheless manage a competent review. My judgement is that this paper largely consists of a reformulation of old results in terms of a modern terminology, which does not in itself justify publication in Physical Review Letters. More detailed comments follow:

1) Figure 1 is not prepared in accord with the caption: the authors have forgotten to draw dashed lines.

2) Figures 2c and d are referred to in the text as Figures 4 and 5.

3) The exposition of the behavior shown in Figure 1 in terms of U_1 U_2 and U_3 is a restatement of phenomena known since the time of Coulomb in a language which so far as I can tell does not contribute to their understanding.

4) The real test of the phenomenology is in its ability to explain the results of Ref. 9. These results are extremely interesting, and an illuminating discussion of them would certainly merit a Letter. A reasonable expectation would be that the theory should predict the wavelength of the striations, the twist angle in the axial direction, or at least predict quantitatively the conditions under which the "spiral staircases" appear as opposed to the plane failure predicted by Mohr and Coulomb. Unfortunately, the phenomenology presented in the paper does not seem rich enough to approach these questions. Without quantitative predictions, I cannot support this paper for publication.

5) Figure 2d shows many bands, which suggests that failure occurs simultaneously on several "staircases." The rationalization in terms of a twisted plane does not even seem consistent with the experimental picture.

6) I would very much like to see a thorough study of this system. The engineering books I have read gloss over the stability issues. But simply rephrasing the behavior in terms of dynamical systems is not the way to learn how complicated instabilities occur.

COPY

Referee B:

Manuscript Number: LE4574

Author: Pierre Fvesque and Didier Sornette

I do not think that this paper in its current form is acceptable for Physical Review Letters. The "dynamical systems" approach appears to me to be just a restatement of the experimental results, either for the global structure or for the planar detect - the latter is expected anytime the system undergoes a symmetry breaking instability and is the same as an equilibrium domain wall. Because of this, I am not convinced that the idea of using a three coordinate phase space language is really adding anything in the way of predictive power. Part of my problem is that I did not fully understand the discussion on page 7 of the shear band experiment and the proposed explanation. Since the experiment is not published in a particularly accessible place, more explanation is called for.

Article refusé PRL LZ 7720: P. Evesque ; Poudres & Grains 11 (4) 58-59 (décembre 2000); The jamming surface of granular matter determined from soil mechanics results

Cet article aété soumis le 17 décembre 2000, et rejeté le 24 Octobre 2001, avec des arguments qui ne m'ont pas satisfaits.
Il a été publié sans réel amendemant dans Poudres & Grains (P.Evesque, Poudres & Grains 11 (4) 58-59 (décembre 2000)).

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Châtenay, le 17 december 2000

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USA

Objet :

Dear Sirs,

Please find enclosed 4 copies of a paper entitled "Identification of the jamming surface using soil mechanics results", author Pierre Evesque, which I submit for publication to Phys. Rev. Lett.

Best regards

Pierre Evesque

Ecole Centrale Paris
Laboratoire de Mécanique : Sols, Structures, Matériaux
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Identification of the jamming surface

using soil mechanics results

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e-mail evesque@mssmat.ecp.fr

Abstract:

Classical soil mechanics results are used to propose the equation of the jamming transition surface of granular matter in the (σ, $1/\rho=v$) space, where ρ is the density, v the specific volume and σ the stress really supported by the grain structure. Taking axisymmetric conditions, labelling $q=\sigma_{11}-\sigma_{22}$ and $p=(\sigma_{11}+\sigma_{22}+\sigma_{33})/3$, and considering normal range of pressure (10 kPa-10MPa) the equation of the surface of jamming transition is $v=v_o-\lambda \ln(p/p_o)+\lambda_d \ln(1+q^2/(Mp)^2)$; M is related to the friction angle, $\lambda$and λ_d are two constants which depend on soil characteristics.

PACS #: 45.70 , 64.70.Pf, 83.70.Fn

Jamming transition is a fundamental problem which attracts some interest from physicists recently since it has been addressed a parallel with the glass transition [1]. We do not want to discuss this last point here; but we just want to stress that some information on the jamming transition can be found already in technical literature, even if it is in different words most likely: for instance, the soil mechanics literature speaks of this problem within an other terminology, but it has already identified the law of variation of the minimum density that a soil can exhibit in statics and under a definite stress field. This may help physicists in their investigation. This is just what we want to report.

Consider a dry granular material (as sand) in static condition, submitted to an axial stress field expressed in the principal axis direction as $(\sigma_{11}, \sigma_{22}, \sigma_{33})$, with $\sigma_{11} > \sigma_{22}=\sigma_{33}$; it can be built at different density $\rho=1/v$. However, this density cannot be looser than a given value; this loosest state is called the "normally consolidated state" in the mechanics literature [2,3,4]; it is characterised by its specific volume v_{nc}. v_{nc} is found to depend on the stress field. Labelling $q=\sigma_{11}-\sigma_{22}$, $p=(\sigma_{11}+\sigma_{22}+\sigma_{33})/3$, $\eta=q/p$ and M the ratio q/p at the limit of plasticity, i.e. $M=6\sin\varphi/(3-\sin\varphi)$ with φ the friction angle, one gets the following equation for v_{nc} from experimental fit :

$$v_{nc}=v_{nco}-\lambda \ln(p/p_o) - \lambda_d \ln(1+\eta^2/M^2) \qquad (1)$$

where λ and λ_d are two constants which depend on material. The domain of validity of this equation is (10 kPa, 10 MPa). For smaller pressure range, experiments in micro-gravity experiments have to be performed and are currently being performed by NASA; it is probable that v_{nc} tends to a given limit. For pressure larger than 10 MPa, grain crushing occurs, modifying the v_{nc} law of variation; examples can be found in [3]. λ is about 0.06 granular

matter and sands; an estimate of this value has been tentatively proposed from a microscopic modelling [4,5].

