

## From zero-dimension cavities to free-energy functionals for hard disks and hard spheres

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We present a *systematic approach* to derive fundamental-measure theory free-energy functionals for hard disks and hard spheres, entirely from the exact free energy in the zero-dimensional limit of a narrow cavity which cannot hold more than one molecule. The functionals are within the generic class that includes the previous successful versions, but have the remarkable property to yield the *exact functional* for quasi-one-dimensional density distributions. [S1063-651X(97)50505-8]

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Model systems of hard disks and hard spheres, in two and three dimensions, play central roles in the microscopic theory of liquids [1]. In the last two decades there have been important advances [2] in the development of density-functional approximations for the excess (over the ideal gas) Helmholtz free energy,  $\Phi[\rho] = (F - F_{id})/(k_B T)$ , for an inhomogeneous density distribution,  $\rho(\mathbf{r})$ . These functionals have been used to study interfaces and capillary systems, and to understand the crystallization of a fluid as a strong self-sustained inhomogeneity [2–4]. The model functionals  $\Phi[\rho]$  are usually constrained by previous approximations for the equation of state and the direct correlation function of uniform bulk systems. The choice of the nonlocal dependence of  $\Phi$  on the density  $\rho(\mathbf{r})$  is simplified by the geometrical character of the interactions and there are two main groups of theories: (1) those based on the *pair*-excluded volume (a sphere with radius equal to twice the molecular radius  $R$ ) [2,4,5], and (2) those based on the molecular volume itself and other fundamental geometric measures of the *individual* molecules. The later, under the generic name of fundamental-measure theories (FMT) [6–9], were proven to be superior for the description of the dimensional crossover, namely, the description of bulk systems of reduced dimension as strongly inhomogeneous density distributions in a larger dimension [9]. FMT functionals are able to detect configurations of close-packed  $D$ -dimensional hard spheres, and can address the phase diagram of hard spheres in confined geometries [6,9]. However, correct dimensional crossover can be achieved only by a functional that contains singularities, and these affect its behavior. The FMT functionals behave nicely, and give reliable results for a large class of  $\rho(\mathbf{r})$ , but in view of their approximate nature their singularities may cause unphysical divergences for certain extreme density distributions. These, however, also serve to advance the theory since the elimination of the divergences is achieved by a finer tuning of the functional form. Indeed, recent regularizations of the FMT in the zero-dimensional (0D) limit of a cavity that cannot hold more than one molecule have opened frontiers in the study of crystallization [9].

In this Rapid Communication we present a *systematic approach* to build up regular FMT functionals, within a generic class that includes the previous versions. The approach is

based on the *ultimate* dimensional crossover: the free energy in narrow cavity, which cannot contain more than one molecule. With an average occupation  $N \leq 1$ , in the grand-canonical ensemble, it has an excess Helmholtz free energy  $\Phi^{(D=0)}[\rho] = \varphi_o(N) = N + (1 - N)\ln(1 - N)$  which is independent of the detailed structure of the cavity [9]. This exact result provides a *zero-dimensional* equation of state which should be reproduced from the density functional in any dimension  $\Phi^{(D)}[\rho]$  for any density distribution  $\rho(\mathbf{r})$  restricted to be such that it cannot have nonzero values at two points if they are separated by more than  $2R$ . The correct 0D limit behavior of the functional, which is important for adequate description of the fluid-solid transition [9], is presently used to fully derive FMT functionals which yield the *exact functional* for quasi-1D density distributions.

