

## Path-integral approach to strongly nonlinear composites

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We study strongly nonlinear disordered media using a functional method. We solve exactly the problem of a nonlinear impurity in a linear host and we obtain a Bruggeman-like formula for the effective nonlinear susceptibility. This formula reduces to the usual Bruggeman effective medium approximation in the linear case and has the following features: (i) It reproduces the weak contrast expansion to the second order and (ii) the effective medium exponent near the percolation threshold are  $s=1$ ,  $t=1+\kappa$ , where  $\kappa$  is the nonlinearity exponent. Finally, we give analytical expressions for previously numerically calculated quantities.

The study of the properties of linear heterogeneous media (composites, suspensions) has been the subject of an intense activity for already fifty years (see Refs. 1 and 2). More recently there has been a great interest in nonlinear media.<sup>2</sup> The nonlinear composites are important for technology and also from a fundamental point of view, for which it is important and challenging to understand the interplay between nonlinearity and disorder. There are essentially two types of nonlinear media. (a) Weak nonlinearity: the nonlinearity is small compared to the linear term. This case was studied by many authors and is now relatively well understood.<sup>3-11</sup> (b) Strong nonlinearity: the nonlinearity is here the dominant term and this can happen in essentially two situations. First, there can be a sharp threshold between two different behaviors and this case can model the phenomena of fracture or dielectric breakdown.<sup>12,13</sup> Second, the constitutive law can be a pure power law of the form

$$j = \chi |E|^\kappa E, \quad (1)$$

where  $j$  is the current and  $E$  the electric field. This behavior can be observed in a dielectric illuminated by a laser<sup>2</sup> when the multiphoton processes dominates and the usual linear approximation completely breaks down. Certain cermet resistors, ZnO based varistors<sup>14,15</sup> or disordered alloys<sup>16</sup> can also display this behavior (1).

In a disordered medium, the nonlinear susceptibilities  $\chi$  can fluctuate from point to point and one is interested in the macroscopic effective behavior of such a medium. If the nonlinearity exponent  $\kappa$  is the same for all phases of the medium, then the effective nonlinear susceptibility is well defined and is given by  $j_0 = \chi_e |E_0|^\kappa E_0$ , where  $j_0$  and  $E_0$  are the macroscopic current and electric field, respectively. It is difficult to evaluate  $\chi_e$  and devising a reliable method to compute  $\chi_e$  would allow one to study a variety of other problems such as fracture or dielectric breakdown.

In this strongly nonlinear case, Blumenfeld and Bergman obtained the weak contrast expansion to second order.<sup>17</sup> This expansion was recovered by means of a path integral method.<sup>18</sup> The dilute limit was studied in Refs. 19 and 20. Problems arise when one tries to find an effective medium approximation (EMA) for this type of media. A good EMA should satisfy the two following criteria. (i) It should reproduce the weak-contrast expansion (at least up to the second

order) and the dilute limit (although this last condition is probably very difficult to fulfill for strongly nonlinear media). (ii) Close to the percolation threshold  $p_c$ , the effective nonlinear susceptibility  $\chi_e$  is described by two exponents: For a metal/insulator mixture, one has<sup>21,22</sup>

$$\chi_e \sim (p - p_c)^{t(\kappa)}, \quad (2)$$

where  $p$  is the proportion of the conducting component. For a superconductor-metal mixture, one expects

$$\chi_e \sim (p_c - p)^{-s(\kappa)}, \quad (3)$$

where  $p$  is here the proportion of the superconducting component. Different values for these exponents were proposed. In Ref. 22, the effective medium values are  $t(\kappa) = 1 + \kappa$  and  $s(\kappa) = 1$ , and in Refs. 23 and 24, the exponents are  $t(\kappa) = s(\kappa) = 1 + \kappa/2$ . In both cases, the crossover exponent  $\phi = s + t$  is equal to  $2 + \kappa$ . These two sets of exponents satisfy the duality relation for  $d=2$ :<sup>21</sup>  $t(\gamma) = \gamma s(1/\gamma)$  where  $\gamma = 1 + \kappa$ . So far, numerical results<sup>25</sup> and series analysis<sup>26</sup> suggests that for  $d=2$  the exponents  $s$  and  $t$  are different, ruling out  $s = t = 1 + \kappa/2$  although further numerical studies are necessary to make a definitive statement. An acceptable EMA should predict such kind of values.