When granular matter is saturated with liquid, it is found experimentally that Eq. (1) still holds, but the stress field which has effectively to be considered in Eq. (1) is the effective stress, i.e. the one which is really carried by the grain structure. So owing to the so-called Terzaghi approximation, σ is then equal to the total stress σ_{tot} minus the liquid pressure u_w:

$$\sigma=\sigma_{tot}-u_w \qquad (2)$$

It is found that λ and λ_d does not depend on the presence of saturating liquid.

When considering clays saturated with water, similar results are still valid, and Eq. (1) holds, if Eq. (2) is taken into account. The main difference is that the values of λ and λ_d are a bit larger, since the material is more "compressible". The name "normally consolidated" comes from clays: indeed it is much more complicated to get loose sand samples than clay ones. Examples of behaviour of clays can be found in [3].

It is worth mentioning that the shape of the transition curve in the ($v=1/\rho$, σ) space is convex instead of concave as proposed in ref. [1].

As a final remark, the ensemble of normally consolidated states forms what is called the Roscoe's surface in soil mechanics literature when $q/p=\eta<M$; It forms what is called the Hvorslev's surface when $q/p=\eta>M$. Both surfaces are parts of the same surface [5,6]. Knowing these notations may help physicists in finding more information.

Acknowledgements: CNES is thanked for partial funding.

References:

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[6] P. Evesque, "Topology of the Roscoe's- and Hvorslev's- surfaces in the phase space of soil mechanics", *poudres & grains* **6**, 10-16, (1999), http://prunier.mss.ecp. fr/poudres &grains

CENTRALE PARIS

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Châtenay, le 14 June 2001

The Physical Review Letters
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Ridge NY 11961-9000
USA

Objet : corrected version of # LZ 7720

Dear Sirs,

Please find enclosed 4 copies of the revised version of the paper entitled "Identification of the jamming surface using soil mechanics results", # LZ 7720, author Pierre Evesque, which I submit for publication to Phys. Rev. Lett.

I join also a response to the referee remarks.

I have modified the introduction in order to stress the new result: (i) the paper identifies the jamming transition states to the states called "normally consolidated states" in the soil mechanics literature. (ii) it gives the equation of the jamming transition states. (iii) it gives some keywords of the "soil mechanics literature" which can help physicists finding more information.

I did not find in the literature some reference stressing points i, ii or iii. So I do believe these results are quite new and deserve publication.

Best regards

Pierre Evesque

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Grande Voie des Vignes - F-92295 Châtenay Malabry Cedex
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Identification of the jamming surface

using soil mechanics results

P. Evesque

Lab MSSMat, UMR 8579 CNRS, Ecole Centrale Paris

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Abstract:

Results from classical soil mechanics studies are used to propose an equation for the jamming transition surface of granular matter in σ, $1/\rho=v$ space; in which ρ is the density, v the specific volume and σ the stress actually supported by the granular structure. Taking axisymmetric conditions, labelling $q= \sigma_{11}- \sigma_{22}$ and $p=(\sigma_{11}+ \sigma_{22}+ \sigma_{33})/3$, and considering a normal range of pressures from 10 kPa to 10MPa, then the equation describing the surface of jamming transition is $v=v_o-\lambda \ln(p/p_o)+ \lambda_d \ln(1+q^2/(Mp)^2)$; where M is related to the friction angle, and $\lambda$and λ_d are constants dependant on the soil characteristics.

PACS #: 45.70 , 64.70.Pf, 83.70.Fn

The jamming transition corresponds to the stress-density states under which an heterogeneous fluid starts "freezing", i.e. stops flowing as a normal liquid and develops a strength which enables it to sustain a static stress field. This transition is a fundamental problem that has recently been attracting interest from physicists due to comparisons with the glass transition [1]. We do not want to discuss the latter point here. We would like to stress that some information on the jamming transition is already available in the technical literature, even though it is described in different words. For example, although the soil mechanics literature does not speak of this problem, it has nevertheless already identified the static law describing the variation of the minimum density in a soil as a function of the applied stress field. Obviously, this stress-density state shall be assimilated to the stress-density state at which the jamming transition occurs for this materials. So, the results of soil mechanics may assist physicists in their investigations. This is just what we want to report. Of course, it requires to know the terminology used in soil mechanics. This is given in the following.

