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Continuous freezing in an infinite-range one-dimensional model

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The partition function of the classical one-dimensional hard rod fluid with a residual long range interaction can be evaluated exactly, with the aid of an auxiliary field, in the limit where the range of the potential goes to infinity. If the Fourier spectrum of the residual interaction lacks components at finite wave vector, the infinite range limit recovers the celebrated result of the Kac-Uhlenbeck-Hemmer model of condensation. Otherwise, it predicts a continuous second-order freezing transition.

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I. INTRODUCTION

Much attention has been given, in recent times, to the behavior of matter confined inside one-dimensional channels. A prime example is provided by noble gas adsorbed inside carbon nanotubes. From the point of view of classical statistical mechanics, these systems might be dismissed as completely trivial, since thermal fluctuations will always destabilize any order at $T>0$. However, the weak interactions in the transverse dimensions, such as those occurring when many nanotubes bundle up in three-dimensional structures, conspire to make the physics considerably more interesting, e.g., by stabilizing ordered low temperature phases [1,2]. It turns out that the behavior of these systems is very anisotropic, and the strong correlations that may be present are usually well described by one-dimensional models, with appropriate perturbations [3].

In this paper, I discuss a class of strictly one-dimensional (1D) models that are amenable to exact solution and display nontrivial phase behavior even in one dimension. This is possible when the interparticle interactions are of sufficiently long range, so that a local thermal fluctuation does not prevent particles to the left and to the right from acting cooperatively and maintaining long range order at nonzero temperature. The model I discuss is that of a classical fluid with a pairwise interparticle potential of the form

$$V(x-x')=V_0(x-x')-V_1(x-x'), \tag{1}$$

where V_0 is the hard core potential of range σ and V_1 is a residual interaction of range γ^{-1}. The grand canonical partition function of the model, $\mathcal{Q}$, can be written exactly, after effecting a Hubbard-Stratonovich (HS) transformation, in terms of the grand potential of the hard rod system in an external field (the auxiliary HS field). Let $\mathcal{Q}=\Sigma_{N=0}^{\infty}\zeta^N Q_N$, where ζ denotes fugacity. The N-particle canonical partition function at inverse temperature β is given by

$$Q_N=\frac{1}{N!}\int\prod_n dx_n \exp\left(-\beta V_0+\frac{1}{2}\beta V_1(x_i-x_j)\right). \tag{2}$$

The grand partition function can be expressed as a functional integral over an auxiliary field $\psi(x)$ through the Hubbard-Stratonovich transformation, following Woo and Song [4]:

$$\begin{aligned}\mathcal{Q}=\mathcal{A}\int &\mathcal{D}[\psi(x)]\\ &\times\exp\left(-\frac{1}{2}\int dx\int dx' W_1(x-x')\psi(x)\psi(x')\right)\\ &\times\exp(-\beta\Omega_0[\psi]).\end{aligned} \tag{3}$$

Here, $\Omega_0[\psi]$ is the grand potential of the 1D hard rod system in the external field $\psi(x)$, W_1 is the functional inverse of βV_1, and the normalization constant $\mathcal{A}$ is the determinant of V_1 given by

$$\mathcal{A}=\exp\left(-\frac{1}{2}\mathrm{tr}\ln 2\pi V_1\right)=\exp\left[-\frac{1}{2}\int\frac{dk}{2\pi}\ln 2\pi V_1(k)\right]. \tag{4}$$

It should be emphasized that Eq. (3) is *exact*, provided that W_1 exists. Since an exact solution is available for hard rods, exact solutions of the interacting system can be obtained in the interesting case of infinite range interactions.

Physical interaction potentials decompose naturally as expressed in Eq. (1), although there is some degree of arbitrariness in choosing the mathematical form of V_1. But such arbitrariness is confined to the region near the hard core and thus it is of no consequence to the present discussion.

The remainder of the paper is organized as follows. In Sec. II, the relevant properties of the hard rod system are reviewed, with emphasis on the convexity of the grand potential. In Sec. III, I show that partition function can be evaluated in the saddle point approximation. The approximation becomes exact in the infinite range limit, discussed in Sec. IV, where, in particular, the results of Kac, Uhlenbeck, and Hemmer [5] are recovered for their model of hard rods plus exponential attraction. In Sec. V, I consider potentials with nontrivial momentum dependence in the infinite range limit. Unlike the Kac model, where $\hat{V}_1(k)\sim\delta(k)$ in that limit, a nontrivial momentum dependence allows for a transition to a crystalline phase. This transition is shown to be of second order.

