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The role of liquid films for light transport in dry foams

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Abstract. – We study the role of liquid films for light transport in dry foams based on ray optics. The foams are modelled by two-dimensional Voronoi tessellations with varying degree of disorder. We perform extensive simulations to determine the diffusive limit of light for two models. In model I, we choose a constant intensity reflectance r to explore the effect of disorder. We show that the honeycomb structure sets the right order of magnitude for the diffusion constant D by providing a master curve for $D(r)$, whereas disorder reveals itself in a fine structure. In model II, the reflectance for thin films as determined by Fresnel's formulae is chosen as well as some disorder in the film thickness. We argue that this model reproduces experimental features and the right order of magnitude for the diffusion constant. This suggests that the liquids films in combination with ray optics are relevant for explaining photon diffusion in foams.

Introduction. – Many objects in nature, *e.g.*, conventional colloidal suspensions or thick aligned nematic liquid crystals, are visibly opaque. In such turbid samples, each photon is scattered many times before exiting the material. Therefore, the photon can be considered as a random walker which ultimately leads to a diffusive transport of light intensity [1–3]. The recently developed technique of diffusing-wave spectroscopy (DWS) [4] exploits this diffusive nature of light transport to provide information about the static and dynamic properties of an opaque system.

Recent experiments have applied diffusing-wave spectroscopy to cellular structures like foams which consist of air bubbles separated by liquid films [5, 6]. This suggests that the model for the photon transport based on the random walk picture is still valid. However, there is a debate in the literature about the main mechanism underlying the random walk [6]. A relatively dry foam consists of cells separated by thin liquid films. Three of them meet in the so-called Plateau borders which then define tetrahedral vertices [7]. One suggestion is that light scattering from the Plateau borders [6,8] or vertices is mainly responsible for the random walk. However, experiments seem to imply that scattering from Plateau borders is not the only or most significant mechanism [6, 9]. On the other hand, since the cells are much larger than the wavelength of light, one can employ ray optics and follow a light beam or photon as it is reflected by the liquid films with a probability r called the intensity reflectance. This naturally

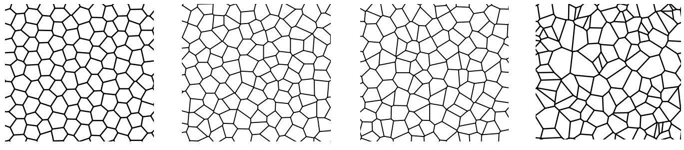

Fig. 1 – Various disordered Voronoi foams. From left to right, the magnitude h of the displacement vector is 0.3, 0.5, 0.6, 2 (in units of the edge length of the initial honeycomb structure) and the disorder in the foams is characterized by the measures (μ_2, η_2).

leads to a random walk of the photons in space [10]. In connection with this ray optics picture, recent experiments and simulations show photon channelling in the Plateau borders [9].

Here we present a study of the second mechanism based on ray optics. In a previous paper, we have already implemented it for the simplest model of a two-dimensional foam, the regular honeycomb structure, using a constant intensity reflectance r [10]. However, the honeycomb structure is highly idealistic. Therefore, in this letter, we extend our studies towards real dry foams in two steps. In a first model, we introduce topological and geometrical disorder based on a Voronoi foam model [11] to investigate the influence of disorder. In a second model, we use the Fresnel formulas to implement the intensity reflectance r with its significant dependence on the incident angle and the film thickness. In addition, disorder in the film thickness is considered. We find that our approach, which combines ray optics and a realistic model for r, reproduces experimental features and the right order of magnitude for the diffusion constant.

Voronoi foam. – As the simplest model of a two-dimensional disordered dry foam, we choose the Voronoi tessellation [11, 12]. For an arbitrary distribution of seed points in a simulation box, Voronoi polygons are constructed in complete analogy to the Wigner-Seitz cells for periodic arrangements of lattice sites. We start with a triangular lattice of seed points, which gives the honeycomb structure, and then systematically introduce disorder by shifting the seed points in randomly chosen directions, whereas the magnitude h of the displacement vector is kept constant. Figure 1 shows typical Voronoi foams with h increasing from left to right which apparently increases the disorder. All our Voronoi tessellations are produced by the software *Triangle* [13]. They have approximately 2870 cells and 8600 edges in the simulation box, a small fraction of which is shown in fig. 1. To simulate photon diffusion in these tessellations, periodic boundary conditions are used.