We can distinguish two different classes of approaches to this problem. A first approach<sup>7,24,27-31</sup> consists in expressing the effective nonlinear susceptibility in terms of the averaged electric field in each component. In Refs. 24,27-29, a kind of a "decoupling approximation" is proposed for calculating these fields, and one obtains a set of coupled equations which is solved numerically. Although the agreement with numerical simulations is generally fairly good, there are a few drawbacks to this method. In particular, this method relies quite heavily on numerics and it is difficult to check some analytical properties. Moreover, the weak-contrast expansion [condition (i)] is usually not recovered and the exponents are difficult to estimate. In particular, the mean-field theory proposed in Ref. 24 does not reproduce the weak contrast expansion but instead the lower bound established by Ponte Castañeda *et al.*<sup>7</sup> In this case,<sup>24</sup> the values of the exponents are  $s = t = \kappa/2 + 1$ . In another series of papers,<sup>30,31</sup> the nonlinear host is linearized up to the second order and the local electric fields are computed in a self-consistent way. With this method, Ponte Castañeda and Kailasam<sup>30</sup> proposed an

effective medium approximation which reproduces the weak contrast expansion, but for which the exponents are difficult to estimate.

The second approach is in the Bruggeman spirit<sup>32</sup> and consists essentially in considering an impurity in an effective host. Bruggeman's theory was reformulated in order to apply to this problem<sup>22</sup> and it was further investigated by different authors.<sup>25,33–35</sup> This approach predicts the effective medium values  $s=1$  and  $t=1+\kappa$  and reproduces the weak contrast expansion to second order. However, all the studies so far are mostly numerical and we propose here the analytical solution. The obtained formula is relatively simple and satisfies conditions (i) and (ii). We give the analytical expressions for numerically estimated quantities.<sup>25,33,35</sup> The only drawback of our result is that the percolation threshold depends on  $\kappa$  (in the same way as in Ref. 35). In the discussion, we address this point and propose a possible way to correct this wrong behavior.

The constitutive relation is  $j=\chi(r)|E|^\kappa E$  and the local energy density associated to it is

$$w[r,E(r)]=\frac{\chi(r)}{\kappa+2}|E|^{\kappa+2}. \quad (4)$$

$E$  is the applied field and for a heterogeneous medium the quantity  $\chi(r)$  at point  $r$  is distributed according to a binary law (a generalization of our method to other types of disorder should be without problems)

$$P[\chi=\chi(r)]=p\delta(\chi-\chi_1)+q\delta(\chi-\chi_2). \quad (5)$$

The total dissipated energy is given by  $W^*=\chi_e|E_0|^{\kappa+2}/(\kappa+2)$ , and can be expressed as a constrained minimum

$$W^*=\left\langle \min_{\bar{E}=E_0, E=-\nabla\phi} \int d^d r w[r,E(r)] \right\rangle. \quad (6)$$

Here, we have assumed that  $W^*$  is a self-averaging quantity in the thermodynamic limit, which allows us to compute the average over the disorder (the brackets  $\langle \cdot \rangle$  denote the average over disorder or equivalently, the spatial average). The minimum in Eq. (6) can be written with the help of path integrals<sup>18</sup>

$$W^*=\lim_{\beta\rightarrow\infty} -\frac{1}{\beta} \ln \int \tilde{\mathcal{D}}E e^{-\beta\mathcal{H}}, \quad (7)$$

where the ‘‘Hamiltonian’’ is  $\mathcal{H}=\int d^d r w[r,E(r)]$  and where the measure is  $\tilde{\mathcal{D}}E=\mathcal{D}(E,\phi)\delta(\bar{E}-E_0)\delta(E+\nabla\phi)$ . The important quantity to study is thus the ‘‘partition function’’

$$Z=\int \tilde{\mathcal{D}}E e^{-\beta\mathcal{H}}. \quad (8)$$

In an earlier paper,<sup>18</sup> we made a perturbation expansion up to the second order in disorder and we recovered known results.<sup>17</sup> We also showed in another paper<sup>36</sup> how to recover Bruggeman's approximation in the functional framework and we recall briefly the idea. We start from the expression (8) and we add and subtract a Gaussian ansatz  $\mathcal{H}_0=\int d^d r w_0[E(r)]$

$$Z=\int \tilde{\mathcal{D}}E e^{-\beta\mathcal{H}_0} e^{-\beta(\mathcal{H}-\mathcal{H}_0)}. \quad (9)$$