II. ONE-DIMENSIONAL FLUIDS

The key to the solution of the interacting 1D problem lies in the hard rod grand potential $\Omega_0[\psi]$. The exact solution of the hard rod system in an external field, found by Percus [6], is given in terms of the density functional $\beta\Omega_0[\rho] \equiv \beta\Omega_0[\psi] - \int dz \rho(z)\psi(z)$. Unfortunately, to my knowledge, no explicit form is available for the grand potential $\Omega_0[\psi]$. Constructing the latter from the former is difficult, because the relation between field and density,

$$\psi(x) + \ln\rho(x) - \ln\zeta = \ln\left[1 - \int_{x-\sigma}^{x} \rho(w)dw\right] - \int_{x}^{x+\sigma} ds \frac{\rho(s)}{1 - \int_{s-\sigma}^{s}\rho(w)dw}, \tag{5}$$

cannot be inverted in any simple manner to yield an expression for $\rho[\psi]$ in an arbitrary field. On the other hand, the functional derivatives of $\Omega_0[\psi]$ have a simple expression in terms of the density, a fact that will prove very helpful in the following sections. Thus, the first derivative is simply the negative of the density in the presence of the external field,

$$\frac{\delta\beta\Omega_0[\psi]}{\delta\psi(x)} = -\rho(x), \tag{6}$$

and the second derivative is the Ursell function

$$\frac{\delta^2\beta\Omega_0[\psi]}{\delta\psi(x)\,\delta\psi(x')} = -\frac{\delta\rho(x)}{\delta\psi(x')} = -S_0(x,x'). \tag{7}$$

Of course, the two formulations in terms of ρ and ψ are equivalent, and many useful mathematical properties of the grand potential can be derived from the properties of the density functional $\Omega_0[\rho]$:

$$\beta\Omega_0[\rho] = \int_{-\infty}^{\infty} dz\rho(z)\left[\ln\left(\frac{\rho(z)}{\zeta\left(1 - \int_{z-\sigma}^{z} dw\rho(w)\right)}\right) - 1\right]. \tag{8}$$

Of particular interest are the expressions for the direct correlation functions [6]:

$$\begin{aligned} c_n(z_1, \ldots, z_n) &\equiv \frac{\delta^{n-1}[\psi(z_1) + \ln\rho(z_1)]}{\delta\rho(z_2)\cdots\delta\rho(z_n)} \\ &= -(n-2)!\sum_{i=1}^{n} \frac{\prod_{j\neq i}[\epsilon(z_i - z_j)\epsilon(z_j - z_i + \sigma)]}{\left[1 - \int_{z-\sigma}^{z}\rho(w)dw\right]^{n-1}} \\ &\quad -(n-1)!\int dz \frac{\rho(z)\prod_{j=1}^{n}[\epsilon(z - z_j)\epsilon(z_j - z + \sigma)]}{\left[1 - \int_{z-\sigma}^{z}\rho(w)dw\right]^{n}}. \end{aligned} \tag{9}$$

Note that all c_n*'s are negative or zero everywhere in* $\mathcal{R}^n$.

Noting that $\delta\beta\Omega_0[\rho]/\delta\rho(z) = -\psi(z)$, from Eq. (9) it follows that

$$\frac{\delta^n\beta\Omega_0[\rho]}{\delta\rho(z_1)\cdots\delta\rho(z_n)} = -c_n(z_1, \ldots, z_n) + \frac{\delta^{n-1}\ln\rho(z_1)}{\delta\rho(z_2)\cdots\delta\rho(z_n)}. \tag{10}$$

The negativity of the correlation functions [Eq. (9)] implies that all even-order functional derivatives of Ω_0 are positive definite.