We use two measures to quantify the disorder in the foam. First, the number of sides of a cell s is a random variable. From Euler's theorem applied to a polygonal tessellation, it follows that $\langle s \rangle = 6$, where $\langle \ldots \rangle$ denotes averaging over all cells [11]. We use the second moment of the edge distribution, $\mu_2 = \langle (s-6)^2 \rangle$, to characterize the *topological* disorder of the foam [11], *i.e.*, the deviation from hexagons. Secondly, the length l of an edge is another natural random variable. We find that in our samples the average edge length $\langle l \rangle$ deviates only slightly from the initial value l_0 of the honeycomb structure. However, the second moment $\eta_2 = \langle (l - \langle l \rangle)^2 \rangle / \langle l \rangle^2$ exhibits considerable variations. We use it to characterize the *geometric* disorder of the foam. Both measures for disorder are indicated in fig. 1 as (μ_2, η_2). Note first that the last Voronoi foam is close to a Poisson foam [$(\mu_2, \eta_2) = (1.781, 0.416)$], which is considered as a *complete spatial random* pattern and which, in principle, allows the analytical evaluation of the moments of various distribution functions [12]. Secondly, in experiments of the temporal evolution of 2D soap froth, Stavans and Glazier found a stationary scaling regime with $\mu_2 = 1.4 \pm 0.1$ [14] which agrees with one of our disordered Voronoi foams used below.

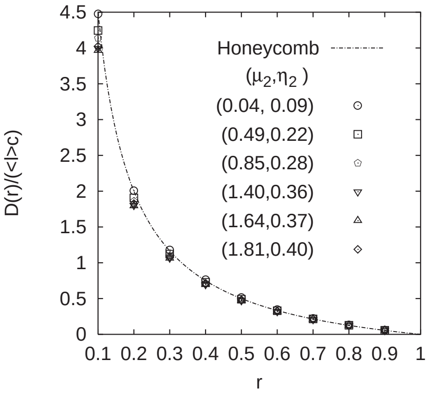

Fig. 2

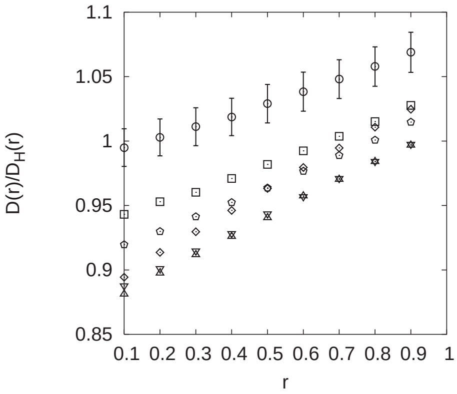

Fig. 3

Fig. 2 – The diffusion constant (in units of average edge length $\langle l\rangle$ times light velocity c) as a function of intensity reflectance r, for various disordered foams. Monte Carlo simulation results and $D_{\rm H}(r)$ are denoted, respectively, by points and the full line.

Fig. 3 – The diffusion constant $D(r)$ plotted relative to $D_{\rm H}(r)$ as a function of intensity reflectance r, for various disordered foams as indicated in the legend of fig. 2.

In the following we model the photon paths in a Voronoi tessellation as a random walk with rules motivated by ray optics, *i.e.*, an incoming light beam is reflected from an edge with a probability r or it traverses the edge with a probability $t = 1-r$. This constitutes a persistent random walk since the new direction chosen by the photon depends on the direction of the previous step [15,16]. Persistent random walks are employed in turbulent diffusion [17], polymers [18], diffusion in solids [19], and in general transport mechanisms [20]. Our work is also related to transport processes in disordered Voronoi networks [21]. We performed extensive numerical simulations, whose details are explained in ref. [10], to mimic the random walk in various disordered samples and to determine the diffusion constants for the following two models.