Consider a dry granular material (e.g. sand) under static conditions, and subject to an axial stress field. The latter can be expressed along the principal axis direction as (σ_{11}, σ_{22}, σ_{33}), with $\sigma_{11} > \sigma_{22}=\sigma_{33}$. It can exist at different densities, $\rho=\rho_s v_s/v$, *where* ρ_s *is the density of the bulk solid.* However, ρ, cannot be lower than a given value. In the mechanics literature this loosest state is called the "normally consolidated state" [2,3,4] and is characterised by its specific volume, v, *labelled* v_{nc}. The value of v_{nc} is found to depend on the stress field. Labelling $q=\sigma_{11}-\sigma_{22}$, $p=(\sigma_{11}+\sigma_{22}+\sigma_{33})/3$, $\eta=q/p$ and M the ratio q/p at the limit of plasticity, *i.e.* $M=6\ \sin\varphi/(3-\sin\varphi)$ with φ the friction angle, one gets from an experimental fit, the following expression for v_{nc} :

$$v_{nc}=v_{nco}-\lambda \ln(p/p_o) - \lambda_d \ln(1+\eta^2/M^2) \qquad (1)$$

where λ and λ_d are two constants that depend on the material. The pressure range over which this equation is valid is from 10 kPa, 10 MPa. For lower pressures, experiments under micro-gravity conditions are required that are currently being carried out by NASA. At low pressures it is probable that v_{nc} tends to a given limit. For pressures larger than 10 MPa, grain crushing occurs, and this modifies the v_{nc} law mentioned above. Examples of this behaviour can be found in [3]. For granular matter and sands, the value of λ is about 0.06; an estimate of this value has been tentatively proposed from a microscopic model [4,5].

When granular matter is saturated with liquid, it is experimentally found that Eq. (1) still holds, but the stress field which needs to be considered in Eq. (1) is the effective stress, i.e. the one which is really supported by the grain structure. Owing to the so-called Terzaghi approximation, σ is then equal to the total stress σ_{tot} minus the liquid pressure u_w:

$$\sigma=\sigma_{tot}-u_w \qquad (2)$$

It is found that λ and λ_d do not depend on the presence of saturating liquid.

Similar conclusions hold for clays saturated with water, and Eq. (1) is valid provided that Eq. (2) is taken into account. The main difference is that the values of λ and λ_d are slightly larger, since the material is more "compressible". In fact the term "normally consolidated" comes from clays: indeed it is much more complicated to obtain loose sand samples than loose clay ones. Examples of the behaviour of clays can be found in [3].

It is worth mentioning that the shape of the transition curve in the ($v=1/\rho$, σ) space is convex and not concave as proposed in ref. [1].

As a final remark, the ensemble of "normally consolidated states" forms what is called in the soil mechanics literature, the Roscoe's surface *[2,4,7,10]* when $q/p=\eta<M$. When $q/p=\eta>M$, it forms what is called the Hvorslev's surface. Both surfaces are parts of the same

surface [4]. Knowing these notations *and keywords* may help physicists obtain more information, *but this does not suppress the necessity of reading, learning and thinking.*

For instance, Eq. (1) is just the combination of Eq. (2.10 bis) and (2.41) (p.79) of Britto & Gunn book [8]. Eq. (1) can be found in [3], (first Eq. of p.26 of [3]). Normal consolidation pertains to the list of keywords of [7], of [8] (indexing to pp. 173-174 of [8]) and of [9] (indexing to pp. 350-51). The Terzaghi principle is cited in [8] too. Experimental data on normal consolidation can be found in [3] and in [2], [10].

Acknowledgements: CNES is thanked for partial funding.

References:

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[7] Ground Engineer's reference book, (F.G. Bell ed., Butterworth, 1987): see Fig. 3.27; see Eq. 3.71, Eq. 3.45 (p. 3/23) ; Eq. ($v=N-k\ ln(p')-l-k)ln(p'_p)$); Fig. 3.27; see in key-word lists: normal consolidation

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*[10] K.H. Roscoe, A.N. Schofield & C.P. Wroth, "On the yielding of soil", Geotechnique **8**, 22, (1958)*

Answer to referee remarks and objections:

1) **The parallel between the jamming transition (limit of the dynamics) and the normally consolidated state (limit of the static condition) has never been done before. If the referees do not agree, can they provide a reference, please. So the idea developed in the article is a new, or there is no new idea in the jamming transition too.**

   The introduction has been changed in order to make this point clearer.

2) Beside this, this paper is aimed at giving (i) the equation of the jamming transition states, (ii) at showing it is concave instead of convex and (iii) at giving key words to physicists who want to find more experimental data on the jamming transition from soil mechanics literature.

3) I have changed slightly the definition of v to be dimensionless. (Thanks for the help).

4) M is defined in the text via its relationship with q/σ_3 and with the friction angle φ. These quantities are defined in all text books [2,3,4] of soil mech.; similar definitions can be found in Technical encyclopaedia ref [6 & 7] see refs below.

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9) New references are given:

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Châtenay, le 20 Septembre 2001

The Physical Review Letters
1 research road
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Ridge NY 11961-9000
USA

Objet : corrected version of # LZ 7720

Dear Sirs,

Please find enclosed 4 copies of the revised version of the paper entitled "Identification of the jamming surface using soil mechanics results", # LZ 7720, author Pierre Evesque, which I submit for publication to Phys. Rev. Lett.