This fact in turn implies that Ω_0 (regarded as a functional of either ψ or ρ) is *convex*. Hence, it has a single minimum. Since a uniform density solution can always be found, the 1D HS system exists *only* in the fluid phase. The density is found as the root of the transcendental equation

$$\frac{\rho}{\zeta} = (1 - \rho\sigma)\exp\left(-\frac{\rho\sigma}{1 - \rho\sigma}\right). \tag{11}$$

Note that although the existence of a single disordered phase is expected in 1D because of fluctuations, the convexity of Ω_0 is a much stronger statement, as it excludes transitions even in mean field theory (MFT) (unlike, e.g., the 1D Ising model, which does display an ordering transition in MFT).

III. THE SADDLE POINT EVALUATION OF THE PARTITION FUNCTION

The functional integral in Eq. (3) can be evaluated by the saddle point method. The saddle point configuration $\psi_0(x)$ is obtained as the solution to the equation

$$\frac{\delta\beta\Omega_0[\psi]}{\delta\psi(x)} + \int dx' W_1(x - x')\psi(x') = 0. \tag{12}$$

Although $\Omega_0[\psi]$ is unknown, this equation can be solved by noting that the left-hand side (lhs) is (minus) the density in the presence of the external field $\psi_0(x)$, by virtue of Eq. (6). Thus, using Eq. (5), one obtains the following equations for the saddle point density (rather than the field):

$$\int dx'\beta V_1(x - x')\rho(x') = -\ln\left[\frac{\rho(x)}{\zeta\left(1 - \int_{x-\sigma}^{x}\rho(w)dw\right)}\right] - \int_{x}^{x+\sigma} ds \frac{\rho(s)}{1 - \int_{s-\sigma}^{s}\rho(w)dw}. \tag{13}$$

Substituting into Eq. (8), one finds the equation of state in the saddle point approximation [4],

$$\beta p = \beta p_0 - \frac{1}{2L}\int dx \int dx'\beta V_1(x - x')\rho(x)\rho(x'), \tag{14}$$

where p_0 is the pressure of the hard rod system at the saddle point density.

Equation (13) admits a unique solution $\overline{\rho}(x)$ provided that form $\delta^2\beta\Omega[\psi]/\delta\psi(x)\delta\psi(x')$ is positive definite, or, equivalently, that

$$-S_0(x-x')+W_1(x-x')>0. \tag{15}$$

Once the saddle point density profile is determined [let us call it $\overline{\rho}(x)$], the saddle point field is obtained as

$$\overline{\psi}(x)=\int dx'\,\beta V_1(x-x')\overline{\rho}(x'). \tag{16}$$

A shift in the functional integration variable $\eta(x)=\psi(x)-\overline{\psi}(x)$ allows one to recast the partition function in the suggestive form

$$\begin{aligned}\mathcal{Q}=\overline{\mathcal{Q}}\mathcal{A}\int \mathcal{D}[\eta(x)]&\\ \times\exp\Bigg[-\frac{1}{2}\int dx\int dx'\,\eta(x)\eta(x')\Bigg(W_1(x-x')&\\ +\frac{\delta^2\beta\Omega_0[\psi]}{\delta\psi(x)\delta\psi(x')}\Bigg|_{\overline{\psi}}\Bigg)\Bigg]\exp\Bigg[-\frac{1}{3!}\int dx\int dx'&\\ \times\int dx''\,\eta(x)\eta(x')\eta(x'')\frac{\delta^3\beta\Omega_0[\psi]}{\delta\psi(x)\delta\psi(x')\delta\psi(x'')}\Bigg|_{\overline{\psi}}\Bigg]\cdots,&\end{aligned} \tag{17}$$

where

$$\begin{aligned}\overline{\mathcal{Q}}&=\exp\left(-\beta\Omega_0[\overline{\psi}]-\frac{1}{2}\int dx\int dx'\,W_1(x-x')\overline{\psi}(x)\overline{\psi}(x')\right)\\ &=\exp\Bigg(\int dx\frac{\overline{\rho}(x-\sigma)}{1-\int_{x-\sigma}^{x}dw\,\overline{\rho}(w)}\\ &\quad-\frac{1}{2}\int dx\int dx'\,\beta V_1(x-x')\overline{\rho}(x)\overline{\rho}(x')\Bigg).\end{aligned} \tag{18}$$

Thus, the partition function is broken down into three factors. The first one, embodied in $\overline{\mathcal{Q}}$, leads to the mean field equation of state; the second one, stemming from $\mathcal{A}$ and from the terms quadratic in η, represents the RPA correction to the equation of state; and the third one contains all higher-order corrections. Note that the higher-order terms multiply *n*-point correlation functions of the hard rod system. The knowledge of their explicit form is not needed in what follows, however. This is because in the infinite range limit, all higher order corrections are shown to vanish.