We consider first a density distribution  $\rho(\mathbf{r}) = N\delta(\mathbf{r})$ , with  $N \leq 1$ , which corresponds to the limit of a narrow spherical cavity in any dimension  $D$ . The exact 0D excess free energy is recovered [9], by an integration by parts, from the following density functional:

$$\Phi_1^{(D)} = \int d\mathbf{r} \varphi_1(\eta(\mathbf{r})) \int d\mathbf{R}_1 \rho(\mathbf{r} + \mathbf{R}_1) w_D(R_1), \quad (1)$$

where  $\mathbf{R}_1$  is fixed to be on a shell of radius  $R$  by,  $w_D(|\mathbf{R}_1|) = s_D^{-1} \delta(R - |\mathbf{R}_1|)$ , normalized by the ‘‘molecular surface area’’  $s_1 = 2$ ,  $s_2 = 2\pi R$ ,  $s_3 = 4\pi R^2$ . The function  $\varphi_1(\eta) \equiv \partial \varphi_o(\eta) / \partial \eta = -\ln(1 - \eta)$  is evaluated at the local packing fraction (at dimension  $D$ )

$$\eta(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') \Theta(R - |\mathbf{r} - \mathbf{r}'|), \quad (2)$$

with the usual Heaviside step function  $\Theta(x)$ . In one dimension,  $\Phi_1^{(1)}$  provides the *exact* functional [10], and it recovers the exact value of  $\varphi_o(N)$  for any other 0D distribution like two  $\delta$  functions,  $\rho(\mathbf{r}) = N_1 \delta(\mathbf{r} - \mathbf{r}_1) + N_2 \delta(\mathbf{r} - \mathbf{r}_2)$  with  $N = N_1 + N_2 \leq 1$  and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \leq 2R$ . In higher dimensions these kind of 0D density distributions, which would represent an elongated cavity like in Fig. 1(a), are not well represented by  $\Phi_1^{(D)}$ , which gives

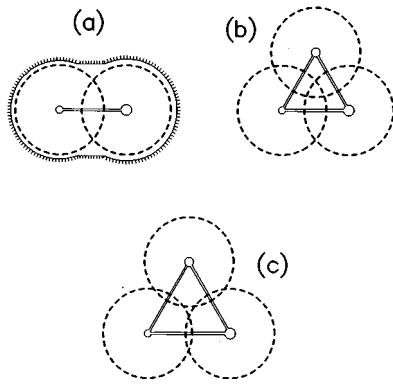


FIG. 1. Sketch of the 0D systems used in the text. The full line shows the available space for the molecular center, which has two (a) or three (b) and (c) narrow subcavities, joined by much narrower channels. The relative volume of the subcavities sets the occupation ratios  $N_i/N_j$ , the channels giving a negligible contribution. The total occupation  $N \leq 1$  will be set by the chemical potential of a reservoir joined to the cavities by channels that are also negligible. The dashed lines show the extent of the molecules at the center of each subcavity within the physical cavity wall (shaded line), which is drawn only in case (a).

$$\Phi_1^{(D)}[\rho] = \varphi_o(N) - \xi_D(r_{12}) \left[ \varphi_o(N) - \sum_{i=1}^2 \varphi_o(N_i) \right]. \quad (3)$$

The deviation from the exact 0D limit is thus found to be a universal function of  $N_1$  and  $N_2$  multiplied by a function  $\xi_D(\mathbf{r})$ . For two and three dimensions, we have

$$\xi_2(\mathbf{r}) = \frac{2}{\pi} \sin^{-1} \left( \frac{r}{2R} \right), \quad \xi_3(\mathbf{r}) = \frac{r}{2R}. \quad (4)$$

We now search for a second contribution to the density functional, a term  $\Phi_2^{(D)}[\rho]$  that corrects this defect in  $\Phi_1^{(D)}[\rho]$  and makes up the exact value  $\varphi_o(N)$ . It has to vanish with a single  $\delta$  function or when the two  $\delta$  functions in  $\rho(\mathbf{r})$  are separated by more than a molecular diameter, and within the FMT scheme we expect it to include the nonlocal dependence through  $\eta(\mathbf{r})$  and  $w_D(\mathbf{r})$ . This is obtained by

$$\Phi_2^{(D)}[\rho] = \int d\mathbf{r} \varphi_2(\eta(\mathbf{r})) \prod_{i=1}^2 \int d\mathbf{R}_i \rho(\mathbf{r} + \mathbf{R}_i) \times w_D(R_i) P_D(\mathbf{R}_1, \mathbf{R}_2). \quad (5)$$

The dependence on  $N_1$  and  $N_2$  in Eq. (3) dictates the functional form of  $\varphi_2(\eta) = \partial^2 \varphi_o(\eta) / \partial \eta^2 = (1 - \eta)^{-1}$ . The kernel  $P_D(\mathbf{R}_1, \mathbf{R}_2)$  couples the integrals over  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , and it is determined by the geometrical factor  $\xi_D(r_{12})$  in Eq. (4), with  $r_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$ .