Model I. – Here we assume that the edges of the Voronoi cells have a constant reflectance r. In fig. 2 we plot the diffusion constant as a function of r for various disordered Voronoi foams, as indicated in the legend, and compare it to the diffusion constant $D_{\rm H}(r) = \frac{1-r}{2r}\langle l\rangle c$ of the unperturbed honeycomb structure with an edge length $\langle l\rangle$ and an injection angle of 60° relative to one edge [10]. Remarkably, all the diffusion constants of the disordered samples are similar to $D_{\rm H}(r)$, which therefore provides a master curve. So topological and geometrical disorder have no strong effect on the diffusion constants and the honeycomb structure gives the right order of magnitude. We increase the resolution by plotting $D(r)/D_{\rm H}(r)$ *vs.* r in fig. 3. For the honeycomb structure such a plot reveals a variation of the diffusion constant with the injection angle, as demonstrated in fig. 5 of ref. [10]. Even for the slightest disorder, all the curves for different injection angles collaps on a single curve, which is shown in fig. 3. However, it is surprising that the diffusion constant still deviates from the usual $(1-r)/r$ law (as seen in the honeycomb structure), since it contains an additional factor linear in r, as fig. 3 clearly reveals. So features of the honeycomb structure are still preserved. Furthermore, fig. 3 shows that the linear correction of the diffusion constant significantly depends on the different disordered samples. So the diffusion constant is sensitive to the amount of disorder in the Voronoi foam. We tried to understand this "fine structure" within an effective cage model where we assumed that the photons move from one cell to

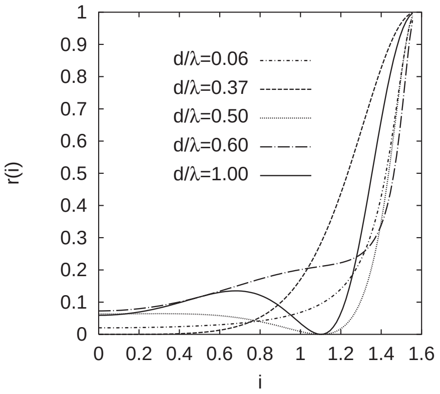

Fig. 4

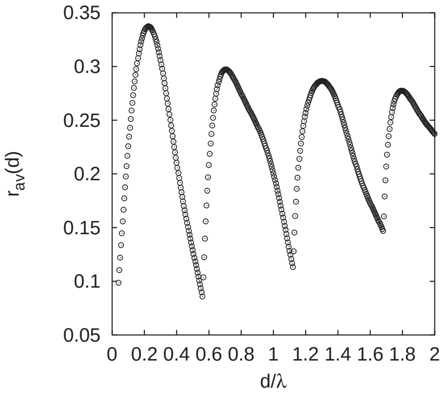

Fig. 5

Fig. 4 – Intensity reflectance as a function of angle of incidence i for various film thicknesses d/λ as given by eq. (1).

Fig. 5 – Angular averaged reflectance $r_{\rm av} = \frac{2}{\pi}\int r(i){\rm d}i$ as a function of d/λ.

the other during transmission and that during reflection they just stay at their positions and change their direction according to some probability function. We determined the diffusion constant for this model analytically by setting up the appropriate master equation. We indeed find, apart from the $(1-r)/r$ law, an additional factor linear in r. However, the slope is negative and the offset is larger than 1, just contrary to what we find in fig. 3. Our current guess is that the features in fig. 3 depend on local correlations within the Voronoi foam which are hard to describe in an effective random walk model.

Model II. – In the second model, we consider edges with a finite thickness d and apply the reflectance r of a thin film of refractive index n that now depends on the angle of incidence i (measured with respect to the normal of the film). Summing up all possible multiple refraction paths in the film and applying Fresnel's formulae to each refraction event, one obtains, in the case of the electric field perpendicular to the plane of incidence [22],

$$r(i)=\frac{2r_{12}^2[1-\cos(i_0)]}{1+r_{12}^4-2r_{12}^2\cos(i_0)}\,,\quad r_{12}=\frac{\cos(i)-\sqrt{n^2-\sin^2(i)}}{\cos(i)+\sqrt{n^2-\sin^2(i)}}\,,\quad i_0=4\pi\frac{d}{\lambda}\sqrt{n^2-\sin^2(i)}. \quad (1)$$