I make appeal of your decision on August 30, 2001.

May I suggest as a third referee,

Prof. P.G. de Gennes, Collège de France, Paris,
Dr Didier Sornette, UCLA, and Nice (France)
Prof. S. Nagel Univ. Chicago

I join also a response to the referee remarks.

Referee B:

This paper makes the link between a problem to which a solution has not been given yet (i.e. the jamming transition) and experimental results.

I believe that reading is an active way of research.

NASA experiments is out of the scope of this paper.

Referee A:

This jamming-surface problem is an up-to-date problem, which interests physics literature.

There is no new physics, except that this paper shows an example, allows to introduce new data on the jamming transition,demonstrates that the surface is concave instead of convex, which was not known.

Nobody in the physics community was able to make the parallel prior this paper. Nobody in the mechanics community has made the parallel too, which means probably that the paper of Nagel et al. have not been understood by this community. I hope this paper will make the bridge between the two community.

Best regards

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Submitted to PRL on 17/12/00; # LZ7720 Corrections after referee reports 20/5/2001

Identification of the jamming surface using soil mechanics results

P. Evesque

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92295 CHATENAY-MALABRY, France,

e-mail evesque@mssmat.ecp.fr

Abstract:

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Re: LZ7720
Identification of the jamming surface using soil mechanics results
by P. Evesque

Dr. P. Evesque
Ecole Cent. Paris, Lab. de
Mecanique, Sols, Struc., Mat.
Grande Voie des Vignes
F-92295 Chatenay
Malabry, Cedex FRANCE

1 May 2001

Dear Dr. Evesque:

The above manuscript has been reviewed by our referee(s).

The resulting reports include a critique which is sufficiently adverse that we cannot accept your paper on the basis of material now at hand. We enclose pertinent comments.

If you feel that you can overcome or refute the criticism, you may resubmit to Physical Review Letters. Please accompany any resubmittal by a summary of the changes made, and a brief response to all recommendations and criticisms.

Yours sincerely,

Reinhardt B. Schuhmann

Reinhardt B. Schuhmann
Associate Editor
Physical Review Letters

enc.

0004–s2n

COPY

Referee A

This is, of course, an interesting Note, emphasizing that the behavior of sand piles (and more complex soil assemblies) have been already much studied by civil engineers, so that the empirical laws of soil failure are known and available and of probable interest to physicists concerned with 'fragile matter'.

I do think the letter approximately meets the PRL requirements of validity, importance and broad interest. It is not self-contained however,(what is a "friction angle", i.e., M??, ; what are the units of l ? (0.06 what? It should have a volume unit, or be unitless such as a fractional packing or something like that. The reader is not told. On the other hand, vnc is called a "specific volume", so it should be volume per gram???)

I do NOT think the letter meets the requirement of "Important Fundamental Research". The author has made a pertinent, interesting and I believe correct, connection between the soil mechanics literature and the timely topic of "jamming". While this is useful, there are no new results reported, so I don't think it is "new" in that sense.
Incidently, I spent several hours in the library pouring over soil mechanics books, such as

"Principles of Soil mechanics," R.F. Scott, Addison-Wesley, London, 1963.
"Critical State Soil Mechanics via Finite Elements", Britto and Gunn, Ellis Horwood series in Civil Engineering, (1987).
"Stress Strain Behavior of Soils", R.H.G. Parry Ed, 1971 (GT Foulis & Co, London)
"Shear Strength of Cohesive Soils", ASCE Proceedings, 1961
"Developments in Soil mechanics", Thomas Telford, London, 1983)

and I was unable to find equation 1 (though something near to it I did find). Please give a reference. I could also find nowhere the term "normally consolidated state". As it stands, it is still not too helpful for a physicist.

Publish as a comment?

COPY

Referee B

Identification of the jamming surface using soil mechanics results
P.Evesque (LZ7720)

Prof. Evesque has provided a very brief account explaining how some results that are apparently well known in the field of soil mechanics can be arranged to provide a description that is relevant to physicists. The investigation concerns the nature of a surface, the jamming surface, which separates qualitatively distinct kinds of particulate configurations. There is also a brief discussion that indicates the role and affect of a liquid that saturates the space between the particles.

It is very difficult to evaluate this manuscript. Firstly there are very few details (for instance surrounding experimental support for equation (1) and the definition of p_0) and secondly the major 'result' appears to be an awareness of soil mechanics literature (supported by unexplained references to Terzaghi approximation, Roscoe's surface and Hvorslev's surface etc.). The manuscript contains several loose expressions, e.g. 'density can not be looser than a given value' and 'it is probable that v_{no} tends to a given limit', which could be strengthened to increase the value of the account.

I cannot see how, in its present form, this Letter would contribute to an improved understanding of granular mechanics. It is unlikely that the level of description would make this account accessible to a general reader of Physical Review Letters. I cannot recommend publication.