For hard disks ( $D=2$ ) we find  $P_2(\mathbf{R}_1, \mathbf{R}_2) = 4\pi R^2 x(1-x^2)^{1/2} \sin^{-1}(x)$ , with  $x = r_{12}/(2R)$ . The integration over  $\mathbf{r}$  in Eq. (5) may be carried out over the intersection of the two circular shells,  $w_2(R_1)$  and  $w_2(R_2)$  to give a useful simpler form:

$$\Phi_2^{(2)} = \int d\mathbf{r}' \frac{\sin^{-1}(r'/R)}{\pi} \int d\mathbf{r} \rho(\mathbf{r}_+) \rho(\mathbf{r}_-) (\varphi_2^+ + \varphi_2^-),$$

where  $\mathbf{r}_\pm = \mathbf{r} \pm \mathbf{r}'$  and  $\varphi_2^\pm = \varphi_2(\eta(\mathbf{r} \pm \hat{\mathbf{u}}(R^2 - r'^2)^{1/2}))$  and  $\hat{\mathbf{u}}$  is a unit vector normal to  $\mathbf{r}'$ . The density functional  $\Phi^{(2)} = \Phi_1^{(2)} + \Phi_2^{(2)}$  has been built to recover the exact 0D limit for a single molecule in a class of 0D cavities, yet leads to remarkable results for the excess free energy of general density distributions. We have checked that  $\Phi^{(2)}[\rho]$  gives the exact 0D value for arbitrary combinations of  $m\delta$  functions when there is a region with common overlap, where  $\eta(\mathbf{r})$  is equal to the total cavity occupation  $N = \sum N_i$ , as in Fig. 1(b). If we apply  $\Phi^{(2)}[\rho]$  to a strictly one-dimensional density distribution  $\rho(x, y) = \rho_1(x) \delta(y)$ , we recover the exact density functional for hard rods [10]. Applied to a homogeneous density distribution, this gives the excess free energy per molecule  $\Phi^{(2)}/N = \varphi_1(\eta) + \eta \varphi_2(\eta)$  which corresponds to the scaled particle equation of state for hard disks [11]. However,  $\Phi^{(2)}[\rho]$  cannot reproduce the 0D limit in cavities like Fig. 1(c), with a density distribution made of three  $\delta$  functions, separated by less than  $2R$  but without a region of triple overlap where  $\eta(\mathbf{r})$  is equal to the total occupation  $N$ . Within the FMT framework these are “lost cases,” which cannot be described through  $\eta(\mathbf{r})$ . The failure in the description of these cases has to be related to the difference between the exact and the scaled-particle equations of state. These “lost cases” disappear, however, not only in the strict 1D limit but also in quasi-1D systems, when the molecules are restricted to a channel of width less than  $\sqrt{3}R$ , for which  $\Phi^{(2)} = \Phi_1^{(2)} + \Phi_2^{(2)}$  is likely to be the exact density functional.

The FMT approximation for hard disks, previously proposed by one us [7], in terms of scalar and vector weighted densities, takes  $P_2^{\text{app}}(\mathbf{R}_1, \mathbf{R}_2) = \pi(R^2 - \mathbf{R}_1 \cdot \mathbf{R}_2)$ . This functional form is similar to the exact kernel for  $r_{12} \ll R$ , which gives  $P_2(\mathbf{R}_1, \mathbf{R}_2) = 2\pi(R^2 - \mathbf{R}_1 \cdot \mathbf{R}_2) + O(r_{12}^4)$ . The truncation at the first term changes by a factor of 2 the contribution of  $\Phi_2^{(2)}$  to the bulk equation of state, and the former approximation is recovered as a truncated and renormalized expansion. We also note that the 2D analog of [8], namely, a FMT functional for hard disks in terms of only scalar weighted densities which is completely equivalent to that of [7], can be derived by another approach [12] that utilizes the 0D limit as a “generating function” for the FMT functional and imposes the scaled-particle bulk equation of state. A deeper understanding of the interconnection between these methods is desirable.