IV. THE INFINITE RANGE LIMIT AND THE KAC-UHLENBECK-HEMMER MODEL

Consider the following residual interaction:

$$V_1(x)=\alpha\gamma\exp(-\gamma|x|). \tag{19}$$

This is the model studied by Kac *et al.* [5]. They showed that the partition function in the thermodynamic limit is given by the largest eigenvalue of the kernel of a certain linear integral equation. They studied the limit $\gamma\to 0$ and found that the exact equation of state of the system has precisely the van der Waals form (below the critical point, it must be complemented by the Maxwell construction).

The result of Kac *et al.* is recovered promptly in the functional integral formalism exposed in the preceding section. To begin, note that in the limit $\gamma\to 0$, $\hat{V}_1(k)\sim 2\pi\alpha\gamma\delta(k)$, that is, the only Fourier component of the potential that survives is at $k=0$. Then from Eq. (15), it follows that any saddle point configuration $\rho(x)$ must be a constant (since the Fourier transform of Eq. (15) can be satisfied only at $k=0$). Therefore, in the saddle point approximation, the equation of state [cf. Eq. (14) or Eq. (18)] is the van der Waals equation

$$p\equiv\frac{T}{L}\log\overline{\mathcal{Q}}=\frac{T\rho\sigma}{1-\rho\sigma}-\alpha\rho^2. \tag{20}$$

Next, I show that the saddle point approximation becomes exact in the limit $\gamma\to 0$. To see this, note first that the determinant of V_1 becomes singular in this limit, so that prefactor $\mathcal{A}$ diverges. To eliminate the divergence, a change of variable is needed: $\eta(x)=\gamma\eta'(x)$. Equation (17) can be recast in the form

$$\begin{aligned}\mathcal{Q}/\overline{\mathcal{Q}}=\mathcal{A}'\int \mathcal{D}[\eta'(x)]\exp\Bigg[-\frac{1}{2}\gamma^2\int dx\int dx'\,\eta'(x)\eta'(x')&\\ \times\Bigg(W_1(x-x')+\frac{\delta^2\beta\Omega_0[\psi]}{\delta\psi(x)\delta\psi(x')}\Bigg|_{\overline{\psi}}\Bigg)\Bigg]&\\ \times\exp\Bigg[-\frac{1}{3!}\gamma^3\int dx\int dx'\int dx''\,\eta'(x)\eta'(x')\eta'(x'')&\\ \times\frac{\delta^3\beta\Omega_0[\psi]}{\delta\psi(x)\delta\psi(x')\delta\psi(x'')}\Bigg|_{\overline{\psi}}\Bigg]\cdots.&\end{aligned} \tag{21}$$

One may regard Eq. (21) as generating a perturbation series in γ [7], and it is immediately apparent that the terms of third or higher order all vanish for $\gamma\to 0$, since the correlation functions of the hard rod system are finite. Direct evaluation of the Gaussian term now yields

$$\begin{aligned}\mathcal{Q}/\overline{\mathcal{Q}}&=\exp\left(\frac{1}{2}\int\frac{dk}{2\pi}\ln[1-\rho\hat{S}_0(k)\beta\hat{V}_1(k)]\right)\\ &\to\exp\left(\frac{1}{2}\gamma\beta\alpha\rho\hat{S}_0(0)\right)\to 1,\quad \gamma\to 0.\end{aligned} \tag{22}$$

Thus, $\mathcal{Q}=\overline{\mathcal{Q}}$, and the van der Waals equation of state is exact.