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Re: LZ7720
Identification of the jamming surface using soil mechanics results
by P. Evesque

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Malabry, Cedex FRANCE

30 August 2001

Dear Dr. Evesque:

The above manuscript has been reviewed by our referee(s).

A critique drawn from the report(s) is enclosed. On this basis, we judge that the paper is not appropriate for Physical Review Letters, but might be suitable for publication in another journal, possibly with some revision. Therefore, we recommend that you submit your manuscript elsewhere. In accordance with our standard practice (see enclosed memo), this concludes our review of your manuscript.

Yours sincerely,

Jerome Malenfant
Senior Assistant Editor
Physical Review Letters

0001-T1LD

Second Report of Referee B

COPY

Identification of the jamming surface using soil mechanics results
P.Evesque (LZ7720)

This brief account expresses a belief that two surfaces in the phase space of dense particulate systems, identified by two different disciplines, are coincident. This surface separates static, or jammed, states of a particulate assembly from those that represent less dense systems and more mobile particles. The account is very brief and difficult to evaluate in isolation. An indication of the nature and strength of experimental support for equation (1) would improve the account. What experiments have been performed in the range 10 kPa to 10 Mpa and what experiments are being carried out at NASA? The cross-disciplinary identification facilitates the author to form an equation for the 'jamming' surface but it is difficult to assess the validity of the equation in the new (physics) regime. Whilst the argument is plausible it does not demonstrate how the initial conjecture has been evaluated? Although the account could be considered novel it is not clear that it is reporting 'substantial research' and, therefore, does not satisfy the criteria for publication in Physical Review Letters. I cannot recommend publication.

Second Report of Referee A (LZ7720 Evesque,P)

COPY

I have now read the author responses and the new revision several times. I agree with the author that he has identified a connection in the soil mechanics literature to the jamming transition in physics. I do not think that there is significant new physics in the connection as it is here presented (though new physics is certainly possible, if not indeed probable), since equation 1 (the basic result of the article) is completely empirical and the author does not discuss its physical basis or interpretation.

The present work supplies no new physical insights or information that I can see, though it does point out a promising and fruitful area of application for future results in "jamming" physics.

Date: Wed, 24 Oct 2001 15:13:55 -0400 (EDT)
From: Physical Review Letters <prl@ridge.aps.org>
To: evesque@mssmat.ecp.fr
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Re: LZ7720
Identification of the jamming surface using soil mechanics results
By: P. Evesque

Dear Dr. Evesque,

The complete file concerning the above manuscript has been reviewed by a Divisional Associate Editor. The enclosed comments advise against publication in Physical Review Letters. The Editors accept this advice.

Your appeal has been considered, and our decision to reject is maintained.

Sincerely yours,

Robert Garisto
Senior Assistant Editor
Physical Review Letters
Email: prl@aps.org
Fax: 631-591-4141

Report of Divisional Associate Editor (LZ7720 Evesque,P)

This paper makes a connection between results in soil mechanics and the jamming transition in granular matter. The author admits the paper is mostly a form of literature research. There is are new results reported, only an attempt to make known to the physics community some results from the field of soil mechanics. This information might be worthwhile as part of a longer research paper or maybe as a very short paper in a specialized granular matter journal, but certainly does not conform to the criteria for publication in PRL, namely new original research of broad interest. Thus, I see no reason to overturn the recommendations of both reviewers to reject this paper for publication in PRL.

-- Jan Tobochnik, Physics Chair
Departments of Physics and Computer Science Editor,
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J. Tobochnik
Divisional Associate Editor

Article soumis à Int. J. of Geomechanics par Evesque et Adjémian et rejeté en Février 2002

Etant donné les critiques, nous avons préféré édité cet article dans Poudres & Grains. (Poudres & Grains **12** (7), 115-121 (octobre 2001))

Ce travail a donné lieu à la thèse de F. Adjémian,

à une partie de F. Adjémian ; Eur. Phys. J. **E 9**, 253-259 (2002), "*Stress fluctuations and macroscopic stick-slip in granular materials"* , P. Evesque,

à F. Adjemeian & P. Evesque , Different regimes of stick-slip in granular matter : from quasi periodicity to randomnessIn Quasistatic deformations of particulate materials, (K. Bagi ed., publishing company of BUTE, Budapest, 2003), pp. 5-13; proceedings of the QuaDPM'03, Budapest Hungary, 22-25 August 2003, pp 5-13;

F. Adjemeian, P. Evesque & X. Jia, Acoustic speckle and diffusion as a probe of contact distribution ;In Quasistatic deformations of particulate materials, (K. Bagi ed., publishing company of BUTE, Budapest, 2003), pp. 15; proceedings of the QuaDPM'03, Budapest Hungary, 22-25 August 2003, pp. 15; ISBN 963 420 748 0

F. Adjémian & P. Evesque , Experimental study of stick-slip behaviour, International Journal for Numerical and Analytical methods in geomechanics [Int. J. Numer. Anal. Meth. Geomech.] 28, 501-530 (2004) 10:1002/nag350

F. Adjémian & P. Evesque Erratum on "Stress fluctuations in granular matter: Normal vs. seismic regimes in uniaxial compression test" (P&G 13,4 (2002); Poudres & Grains 14 (1), pp. 4-7, (2004)

à un artricle dans Powders & Grains 2005 : F. Adjémian, P. Evesque & X. Jia; Ultrasonic experiment coupled with triaxial test for micro-seismicity detection in granular media ; Powders & Grains 2005, Stuttgart, July 18-22, 2005, in Powders & Grains 2005, (Garcia-Rojo, Herrmann, McNamara ed., Balkema 2005), pp. 281-285

et à une collaboration avec X. Jia.