Considering now 3D hard spheres we find that the kernel in Eq. (5) is  $P_3(\mathbf{R}_1, \mathbf{R}_2) = 4\pi R(R^2 - \mathbf{R}_1 \cdot \mathbf{R}_2)$ , which gives rise to exactly the same second term  $\Phi_2^{(2)}[\rho]$  in the functional as in the previous versions of the FMT for hard spheres [6,9]. The density functional  $[\Phi_1^{(3)} + \Phi_2^{(3)}]$  is known [9] to yield the exact free energy and pair direct correlations in the uniform 1D limit. We find, however, that in fact it yields the exact 1D functional in the general 1D limit, i.e., it has an exact dimensional crossover to 1D, and it is probably exact for quasi-1D systems, restricted to tubes of diameter less than  $\sqrt{3}R$ . However,  $[\Phi_1^{(3)} + \Phi_2^{(3)}]$  fails to reproduce the exact 0D limit in cases like Fig. 1(b), with  $\rho(\mathbf{r}) = \sum_{i=1,3} N_i \delta(\mathbf{r} - \mathbf{r}_i)$  which were well described in two dimensions. The result for these cases is now

$$\begin{aligned} \Phi_1^{(3)}[\rho] + \Phi_2^{(3)}[\rho] &= \varphi_o(N) - \zeta(r_{12}, r_{23}, r_{31}) \\ &\times \left[ \varphi_o(N) - \sum_{\{ij\}} \varphi_o(N_i + N_j) \right. \\ &\left. + \sum_{i=1,3} \varphi_o(N_i) \right], \end{aligned} \quad (6)$$

where  $\{ij\}$  runs over the pairs 12, 23, and 31. The function  $\zeta$  is defined in geometrical terms [13] and takes values between 0 and 1, for any triangle with the three sides  $r_{12}$ ,  $r_{23}$ , and  $r_{31}$ , less than  $2R$ . Again we search for an extra term,  $\Phi_3^{(3)}[\rho]$ , in the density functional that makes up the exact value  $\varphi_o(N)$  for cavities like Fig. 1(b), and vanishes in cavities like Fig. 1(a), which were already well described by  $[\Phi_1^{(3)} + \Phi_2^{(3)}]$ . The correct dependence with respect to  $N_i$  is given by

$$\begin{aligned} \Phi_3^{(3)}[\rho] &= \int d\mathbf{r} \varphi_3(\eta(\mathbf{r})) \prod_{i=1,3} \int d\mathbf{R}_i \rho(\mathbf{r} + \mathbf{R}_i) \\ &\times w_3(R_i) Q(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3). \end{aligned} \quad (7)$$

with  $\varphi_3(\eta) = \partial^3 \varphi_o(\eta) / \partial \eta^3 = (1 - \eta)^{-2}$ . Previous versions of the FMT functional [6–9] have this structure but the geometrical dependence, in the kernel  $Q(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ , was set (implicitly [6] or empirically [8]) to recover the equation of state and the correlations in the bulk fluid, as given by the Percus-Yevick approximation. In a recent version [9] the structure of this kernel was changed to avoid divergences in the 0D limit, but the regularization was only partial, and  $\Phi_3^{(3)}$  would still diverge in cavities like Figs. 1(a) and 1(b). We may now obtain  $Q(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$  from the function  $\zeta(r_{12}, r_{23}, r_{31})$ , with  $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ , to recover the exact 0D. This gives a fully regularized  $\Phi_3^{(3)}$ , although the geometrical definition of  $\zeta$  is cumbersome (see [13]). For small values of the arguments we may expand  $\zeta$  with a leading term

$$\zeta(r_{12}, r_{23}, r_{31}) = (4\pi R^3)^{-1} |\mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)| + \dots \quad (8)$$