V. SECOND-ORDER FREEZING TRANSITION

The Kac potential can be used as a model of the liquid-gas transition. However, it cannot display a transition to a crystalline phase, because in the infinite range limit, it loses all nontrivial momentum components. Consider instead a residual interaction of type

$$V_1(x)=\alpha\gamma\exp(-\gamma|x|)\cos(bx). \tag{23}$$

This interaction can be viewed as an extension of the Kac model to the complex plane, and can be expected to generate a crystalline phase, i.e., a state with broken translational invariance, at low temperature. To look for such a phase, consider the Fourier transform of the potential

$$\hat{V}_1(k)=\alpha\gamma^2\left[\frac{1}{\gamma^2+(b+k)^2}+\frac{1}{\gamma^2+(b-k)^2}\right]. \tag{24}$$

In the limit $\gamma\to 0$, it vanishes everywhere except for points $k=\pm b$. It then follows that the Fourier transform of the density, $\hat{\rho}(k)$, must have support on a discrete set of points or else the lhs of Eq. (13) is identically zero. This implies that a solution for the density can be sought in the form of a cosine series [8]:

$$\rho(x)=\sum_{n=0}^{\infty}\rho_n\cos(nbx). \tag{25}$$

The solution of this model now follows quite closely that of the Kac model, exposed in the preceding section. In particular, in the limit $\gamma\to 0$, determinant $\mathcal{A}$ is again singular, the singularity is removed by rescaling the field by a factor of γ so that random-phase appoximation and higher order corrections again vanish for $\gamma=0$. The only remaining task is the solution of the saddle point equation, Eq. (13), which now becomes

$$\beta\alpha\rho_1\cos(bx)=-\ln\left[\frac{\rho(x)}{\zeta\left(1-\int_{x-\sigma}^{x}\rho(w)dw\right)}\right]-\int_{x}^{x+\sigma}ds\,\frac{\rho(s)}{1-\int_{s-\sigma}^{s}\rho(w)dw}. \tag{26}$$

Equation (26) can be solved numerically with arbitrary accuracy, in principle. Note that it always admits one (and only one) solution of the form $\rho=\rho_{\text{gas}}=\text{const}$. Now, for $\beta\alpha<\hat{S}_0(b)$, the free energy is convex, hence the hessian corresponding to the constant density solution ρ_{gas} is positive, and the solution is the free-energy minimum. But as we increase β (lower temperature) to some value β_c, as soon as Eq. (15) is satisfied, the hessian determinant changes sign, and the constant density solution is no longer a minimum. The fluid phase has disappeared.

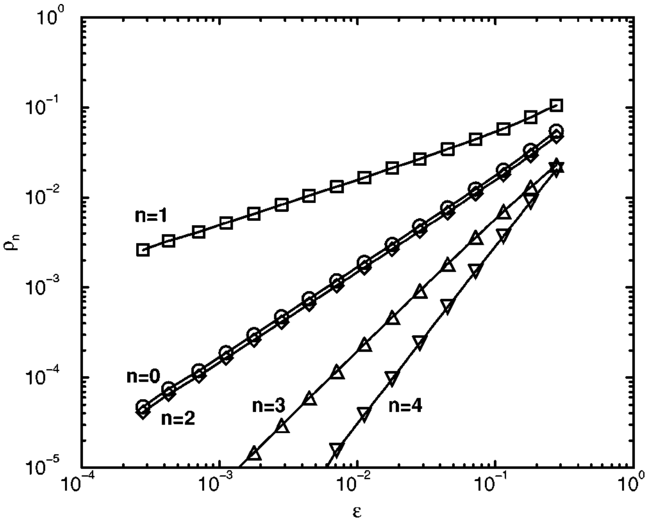

FIG. 1. Log-log plot of the Fourier coefficients of the density versus ϵ. Circles, $\rho_{\text{gas}}-\rho_0$; squares, ρ_1; diamonds, $-\rho_2$; up triangles, ρ_3; down triangles, ρ_4. The calculation was performed for $\sigma=1$, $b=2\pi/4.3$, $\zeta=200$ ($\rho_{\text{gas}}=0.797$).