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February 26, 2002

Dr. Pierre Evesque
Ecole Centrale Paris
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FRANCE

Dear Dr. Evesque:

Enclosed are two reviews and one marked copy on your paper entitled, *Study of Stick-Slip Behaviour*. One reviewer suggests that the paper be resubmitted after detailed revision, while the other recommends rejection. Under the circumstance, in the present form, the paper is not recommended for publication in this journal

However, if you wish to consider revising the paper as per the reviewers' suggestions, I would be glad to send it for another review. In that case, please attend to the following items as marked:

- ☑ Revise the manuscript as per enclosed reviews and send me three/four copies of the revised version. Indicate in the margins of one of the copies locations where the review comments are complied with.
- ☐ Submit as Short Communication.
- ☑ Make any other appropriate changes in the manuscript.
- ☑ Attend to enclosed check list.
- ☐ Originals of _____text and _____figures are enclosed.
- ☑ Marked copy/copies are enclosed. (1)

With best wishes.

Sincerely yours,

C. S. Desai

Enclosures

Reviewer's Comments on "Study of Stick-Slip Behaviour" (Evesque and Adjemian)

#1

The experimental work and analysis reported on in this paper is of general interest to geotechnical community and provides some interesting results. However, I believe the work has some serious flaws that need to be addressed before the work can be published. These are enumerated below. There are also a number of other comments of a more editorial nature that should be considered.

Principal comments:

1. While the authors make reference to the fact that their measures of stress and strain used in analyzing their data (simple engineering stress and strain) are not adequate, the implications of this are not addressed and could have significant impact on the conclusions. The deformations measured during the experiments are very large and serious errors result from using simple engineering stress-strain measures. At a minimum, the authors should re-analyze the data using a strain/deformation measure compatible with the large deformations and an associated work-conjugate stress measure. I suspect that if this were done, some of the conclusions regarding the magnitude of the stress drops and changes in the nature of the stick-slip process with confinement and strain rate will change.

2. The authors refer to the fact that sample size is a significant factor affecting their results. It is not clear what specifically they mean by this, but I assume they are referring to specimen volume relative to a characteristic volume element. I would submit that there is another effect that is not being considered that clearly shows up in the data. The material "A" samples have different aspect ratios ranging from a height to diameter of 1.22 down to 1.0. Clearly, all other parameters being constant, the change of aspect ratio will dramatically affect the results because, for ratios below 2.0, the end effects are significant, e.g. reducing the aspect ratio has the same effect as increasing the confinement. For this reason, all standard test methods require samples with aspect ratios of 2.0 or greater to avoid this problem. The effect clearly shows up in Table 1 and in the comparison of plots in several Figures. In Table 1, the reported friction angle correlates exactly with sample aspect ratio. The other problem is the ratio of particle/grain size to sample diameter. For samples with a diameter greater than 20 particle diameters, the effect of particle size should be minimal other than the possible effect of particle size on strength (strength should scale as the square root of the particle size). For "B" type samples, this effect could have an impact on the results. Clearly the authors need to be comparing results from samples with only a limited number of independent variables. Therefore, it is strongly suggested that some additional tests be performed where the sample aspect ratios are kept constant, sample diameter to particle size is greater than 20, and the particle sizes and sample volumes are varied. I think this will result in quite different conclusions than

those derived in the current paper. For example the characteristic volume element will turn out to be quite a bit smaller than proposed.

3. The authors make no mention of the effect of machine stiffness on their observed results. In dynamic micro-failure events, the energy stored in the system (loading machine plus specimen) plays a key role in driving the dynamics of the deformation. For example in a compliant system, fractures or frictional slips will have a completely different character than those produced by the same material in a very stiff loading machine. The result is that the reported δq values for frictional slips in the tests are as much a function of the machine stiffness as the material. The authors could demonstrate the machine stiffness effect by conducting similar tests where a spring of known stiffness is inserted between the specimen and the loading ram. By using springs of different stiffnesses, the machine effect can be estimated and the effect on the results accounted for.

Editorial Comments:

1. The authors include a lot of stress-strain plots for comparison to evaluate the effect of certain variables. It would be very helpful if all the plots were on the same scale. Different scales make it very difficult for the reader to grasp the comparison.

2. The manuscript, as a whole is too long, a concerted effort should be made to make it more concise.

3. The manuscript would benefit from a detailed editing. There are several places where concepts are lost in the translation. Several of the Figures also need editing to make the notation consistent throughout.

4. Figure 8a is the wrong plot (should be same plot as Figure 7a).

Summary:

The work reported in this paper has potential but also has flaws that need to be corrected before it is ready for publishing. I recommend, therefore, that the authors consider the comments above and re-submit the article at a later date.