The truncation at this first term keeps the exact cancellation of any divergence which may arise at the overlap of two spherical shells (when  $\mathbf{R}_i = \mathbf{R}_j$ ), and it cancels out for any linear density distribution (because  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ , and  $\mathbf{R}_3$  are coplanar), as required to recover the exact form of  $[\Phi_1^{(3)} + \Phi_2^{(3)}]$  for those cases. The 0D cavities represented in Fig. 1(c), in which  $\eta(\mathbf{r})$  never takes the value  $N = \sum N_i$ , have  $\zeta = 1$ . As in 2D, these are “lost cases” for the FMT, because there is no triple intersection of the spherical shells in Eq. (7), and  $\Phi_3^{(3)}$  vanishes.

The free-energy density functional for hard spheres  $\Phi^{(3)} = \Phi_1^{(3)} + \Phi_2^{(3)} + \Phi_3^{(3)}$  has been built, within the FMT, from the properties of a single molecule in a 0D cavity, but it also provides an approximation for the bulk equation of state, through the excess free energy per molecule in a bulk system, which is

$$\begin{aligned} \Phi^{(3)}/N &= \varphi_1(\eta) + 3\eta\varphi_2(\eta) + \frac{3}{2}\eta^2\varphi_3(\eta) \\ &\times \left[ \int d\mathbf{r}_{12} \int d\mathbf{r}_{23} \frac{\zeta(r_{12}, r_{23}, r_{31})}{(4\pi R^3)^2} \right], \end{aligned} \quad (9)$$

where we integrate  $\zeta$ , over all the triangles with one vertex at the origin, excluding the “lost cases” which have  $\zeta = 1$  but do not appear in Eq. (7). This integral is  $(\pi/4)^2 \approx 0.6168$ , which gives a rather poor equation of state for hard spheres. However, if we extend the integration to include the FMT “lost cases,” the term in the brackets becomes 1, and we recover from Eq. (9) the Percus-Yevick compressibility equation of state [1] (which in three dimensions is identical to scaled particle), as in the previous FMT functionals. Notice that this extension is incompatible with the FMT form (7), so that the scaled-particle equation of state cannot be achieved within a FMT functional based entirely on the 0D limit. The expansion (8) suggests the approximation of using in Eq. (7) the kernel

$$Q^{\text{appr}}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = 12\pi^2 [\mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)]^2, \quad (10)$$

in which the prefactor was renormalized to be consistent with the scaled-particle equation of state. This approximation for  $\Phi_3^{(3)}[\rho]$  will be free of divergences, it vanishes for any linear density distribution, and it may be expressed in terms of tensor weighted densities [9]. Use of the kernel (10) in Eq. (7) is the equivalent for hard spheres of the previous approximation for hard disks [6].

The functional form of  $\varphi_k(\eta) = \partial^k \varphi_o(\eta) / \partial \eta^k$  in  $\Phi_k^{(D)}[\rho]$  is related in a systematic way to the  $k\delta$ -function distributions. For hard spheres there is no need to go beyond  $k=3\delta$  functions because no new geometrical elements appear. There would be no intersections of, e.g., four spherical surfaces, and the free energy would still be the sum of surface, line, and dot contributions, with the same basic structure as in the case with  $k=3\delta$  functions. Likewise, for hard disks there is no need to go beyond  $k=2\delta$  functions. Our 0D analysis is capable to recapture the scaled-particle dimensional analysis [6] [which leads to the same functions  $\varphi_k(\eta)$ ] directly from the general FMT functional forms (1), (5), and (7) for  $\Phi_k^{(D)}[\rho]$  and without any reference to the bulk thermodynamics. The  $\eta=1$  singularity, which played an important role (as “ideal liquid”) in the original development of the FMT [6], is now shown to emanate from the corresponding singularity in the 0D limit. The influence of the FMT 0D “lost cases” grows with the dimension: they do not exist in one dimension, they do not interfere with the scaled particle equation of state in two dimensions (they do not change the contribution of  $\varphi_2$ ), but they are very important for the contribution of  $\varphi_3$  in three dimensions. This is in accordance with the decreasing accuracy of the Percus-Yevick approximation with increasing dimensions [6]. We also note that for parallel hard squares and cubes, the FMT functionals are generated from the 0D limit in a more complete way [14] than for disks and spheres. Our aim to use the 0D limit as the guide to build fully regularized FMT density functionals has proven to be successful for hard disks with exact results for most 0D cavities. For hard spheres our effort has exposed the intrinsic limits of the FMT, but it also suggests useful approximations like using in Eq. (7) the kernel (10). In summary, we have presented interesting FMT free energy functionals for hard disks and hard spheres, which are exact for a single  $\delta$ -function cavity, and thus appropriate to describe solids. They reduce to the exact *functional* in the