The stable solution to Eq. (26) possesses a modulated density with period $2\pi/b$. [Higher harmonics will also be generated, of course; cf. Eq. (25).] Thus, ρ_1 can be taken as the order parameter of the transition. One verifies that the transition is continuous by noting that all Fourier coefficients ρ_n $(n\geqslant 1)$ vanish as powers of critical parameter $\epsilon=T_c-T/T_c$ with critical indices β_n. For ρ_0, which, of course, does not vanish, exponent β_0 characterizes the approach to ρ_{gas}. The results obtained by solving Eq. (26) numerically are summarized in Fig. 1, which shows a log-log plot of the first few coefficients ρ_n versus ϵ (for $n=0$, I have plotted $\rho_{\text{gas}}-\rho_0$; for $n=2$, I have plotted $-\rho_2$). A conjugate gradient algorithm [9] was adopted. The following parameters were used: hard core radius $\sigma=1$; $b=2\pi/4.3$, $\zeta=200$ (corresponding to a density of about 0.8). The following numerical values of the indices β_n were found for $n=0,\ldots,4$: 0.998, 0.502, 0.999, 1.46, 1.96. Thus, one concludes that, for $T\to T_c^-$,

$$\rho_1\propto\epsilon^{1/2}, \tag{27}$$

as expected, since MFT is exact for this model. All other coefficients are found to be proportional to integer powers [10] of the order parameter,

$$\rho_n\propto\rho_1^n\propto\epsilon^{n/2},\quad n>1. \tag{28}$$

Furthermore, the excess density of the crystalline phase vanishes at the transition as the square of the order parameter,

$$\rho_0-\rho_{gas}\propto\rho_1^2\propto\epsilon. \tag{29}$$

Thus, the density changes continuously upon crystallization.

VI. CONCLUSIONS

In this paper, I have presented a simple model of one-dimensional particles with long range interactions that possess nontrivial components in momentum space. In the infinite range limit, the model is amenable to exact solution and displays a crystallization transition. This transition is of second order with mean field critical exponents.

The solution of this model, which is an extension of the Kac model of the liquid-gas transition, confirms recent results, based on density functional theory and Monte Carlo simulations, which found continuous freezing of atoms confined within three-dimensional arrays of narrow channels [3]. There are many physical systems where such transitions may be observable. Examples include an array of atoms confined (or intercalated) within carbon nanotubes [11,1], and also inclusion compounds, in which guest molecules are laterally confined, but retain axial mobility, inside a host crystalline matrix [12]. Similar phenomena are often discussed in the context of 2D colloidal particles in an external modulated laser field [13].

What these systems have in common is that order in the transverse dimensions is imposed by an external structure. Long range order in the axial dimension is the only nontrivial occurrence, and is stabilized by the weak transverse interparticle interactions. Hence, modeling the physics with an infinite range one-dimensional interaction renders the problem mathematically tractable without altering the essence of the physics. This is essentially the physics of packing of hard spheres in one dimension, a trivial problem with an exact solution, unlike the counterpart in higher dimension.

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[1] M.M. Calbi, M.W. Cole, S.M. Gatica, M.J. Bojan, and G. Stan, Rev. Mod. Phys. **73**, 857 (2001).
[2] C. Carraro, Phys. Rev. B **61**, R16 351 (2000).
[3] C. Carraro, Phys. Rev. Lett. **89**, 115702 (2002).
[4] H.-J. Woo and X. Song, J. Chem. Phys. **114**, 5637 (2001).
[5] M. Kac, G.E. Uhlenbeck, and P.C. Hemmer, J. Math. Phys. **4**, 216 (1963).
[6] J.K. Percus, J. Stat. Mech. **15**, 505 (1976).
[7] The adimensional coupling could be taken to be $\gamma\sigma$.
[8] The choice of a cosine series, rather than a more general Fourier series, corresponds to fixing the position crystal lattice as a whole with respect to the origin. This choice is arbitrary and inconsequential to the physics.
[9] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C*, 2nd ed. (Cambridge University Press, Cambridge, 1992), Chap. 10.
[10] Integer values are found within numerical accuracy. There is no doubt, of course, that the true values are indeed integers.
[11] W. Teizer, R.B. Hallock, E. Dujardin, and T.W. Ebbesen, Phys. Rev. Lett. **82**, 5305 (1999).
[12] A.A. Khan, S.T. Bramwell, K.D.M. Harris, B.M. Kariuki, and M. Truter, Chem. Phys. Lett. **307**, 320 (1999).
[13] L. Radzihovsky, E. Frey, and D.R. Nelson, Phys. Rev. E **63**, 031503 (2001).