We expand the second exponential and resum it keeping only the contribution at the same point

$$\begin{aligned} e^{-\beta(\mathcal{H}-\mathcal{H}_0)} &= \sum_{k=1}^{\infty} \left[ \int d^d r \{w[r,E(r)]-w_0[E(r)]\}^k \right] \\ &\simeq \int d^d r \sum_{k=1}^{\infty} \{w[r,E(r)]-w_0[E(r)]\}^k \\ &\simeq \int d^d r e^{-\beta\{w[r,E(r)]-w_0[E(r)]\}} \end{aligned} \quad (10)$$

(here and in the following, we omit unimportant volume factors and cutoffs). The partition function  $Z$  is thus given by

$$Z \simeq \int d^d r \int \tilde{\mathcal{D}}E e^{-\beta\mathcal{H}_0} e^{-\beta\{w[r,E(r)]-w_0[E(r)]\}}. \quad (11)$$

The following physical picture can be associated with this approximation. The background is described by  $\mathcal{H}_0$  and at point  $r$  there is an impurity described by  $w-w_0$ . The ideal case would be to take a nonlinear background described by an effective nonlinear susceptibility  $\mathcal{H}_0=[\chi_e/(\kappa+2)]\int|E|^{\kappa+2}$  and a nonlinear impurity, which is so far impossible to compute. We thus have to resort to a further approximation. The averaged value of the electric field is fixed and given by  $\bar{E}=E_0$ . It is thus reasonable to assume that the electric field in the background will not fluctuate too much (at least far from the impurity) and we can expand the nonlinear background around  $E(r)=E_0$ . We write  $E(r)=E_0+\varepsilon(r)$  and expand up to the second order in  $\varepsilon$

$$\begin{aligned} w_0 &\simeq \frac{\chi_e}{\kappa+2} E_0^{\kappa+2} + E_0^\kappa E_0 \varepsilon(r) \\ &+ \frac{1}{2} E_0^\kappa \sum_{i,j} \varepsilon_i(r) \left( \delta_{ij} + \kappa \frac{E_{0i} E_{0j}}{E_0^2} \right) \varepsilon_j(r) \end{aligned} \quad (12)$$

while we keep the exact expression for  $w=[\chi/(\kappa+2)]|E|^{\kappa+2}$ . The final picture is then the following: we compute exactly the perturbation induced by a nonlinear impurity in the nonlinear *linearized* effective medium. In addition to allow calculations, this scheme ensures that the weak-contrast expansion will be recovered. The numerical study of this problem can be found in Refs. 25,33,35.

The path integral (11) together with the approximation (12) can be computed and after some calculations, one is led to

$$Z \simeq e^{-\beta\chi_e E_0^{\kappa+2}} \int d^d u e^{-\beta\mathcal{M}(u)} \quad (13)$$

with

$$\begin{aligned} \mathcal{M}(u) &= \frac{\chi(r)}{\kappa+2} u^{\kappa+2} + \chi_e E_0^\kappa u E_0 \\ &+ \frac{\chi_e E_0^\kappa}{2} (E_0 + u) \left( 1 - \frac{1}{I} + \kappa \frac{E_0 \otimes E_0}{E_0^2} \right) (E_0 + u), \end{aligned} \quad (14)$$

where  $u$  is a  $d$ -dimensional vector. The quantity  $I$  is given by

$$I(d, \kappa) = \frac{S_{d-1}}{S_d} \int_0^\pi d\theta \sin^{d-2} \theta \frac{\cos^2 \theta}{1 + \kappa \cos^2 \theta}, \quad (15)$$

where  $S_d = 2\pi^d / \Gamma(d/2)$  is the surface of the  $d$ -dimensional sphere. In the linear case,  $I(d, \kappa=0) = 1/d$ , and for  $d=2,3$ , one has<sup>17,18</sup>

$$I(2, \kappa) = \frac{1}{\kappa} \left( 1 - \frac{1}{\sqrt{1+\kappa}} \right), \quad (16)$$

$$I(3, \kappa) = \frac{1}{\kappa} \left( 1 - \frac{1}{\sqrt{\kappa}} \arcsin \sqrt{\frac{\kappa}{1+\kappa}} \right). \quad (17)$$