Figure 4 illustrates r as a function of the angle i for different thicknesses d/λ and the refractive index $n = 1.34$ of water. For films as thin as a common black film ($d \approx 30\,{\rm nm}$ or $d/\lambda = 0.06$ for $\lambda = 500\,{\rm nm}$) [7], the reflectance is very small but sharply increases to 1 close to grazing incidence ($i = \pi/2$). Increasing the thickness d, oscillations in $r(i)$ start to enter at $d = \lambda/(2n)$ due to the constructive and destructive interferences of the multiple refraction paths. We numerically determined an angular averaged reflectivity $r_{\rm av} = \frac{2}{\pi}\int r(i){\rm d}i$ to illustrate the overall effect of d. In fig. 5, $r_{\rm av}$ is plotted as a function of d/λ. The reflectance for electric fields parallel to the plane of incidence shows the same qualitative behavior. Especially, in the angular averaged reflectivity the characteristic minima are situated at approximately the same values d/λ as in fig. 5, although the absolute values are by a factor of 2 smaller. Therefore, we only used eqs. (1) in simulating the photons' random walk. Furthermore, in our model we introduce some additional randomness in the thickness of the film d assuming that it is

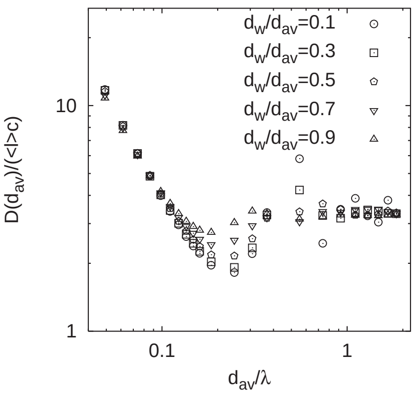

Fig. 6

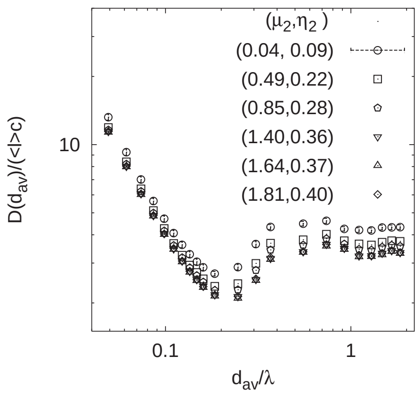

Fig. 7

Fig. 6 – The diffusion constant as a function of $d_{\rm av}/\lambda$ for the disordered sample $(\mu_2, \eta_2) = (1.81, 0.4)$ with various thickness distributions. Other disordered samples show the same behavior.

Fig. 7 – The diffusion constant $D(d_{\rm av})$ as a function of $d_{\rm av}/\lambda$ for various disordered foams with $d_{\rm w}/d_{\rm av} = 0.5$. Other thickness distributions show the same behavior.

uniformly distributed in $[d_{\rm av} - d_{\rm w}, d_{\rm av} + d_{\rm w}]$, where $d_{\rm av}$ denotes the average thickness and $d_{\rm w}$ the width of the distribution. We will comment below on this assumption.

In fig. 6, we plot the diffusion constant D in units of $\langle l \rangle c$ as a function of $d_{\rm av}/\lambda$ for the most disordered Voronoi foam but different $d_{\rm w}$. For small disorder in the film thickness ($d_{\rm w}/d_{\rm av} = 0.1$), D is clearly oscillating when $d_{\rm av}/\lambda$ decreases from 2. It then reaches a pronounced minimum at around $d_{\rm av}/\lambda = 0.23$ and finally monotonically increases. This behavior is in complete agreement with the plot of $r_{\rm av}$ in fig. 5. Disorder in the film thickness decreases the oscillations to an approximately constant D, the minimum nearly vanishes, and the monotonic increase in D for small $d_{\rm av}/\lambda$ does not show a significant dependence on $d_{\rm w}$. In fig. 7 we choose $d_{\rm w}/d_{\rm av} = 0.5$ and plot D as a function of $d_{\rm av}/\lambda$ for different disordered Voronoi foams. Interestingly, the curves have all the same shape but, for increasing disorder in the foams, the first three samples are shifted downward, whereas the three most disordered samples are not distinguishable in the present resolution. So again, disorder shows itself in a quantitative effect on D rather than a qualitative one.