Review of **"Study of stick-slip behaviour"** by Evesque and Adjemian

#2

The authors present an experimental study of the behaviour of a limited number of quartz particles and find that the behaviour is characterized by what they call a stick-slip phenomenon. Although quartz particles are used, this stick-slip phenomenon is apparently not the one usually associated with quartz. This, however, is not clear from the presentation. But it appears that the phenomenon is significant when a limited number of particles are tested, and it disappears (?) when the number of particles is sufficiently large. Unfortunately, the presentation is so flawed that it is difficult to follow it and to judge the quality of the contents. The presentation is rather cursory, wordy, and not concise (language is spoken, structure of sentences and sentences themselves appear to be jotted down as the words come to mind), the experimental technique is not high quality. The overall impression is that of a careless research project and presentation. It is recommended to decline the contribution. The following comments may be considered:

1) p. 4, middle: Detailed explanation of well-known items in soil mechanics are given, but explanations of essential experimental techniques are omitted. The authors should mention and explain the continuous recording of data, since continuous curves are necessary and in fact recorded. Were lubricated ends on the triaxial specimens used? Apparently the volume change was not measured, even though this is easily done, also for dry samples. The area correction is therefore not made in the first place, and the consequences of different types of corrections are explained in a 2-page appendix. Thus, the quality of the experimentation is questionable, and using 2 pages in the journal to explore the consequences of different assumptions seems extravagant and unnecessary, when this is standard soil mechanics techniques today.

2) p. 4, 6 lines from bottom: H = D in some experiments. Were lubricated ends used? Or were the specimens barrel-shaped at the end of the experiments? Quality of data?

3) Table 1: It is difficult to tell how reliable the friction angles are since the volume change was not measured and correct area corrections, especially at large strains, have not been made.

4) p. 5, 7 lines from bottom: " In soil mechanics, the ratio σ_1'/σ_3'...." The statement in this sentence is not correct in general. It depends on whether the samples are drained or undrained. The tendency is correct for undrained tests on dense sand, but not for loose samples, and not for drained tests. Here we are dealing with drained tests, so the statement does not semm to be appropriate.

5) p. 5, 5 lines from bottom: "So the limit ratio at plateau can be interpreted as solid friction." This is not correct. This plateau in undrained tests on this diagram contains effects of a tendency for dilation, and it contains effects of remolding at constant volume. This does not represent solid friction.

6) p. 5, line 7 from bottom: Switch to effective stresses - why? Are we talking about undrained tests? Authors do not appear to be aware of the different behaviours in drained and undrained tests, and they liberally use what they can use for comparison with their own results.

7) p. 6: n is used as a counter here, while it represents the porosity on p. 5, line 3.

8) p. 7, line 4: v is velocity here, while it represents the volume in line 2 of section II.

9) p. 7, line 10 and 11: Cap V used for velocity here (see previous comment).

10) p. 7, line 10: Is m the mass of the block, not the slider?

11) Figs. 4c and 5a: Indicate rates in the 4th sections of the tests.

12) Figs. 5a and 5b: "For instance similar Δq amplitudes are obtained for the three $d\varepsilon_1/dt$ = V/H strain rates in Figs. 5a and 5b." How is this seen? For the same strain rate? The vertical scales are not the same in Figs. 5a and 5b - difficult to judge.

13) Figs. 6a, 6c, and 6e: Comparisons are difficult, because none of the coordinate axes are the same. How can the reader follow the arguments, when the points being made are extremely difficult to observe on the figures?

14) p. 8, second paragraph in section III.1.2: "In next part..." This is not understood at all.

15) p. 8, line 6 from bottom: V>0.18 mm/mn should be 0.18 mm/min.

16) p. 8, near middle: Piston speed is given in s^{-1}, whereas velocities are given in the figures in mm/min. The sample heights play a role in the comparisons of these deformation rates and strain rates. How can the reader get anything out of this presentation?

17) Figs. 4, 5, 6,: Comparisons of velocities are made in mm/min, while the sample height changes. Should results be compared in terms of deformation rates or in terms of strain rates? Are these test data actually comparable? They appear to correspond to different strain rates. The authors need to explain the data in much more detail and make the comparisons before presentation of the essentially raw data to the reader.

The contents of this paper may be of interest after the data have been thoroughly analysed (!), but it is not the readers job to make the analyses.

18) Fig. 7: Again, the reader is being asked to observe the behaviour in 6 diagrams, none of which have comparable scales on the ordinates or the abscissas. - And the results correspond to different sample heights, while the deformation rates are given in mm/min, i.e. different strain rates!

At this point it was clear that this contribution would be declined, and the remainder of the paper was not reviewed.

Article PRL_LSK8l3 refusé en Août 2002 par Phys Rev Lett : "Comment on "Coexistence of two granular temperatures in binary vibrofluidized beds" by Pierre Evesque

Je n'ai pas accepté considérer les reproches de Phys Rev Lett. Il a été publié sans réel amendemant dans Poudres & Grains en Avril 2002 (P. Evesque, Poudres & Grains 13 (2), 20-26 (2002), " Are Temperature and other Thermodynamics Variables efficient Concepts for describing Granular Gases and/or Flows **?**")

$>>n\ m/d^2$ so that the piston mass can be considered as infinite for collision rules. We assume also that bead-bead and bead-piston collisions are both governed by the same restitution coefficient ε and that we can neglect the air effect. Let us also neglect particle rotation, stating for instance that the rotation kinetic energy behaves as the mean translation kinetic energy.