We are interested in the large  $\beta$  limit [Eq. (7)] so we can apply the saddle-point method to the integral (13). The saddle point  $u_*$  is parallel to  $E_0$  and is given by

$$u_*(x) = \frac{-E_0(\kappa - 1/I)}{1 - 1/I + \kappa - u_*^\kappa/x E_0^\kappa}, \quad (18)$$

where here  $x = \chi_e / \chi$ . One can note that  $u_*$  is the electric field in the nonlinear impurity embedded in the linearized effective homogeneous host. The effective energy  $W^* = -(1/\beta) \langle \ln Z \rangle$  is then given by  $W^* = W_0 + \Delta W$  where  $W_0 = [\chi_e / (\kappa + 2)] E_0^{\kappa+2}$ . The natural self-consistent condition  $\Delta W = 0$  can be rewritten for the binary disorder (5) under the form<sup>22,35</sup>

$$p f\left(\frac{\chi_e}{\chi_1}\right) + q f\left(\frac{\chi_e}{\chi_2}\right) = 0, \quad (19)$$

where

$$\begin{aligned} f(x) &= \frac{1}{x} \frac{v_*^{\kappa+2}}{\kappa+2} - \frac{1}{\kappa+2} + 1 + v_*(x) \\ &- \frac{1}{2} [1 + v_*(x)]^2 \left( 1 - \frac{1}{I} + \kappa \right), \end{aligned} \quad (20)$$

where  $v_*(x) = u_*(x)/E_0$  is given by Eq. (18). This equation (19) [together with Eqs. (18) and (20)] is our main result, and we will now discuss it.

In the linear case ( $\kappa=0$ ), one can easily check that Eq. (19) reduces to Bruggeman's<sup>32</sup> equation. Moreover, in the one-dimensional case, one recovers the exact result  $1/\chi_e = \langle 1/\chi^{1/(\kappa+1)} \rangle^{\kappa+1}$ .

As expected, the weak contrast expansion is recovered up to the second order, namely,

$$\chi_e \approx \langle \chi \rangle - \frac{\kappa+2}{2\langle \chi \rangle} \langle \delta\chi^2 \rangle I(d, \kappa). \quad (21)$$

This fact is not surprising since we used as an ansatz  $\mathcal{H}_0$  the nonlinear effective medium linearized up to second order.

Our approximation will not reproduce the exact dilute limit, since the nonlinear host is linearized. Instead, we will obtain the following expansion to the first order in concentration (exact for  $\kappa=0$ ):

$$\chi_e \approx \chi_1 + q(\kappa+2)\chi_1 f\left(\frac{\chi_1}{\chi_2}\right), \quad (22)$$

where  $q$  is the fraction of component  $\chi_2$ .

The critical behavior is determined by  $f(x)$  for  $x \approx 0$  and  $x \rightarrow \infty$ .<sup>22,35</sup> One obtains from Eqs. (18), (20)  $f(x \approx 0) \approx f(0) - a(\kappa+1)x^{1/(\kappa+1)}$ , where

$$\begin{aligned} f(0) &= -\frac{1}{\kappa+2} + \frac{1}{2} + \frac{1}{2I} - \frac{\kappa}{2}, \\ a &= \frac{1}{\kappa+2} \left( -\frac{1}{I} + \kappa \right)^{(\kappa+2)/(\kappa+1)}. \end{aligned} \quad (23)$$

For  $x \rightarrow \infty$ , one has  $f(x) \approx f(\infty) + b/x$ , where

$$f(\infty) = -\frac{1}{\kappa+2} + 1 - \frac{1+2(-1/I+\kappa)}{2(1-1/I+\kappa)}, \quad (24)$$

$$b = \frac{1}{\kappa+2} \left( \frac{1/I-\kappa}{1-1/I+\kappa} \right)^{\kappa+2}. \quad (25)$$