An important parameter for foams is the volume fraction ε of the liquid phase. The question of how the film thickness $d_{\rm av}$ depends on ε is controversal in the literature. On the one hand, it is assumed that $d_{\rm av}$ is set by the interfacial forces, *i.e.*, independent of ε. However, with $d_{\rm av} \approx 30\,$nm (common black film) [23, 24] and $d_{\rm av} \approx 100\,$nm [25] different values are stated. On the other hand, a linear relationship $d_{\rm av} \propto \varepsilon$ is reported with film thicknesses up to 2000 nm [26]. The last reference might also justify our assumption that the film thickness in a real foam shows some distribution about an average value. We already showed that such a distribution decreases the oscillations of D when $d_{\rm av}/\lambda$ is changed. These missing oscillations were used in ref. [6] to argue against the importance of the films for the photon diffusion. Here we present a mechanism to reduce them. However, even for vanishing $d_{\rm w}$, oscillations do not occur for $d_{\rm av}/\lambda < 0.2$, as demonstrated in fig. 6. In ref. [6], it was also observed that the diffusion constant hardly depends on the wavelength of light in the visible spectrum. The constant D for $d_{\rm av}/\lambda > 0.3$ for the most disordered foams in fig. 6 reproduces this fact. However, for $d_{\rm av}/\lambda < 0.2$, we predict an increase of D with decreasing λ^{-1}. In ref. [6] the dependence on λ was not reported for very dry foams, so it is not clear in which regime of the averaged film thickness the measurements were performed. Therefore, an experimental confirmation of our prediction would be a strong argument for the approach presented here.

The diffusion constant D is linked to the transport mean free path l^* via $D = cl^*/m$, where m is the spatial dimension. Detailed studies of l^*/a as a function of ε, where a is the average bubble diameter, were undertaken by Durian and collaborators [6]. If we choose $a = 2\langle l \rangle$ for the Voronoi foams, as suggested by a hexagon, we can directly compare our results to fig. 3 in ref. [6]. There, l^*/a increases from 2 to 20 for decreasing ε, whereas in our case l^*/a varies between 2 and 12 (for $d_{\rm av} \approx 30\,\rm nm$). This quantitative agreement for l^*/a serves as a strong argument for our approach concentrating on the films and ray optics. If it were of minor importance in the photon diffusion, it would give much larger transport mean free paths. Of course, our studies were done in 2D. However, we speculate that they also apply to the three-dimensional foams of ref. [6]. Although this has to be confirmed by appropriate simulations, we already have hints for this speculation. The l^* of one-dimensional photon paths in the honeycomb lattice is by a factor of $\sqrt{3}/2$ smaller than the l^* of two-dimensional paths with an injection angle of 60° [10]. Such a factor would not spoil our quantitative agreement. Furthermore, the steady increase in l^*/a observed in ref. [6] for decreasing ε in dry foams is directly comparable to the behavior in fig. 6 for $d_{\rm av}/\lambda < 0.2$.

Finally, we comment on the very appealing idea of photon channeling in foams as reported in ref. [9]. We implicitly include photon paths which preferentially move in the "liquid phase" since the reflectance r in eq. (1) includes multiple refraction paths. However, there is an important difference; whereas in our treatment the multiple refraction paths interfere constructively and destructively, this effect seems to be not taken into account in the simulations of ref. [9].

Conclusion. – We have presented a detailed study of the role of films for light transport in disordered 2D Voronoi foams. We show that the amount of disorder has a quantitative effect on the diffusion constant rather than a qualitative one which might depend on local correlations within the Voronoi foam. We speculate that the results within model II can be directly compared to measurements of the transport mean free path in 3D. Based on a quantitative agreement, we then argue that the liquid films play a significant role for explaining light diffusion in foams. This reasonable assumption, however, needs a confirmation by simulations using 3D model foams. To test our results within model II, measurements of the transport mean free path as a function of the wavelength of light for very dry foams would be helpful.

So far, we cannot exclude the importance of light scattering from Plateau borders or vertices for the diffusive behavior of light. A simple estimate where the vertices in 2D with a radius of curvature $R \ll \langle l \rangle$ are viewed as isolated scatterers leads to a transport mean free path of $l^*_{\rm S} \propto \langle l \rangle^2/R$. This can become comparable to $l^*/2\langle l \rangle \approx 12$, which we find within model II in the common black-film limit. To clarify this question in future, we aim at a model which combines both mechanisms. Also, an extension of our ray-optics approach to wet foams and, as already stated, to 3D is envisaged. Clearly, we are progressing towards a detailed understanding of the mechanisms underlying light diffusion in foams.