The equality between inertial mass and gravity mass imposes that the mass m of the particles does not play any part in determining the particle -trajectories and -speeds because it intervenes neither in the free-flight dynamics nor in the collision characteristics, as far as the restitution coefficient ε remains independent of the speed V. This leads to predict that two sets of identical particles having the same diameter and the same coverage ratio n and submitted to the same vibration excitation will vibrate similarly even if the two particles have different masses m_1 and m_2, the restitution coefficient being assumed the same, *i.e.* $\varepsilon_1=\varepsilon_2$. It means that these particles will get the same typical speed $\underline{V}$, independently of m. So, $\underline{V}=\underline{V}_1=\underline{V}_2$. Of course, $\underline{V}$ depends on the other experimental parameters which are a, ω, ε, n, g, d; in particular, one expects that the larger a and/or ω the larger the grain speed so that dimensional analysis leads writing:

$$\underline{V}= a\omega\, f\{\varepsilon, n, d/a, gd/(a\omega)^2\} \qquad (1)$$

where f is a function of 4 dimensionless parameters. Indeed, as m/m=1 and m/M=0 are both independent of m, dimension analysis confirms also that **Eq. (1) is independent of m**. Furthermore, as the "granular temperature" T is defined as $T=\langle mV^2/2\rangle= m\underline{V}^2/2$, **this demonstrates that a vibrator is a "velostat" instead of a thermostat**, which means that it imposes a speed and not a temperature (or a mean kinetic energy). Indeed if we consider two granular gases differing only by the mass m_1 & m_2 of their grains, so that $m_1>m_2$, but $d_1=d_2$, $n_1=n_2$, $\varepsilon_1=\varepsilon_2$, $a_1=a_2$ and $\omega_1=\omega_2$, Eq. (1) imposes $\underline{V}_1=\underline{V}_2$ so that their temperatures T_1 & T_2 are different, their ratio being $T_1/T_2=m_1/m_2$. But the heights H_1 and H_2 of their cloud are equal, *i.e.* $H_1=H_2$, since $\underline{V}_1=\underline{V}_2$.

Let us now investigate the mixing of these two gases in proportion c_1 & c_2, $c_1+c_2=1$, keeping $n=n_1c_1+n_2c_2$ constant: relabelling $T_{1,o}$ & $T_{2,o}$ their temperatures when they are separated ($T_{1,o}$

$> T_{2,o}$) & ($V_{1,o} = V_{2,o}$), and as mixing shall smoothen the temperature difference, one expects then that mixing (i) lets $T_1>T_2$, but that (ii) $T_1-T_2< T_{1,o}-T_{2,o}$, so that it heats up the lighter particles from $T_{2,o}$ to $T_2=T_{2,o}+\Delta T_2$ and cools down the heavier ones from $T_{1,o}$ to $T_1=T_{1,o}-\Delta T_1$ in such a way (i) that $T_1 -T_2 < [T_{1,o}-T_{2,o}]$ and (ii) that the larger c_2 the larger ΔT_1, while the smaller c_1 the larger ΔT_2 . In particular, this analysis does not conclude to the necessity of a thermodynamics equilibrium between the two species so that one shall accept that $T_1 \neq T_2$ in general. Furthermore as the two mean speeds are now different $\underline{V}_1 \neq \underline{V}_2$, one expects that H_1 and H_2 be different too, leading probably to predict the existence of some spatio-temporal segregation.

Let us now compare the characteristics of two granular gases of identical particles under the same excitation (a,ω); as we want to investigate the gaseous case, we limit to small value of n and rather large value of the acceleration $a\omega^2 >> g$. We consider two granular gases with the same number of layers at rest, so that $n_1=n_2 \approx 1$. Be (m_1 ,d_1) & (m_2,d_2) the particle- (mass , size) of each gas respectively. Eq. (1) predicts that their speed $\underline{V}_1$ and $\underline{V}_2$ can be different, due to the difference between d_1 and d_2. However, let us assume that we are investigating the case of a granular gas for which the cloud height H shall be large, *i.e.* H>>d, H>>a. Indeed in this limit, one expects that confinement is due to g, so that H scales as $\underline{V}^2/g$ and that $\underline{V}$ scales as $a\omega$, for a fixed set (n, d, m). This imposes that d/a and $gd/(a^2\omega^2)$ do not play some important part. In turn this assumes that $a\omega^2 >> g$.

At this stage, it is worth noting by passing that the mean free path l_c is given by $l_c=(L^2H)/[N\pi d^2]$ so that it scales as H/n and is independent of d. Furthermore, when n>1, one expects the gas to be not homogeneous along the vertical so that l_c increases with the height in the cloud; this is due to both the action of local collision dissipation and to the mean confining pressure which decreases when the upper layer is approached.