For  $\kappa=0$ , one recovers the known exact expressions<sup>22,35</sup>  $a = d^2$ ,  $b = [d/(d-1)]^2$ ,  $f(0) = d$ , and  $f(\infty) = -d/[2(d-1)]$  [the function  $f$  is defined up to a constant factor, and there is a global additional factor  $1/(\kappa+2)$  in our result]. These four different coefficients were estimated numerically.<sup>25,33,35</sup>

The percolation threshold is given by

$$p_c = \frac{f(\infty)}{f(\infty) - f(0)} = \frac{1}{\kappa+2} \frac{2/I - \kappa}{(-1/I + \kappa)^2} \quad (26)$$

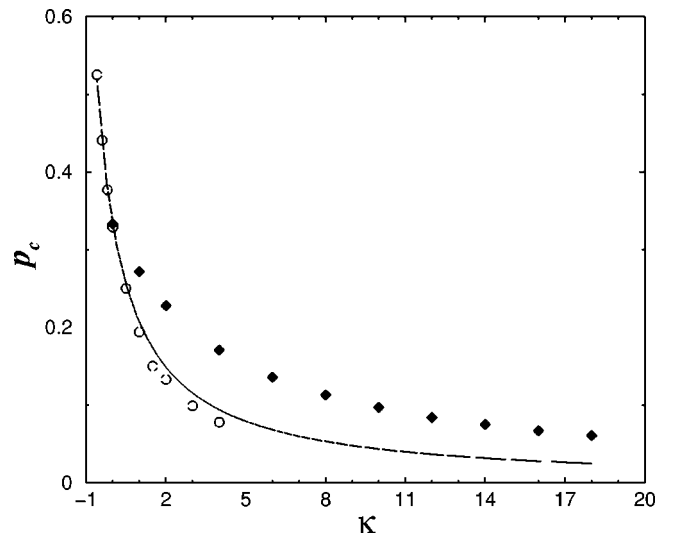


FIG. 1.  $p_c$  versus  $\kappa$  for  $d=3$ . The line is the analytical expression (26), the circles and the diamonds represent the numerical results from Refs. 35 and 25,33, respectively.

and the exponents are  $t(\kappa)=1+\kappa$  and  $s(\kappa)=1$ . In Fig. 1, we compare for  $d=3$  this exact expression for  $p_c$  to numerical results.<sup>25,33,35</sup> It thus seems that the variational method used in Refs. 25,33 does not lead to the correct values of the electric field around the impurity. The fact that the percolation threshold depends on  $\kappa$  is the bad feature of this approximation. However, for  $\kappa$  not too large, or for a contrast not too high this approximation works well. When one adds a linear background of effective conductivity  $\sigma_e$ , an additional dimensionless factor  $\Lambda = \sigma_e / \chi_e E_0^K$  is introduced in the equations. Close to  $p_c$ , the effective conductivity behaves as  $\sigma_e \sim \Delta p^1$  and the effective nonlinear susceptibility as  $\chi_e$

$\sim \Delta p^{1+\kappa}$ . The factor  $\Lambda$  is then diverging and the behavior of  $f$  is modified. One then recovers the Bruggeman value for the percolation threshold  $p_c = 1/d$ . It thus seems that in the one-impurity scheme a linear background is necessary to “regularize” the wrong behavior of  $p_c$ . It might be a way to obtain an EMA satisfying conditions (i) and (ii), and which gives a correct value for  $p_c$ .