quasi-1D limit, and yield the scaled-particle bulk equation of state. They are not exact in certain 0D cavities, but in view of the behavior of well-studied previous functionals [6–9] they should be quite accurate in most cases. The present study and the related approximations open the subject for future work.

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- [1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
- [2] See the recent collection of reviews, *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Dekker, New York, 1992), and in particular the review by R. Evans.
- [3] See, e.g., the reviews M. Baus, *J. Phys. Condens. Matter.* **2**, 2241 (1990); H. Löwen, *Phys. Rep.* **237**, 249 (1994).
- [4] P. Tarazona, *Mol. Phys.* **52**, 81 (1984); P. Tarazona, *Phys. Rev. A* **31**, 2672 (1985).
- [5] W. A. Curtin and N. W. Ashcroft, *Phys. Rev. A* **32**, 2909 (1985).
- [6] Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989); *J. Chem. Phys.* **98**, 8126 (1993); *Phys. Rev. E* **50**, R3318 (1994); *J. Phys. Condens. Matter.* **8**, 9287 (1996); **8**, L795 (1996).
- [7] Y. Rosenfeld, *Phys. Rev. A* **42**, 5978 (1990).
- [8] E. Kierlik and M. L. Rosinberg, *Phys. Rev. A* **42**, 3382 (1990); **44**, 5025 (1991); S. Phan, E. Kierlik, M. L. Rosinberg, B. Bildstein, and G. Kahl, *Phys. Rev. E* **48**, 618 (1993).
- [9] Y. Rosenfeld, M. Schmidt, H. Löwen, and P. Tarazona, *J. Phys. Condens. Matter.* **8**, L577 (1996); *Phys. Rev. E* **55**, 4245 (1997); M. Schmidt, Ph.D. thesis, Mathematisch-Naturwissenschaftlichen Fakultät der Heinrich-Heine-Universität Düsseldorf, 1997.
- [10] J. K. Percus, *J. Stat. Phys.* **15**, 505 (1976).
- [11] H. Reiss, H. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959); H. Reiss, *ibid.* **96**, 4736 (1992); Y. Rosenfeld, *ibid.* **89**, 4272 (1988).
- [12] A. Gonzalez, J. A. White, and R. Evans (unpublished).
- [13] For a given triangle, with vertices  $i=1, 2$ , and  $3$ , and sides  $r_{12}$ ,  $r_{23}$ , and  $r_{31}$ , draw a sphere of radius  $R$  around each vertex. Let  $A_i$  be the area of the sphere at vertex  $i$  which is inside the other two spheres, let  $L_{ij}$  be the length of the intersection line between spheres  $i$  and  $j$ , and let  $L_{ij}^k$  be its partial length inside the third sphere  $k$ . Then we have  $\zeta(r_{12}, r_{23}, r_{31}) = 1 - \sum_i A_i / (4\pi R^2) - \sum_{\{ij\}} [L_{ij}^k r_{ij} / (2RL_{ij})]$ . When the intersection of two spheres is fully contained in the third, or when there is no intersection between two of the spheres, then  $\zeta=0$ . When each pair of spheres has intersection but there is no triple intersection, then  $\zeta=1$ .
- [14] J. A. Cuesta, *Phys. Rev. Lett.* **76**, 3742 (1996); and (private communication).