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REFERENCES

[1] Sheng P. (Editor), *Scattering and Localization of Classical Waves in Random Media* (World Scientific, Singapore) 1990; Sheng P., *Introduction to Wave Scattering, Localization, and Mesoscopic Phenomena* (Academic Press, San Diego) 1995.

[2] Maret G., in *Mesoscopic Quantum Physics, Les Houches, Session LXI*, edited by Akkermans E., Montambaux G., Pichard J.-L. and Zinn-Justin J. (North-Holland, Amsterdam) 1995.

[3] van Tiggelen B. and Stark H., *Rev. Mod. Phys.*, **72** (2000) 1017.

[4] Maret G. and Wolf P. E., *Z. Phys. B*, **65** (1987) 409; Pine D. J., Weitz D. A., Chaikin P. M. and Herbolzheimer E., *Phys. Rev. Lett.*, **60** (1988) 1134; Maret G., *Current Opin. Colloid Interface Sci.*, **2** (1997) 251.

[5] Durian D. J., Weitz D. A. and Pine D. J., *Science*, **252** (1991) 686; *Phys. Rev. A*, **44** (1991) R7902; Earnshaw J. C. and Jaafar A. H., *Phys. Rev. E*, **49** (1994) 5408; Höhler R., Cohen-Addad S. and Hoballah H., *Phys. Rev. Lett.*, **79** (1997) 1154; Cohen-Addad S. and Höhler R., *Phys. Rev. Lett.*, **86** (2001) 4700.

[6] Vera M. U., Saint-Jalmes A. and Durian D. J., *Appl. Opt.*, **40** (2001) 4210.

[7] Weaire D. and Hutzler S., *The Physics of Foams* (Oxford University Press, New York) 1999.

[8] Skipetrov S., private communication (2003).

[9] Gittings A. S., Bandyopadhyay R. and Durian D. J., *Europhys. Lett.*, **65** (2004) 414.

[10] Miri MF. and Stark H., *Phys. Rev. E*, **68** (2003) 031102.

[11] Weaire D. and Rivier N., *Contemp. Phys.*, **25** (1984) 59.

[12] Okabe A., Boots B. and Sugihara K., *Spatial Tessellations, Concepts and Applications of Voronoi Diagrams* (John Wiley & Sons, Chichester) 2000.

[13] Shewchuk J. R., `http://www-2.cs.cmu.edu/~quake/triangle.html`.

[14] Stavans J. and Glazier J. A., *Phys. Rev. Lett.*, **62** (1989) 1318.

[15] Weiss G. H., *Aspects and Applications of the Random Walk* (North-Holland, Amsterdam) 1994.

[16] Haus J. W. and Kehr K. W., *Phys. Rep.*, **150** (1987) 263.

[17] Taylor G. I., *Proc. London Math. Soc.*, **20** (1921) 196.

[18] Flory P. J., *Statistical Mechanics of Chain Molecules* (Interscience, New York) 1969.

[19] Glicksman M. E., *Diffusion in Solids: Field Theory, Solid-state Principles, and Applications* (Wiley, New York) 2000.

[20] Larralde H., *Phys. Rev. E*, **56** (1997) 5004; Boguñá M. and Masoliver J., *Phys. Rev. E*, **58** (1998) 6992; Boguñá M., Porrà J. M. and Masoliver J., *Phys. Rev. E*, **59** (1999) 6517.

[21] Priolo A., Jaeger H. M., Dammers A. J. and Radelaar S., *Phys. Rev. B*, **46** (1992) 14889; Jerauld G. R., Hatfield J. C., Scriven L. E. and Davis H. T., *J. Phys. C*, **17** (1984) 1519.

[22] Reitz J. R., Milford F. J. and Christy R. W., *Foundations of Electromagnetic Theory* (Addison-Wesley, Reading) 1979.

[23] Monnereau C. and Vignes-Adler M., *Phys. Rev. Lett.*, **80** (1998) 5228.

[24] Hilgenfeldt S., Koehler S. A. and Stone H. A., *Phys. Rev. Lett.*, **86** (2001) 4704.

[25] Vera M. U. and Durian D. J., *Phys. Rev. Lett.*, **88** (2002) 088304.

[26] Carrier V., Destouesse S. and Colin A., *Phys. Rev. E*, **65** (2002) 061404.