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- <sup>1</sup>R. Landauer, in *Proceedings of the first Conference on Electrical and Optical Properties of Inhomogeneous Media*, Ohio State University, 1977, edited by J. C. Garland and D. B. Tanner, AIP Conf. Proc. No. 40 (AIP, New York, 1978).
- <sup>2</sup>D. J. Bergman and D. Stroud, *Solid State Phys.* **46**, 147 (1992).
- <sup>3</sup>D. Stroud and P. M. Hui, *Phys. Rev. B* **37**, 8719 (1988).
- <sup>4</sup>X. C. Zeng, D. J. Bergman, P. M. Hui, and D. Stroud, *Phys. Rev. B* **38**, 10 970 (1988).
- <sup>5</sup>X. C. Zeng, P. M. Hui, D. J. Bergman, and D. Stroud, *Physica A* **157**, 192 (1989).
- <sup>6</sup>R. R. Tremblay, G. Albinet, and A.-M. S. Tremblay, *Phys. Rev. B* **45**, 755 (1992).
- <sup>7</sup>P. Ponte Castañeda, G. deBotton, and G. Li, *Phys. Rev. B* **46**, 4387 (1992).
- <sup>8</sup>X. Zhang and D. Stroud, *Phys. Rev. B* **49**, 944 (1994).
- <sup>9</sup>O. Levy and D. J. Bergman, *Phys. Rev. B* **50**, 3652 (1994).
- <sup>10</sup>P. M. Hui, W. M. V. Wan, and K. H. Chung, *Phys. Rev. B* **52**, 15 867 (1995).
- <sup>11</sup>Y.-P. Pellegrini, *Phys. Rev. B* **61**, 9365 (2000).
- <sup>12</sup>B. K. Chakrabarti, *Rev. Solid State Sci.* **2**, 559 (1988).
- <sup>13</sup>*Statistical Models for the Fracture of Disordered Media*, edited by H. Herrmann and S. Roux (North-Holland, Amsterdam, 1990), and references cited therein.
- <sup>14</sup>R. Einziger, *Annu. Rev. Mater. Sci.* **17**, 299 (1987).
- <sup>15</sup>G. A. Niklasson, *Physica A* **157**, 482 (1989).
- <sup>16</sup>M. Osofsky, M. LaMadrid, J.-B. Bieri, W. Contrata, J. Gavilano, and J.-M. Mochel, *Phys. Rev. B* **38**, 8486 (1988).
- <sup>17</sup>R. Blumenfeld and D. J. Bergman, *Phys. Rev. B* **40**, 1987 (1989).
- <sup>18</sup>M. Barthélémy and H. Orland, *Eur. Phys. J. B* **6**, 537 (1998).
- <sup>19</sup>O. Levy and D. J. Bergman, *Phys. Rev. B* **46**, 7189 (1992).
- <sup>20</sup>P. M. Hui and W. M. V. Wan, *Appl. Phys. Lett.* **69**, 1810 (1996).
- <sup>21</sup>J. P. Straley and S. W. Kenkel, *Phys. Rev. B* **29**, 6299 (1984).
- <sup>22</sup>D. J. Bergman, in *Composite Media and Homogenization Theory*, edited by G. dal Maso and G. F. Dell’Antonio (Birkhauser, Boston, 1991).
- <sup>23</sup>P. Ponte Castañeda, *Proc. R. Soc. London* **341**, 531 (1992).
- <sup>24</sup>W. M. V. Wan, H. C. Lee, P. M. Hui, and K. W. Yu, *Phys. Rev. B* **54**, 3946 (1996).
- <sup>25</sup>H.-C. Lee, W.-H. Siu, and K. W. Yu, *Phys. Rev. B* **52**, 4217 (1995).
- <sup>26</sup>Y. Meir, R. Blumenfeld, A. Aharony, and A. B. Harris, *Phys. Rev. B* **34**, 3424 (1986).
- <sup>27</sup>P. M. Hui, Y. F. Woo, and W. M. V. Wan, *J. Phys.: Condens. Matter* **7**, L593 (1995).
- <sup>28</sup>L. Gao and Z.-Y. Li, *Phys. Lett. A* **219**, 324 (1996).
- <sup>29</sup>P. M. Hui, P. Cheung, and Y. R. Kwong, *Physica A* **241**, 301 (1997).
- <sup>30</sup>P. Ponte Castañeda and M. Kailasam, *Proc. R. Soc. London* **453**, 793 (1997).
- <sup>31</sup>P. Ponte Castañeda, *Phys. Rev. B* **57**, 12 077 (1998).
- <sup>32</sup>D. A. G. Bruggeman, *Ann. Phys. (Leipzig)* **24**, 636 (1935).
- <sup>33</sup>H.-C. Lee, K.-P. Yuen, and K. W. Yu, *Phys. Rev. B* **51**, 9317 (1995).
- <sup>34</sup>H.-C. Lee, K. W. Yu, and G. Q. Gu, *J. Phys.: Condens. Matter* **7**, 8785 (1995).
- <sup>35</sup>L. Sali and D. J. Bergman, *J. Stat. Phys.* **86**, 455 (1997); **89**, 1105 (1997).
- <sup>36</sup>Y.-P. Pellegrini and M. Barthélémy, *Phys. Rev. E* **61**, 3547 (2000).