Computer simulation of a quantum particle in a quenched disordered system: Direct observation of Lifshitz traps

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A new sampling technique is introduced for the Monte Carlo evaluation of path integrals. The method is used to study a single quantum particle in a rigid bcc lattice, a fluid, and a quenched disordered array of classical hard spheres. In the latter case, the quantum particle is shown to localize at preferred sites (Lifshitz traps).

By applying a novel quantum-mechanical sampling method, we have succeeded in obtaining exact numerical results on the nature of electronic states in systems with strong (gaslike) topological disorder. A typical physical example is that of heavily doped semiconductors. For such systems, spatial fluctuations in the Hamiltonian are able to sustain extended as well as localized states for noninteracting electrons.[1-3] The presence of extended states in disordered systems can be accounted for with the use of a multiple-scattering formalism.[3] However, Lifshitz argued that there should be exponential tails associated with the energy bands of extended states which are produced by bound states, localized in regions of excess concentrations of attractive impurity centers or in regions deficient in repulsive scatterers.[4] Such fluctuations in the distribution of impurities are called Lifshitz traps.[5-9]

The localized states of an electron in a disordered array of hard-core scatterers were studied by Friedberg and Luttinger with the use of path integrals.[9] The same model has also been the focus of recent approximate analytical work concerning the behavior of an excess electron in a fluid.[10] Friedberg and Luttinger derived an explicit expression for the low-energy density of states and the free energy, and confirmed the intuitive idea of Lifshitz that localization occurs despite the fact that there are no constraints, such as potential-energy barriers, to confine the electron.

The path-integral representation of quantum mechanics[11] is not only useful for the purpose of analytic calculations.[8-10] It also yields algorithms for the numerical simulation of quantum systems.[12-16] In this Rapid Communication, we report the first path-integral Monte Carlo (PIMC) study of a quantum particle in a rigid disordered array of hard spheres. Our results, obtained using a direct-sampling technique,[16] yield evidence for the existence of Lifshitz traps. We also introduce an importance-sampling technique to study a quantum particle solvated in a fluid of hard spheres. Since the configurational distribution of hard spheres is independent of temperature, it can be argued that the equilibrium properties of a quantum particle in an infinitely large disordered array of nonoverlapping *fixed* scatterers are identical to those in a *fluid* system. Therefore, comparison between the results of these independent calculations provides a powerful test of our algorithm.

The PIMC method is based on the isomorphism between the discretized path integral and a classical system composed of a set of particles arranged in a chain.[13] Classical averages over the chain configurations give accurate estimates of the equilibrium properties of the quantum particle, provided that P, the number of particles in the chain, is sufficiently large or, equivalently, when an elementary link in the chain corresponds to propagation for an infinitesimally short time. Since the short-time expansion for steep hard-core potentials is very slowly convergent, chains with large P, typically 10^3–10^4, are needed.[14-16] The coupling between the chain particles, which becomes increasingly strong with P, will allow only small particle displacements. Hence, large-scale fluctuations of the chain configuration are greatly inhibited, and there is a serious danger that the chain will be locked into a locally stable configuration by the excluded volume interaction with the hard spheres. This phenomenon, which is due to nonergodic motion of the isomorphic classical system, is not to be confused with the Lifshitz trap.

To overcome this difficulty we propose a new sampling algorithm, which builds up the chain configuration in stages.[16] First, the gross features of a configuration are established using a chain with the correct thermal wavelength, $\lambda = \hbar (\beta/m)^{1/2}$, but composed of only a few particles. Then, with the configuration of this primary chain held fixed, secondary chains are inserted between adjacent vertices of the primary chain. This basic idea can be applied in a two-stage direct sampling procedure, and it can also be modified to provide an efficient importance-sampling scheme for the primary chain. In the direct method, both primary- (a-) chain and secondary- (b-) chain configurations are sampled from distributions of free chain configurations with the appropriate force constants and boundary conditions for the end points.[16] The insertion of secondary chains is repeated many times, in order to determine an effective weight for each fixed primary-chain configuration. In the importance-sampling scheme, this weight is used as an acceptance criterion for trial moves of primary-chain vertices. This two-stage sampling procedure, the second stage determining a weight for the first, is an application of the superposition principle.[16]

Let us define a density matrix $\rho(\mathbf{r}, \mathbf{r}'; \beta)$ as the ratio K/K^0 of the propagator $K(\mathbf{r}, \mathbf{r}'; \beta)$ and its free value

$K^0(\mathbf{r},\mathbf{r}';\beta)$; K gives the probability for propagation from an initial point r' to a final point r in a time interval $i\tau = \beta\hbar$. If $\{\mathbf{r}_i^a\}$ is the set of coordinates from the P_a primary-chain particles and $\{\mathbf{r}_{j,i}^b\}$ gives the positions of the $P_a(P_b - 1)$ secondary-chain particles, then

$$\rho(\mathbf{r},\mathbf{r}';\beta) \simeq N_a^{-1} \sum \prod_i \bar{\rho}_i(\mathbf{r}_i^a, \mathbf{r}_{i-1}^a;\beta/P_a) \ ,$$

$$\bar{\rho}(\mathbf{r}_i^a, \mathbf{r}_{i-1}^a;\beta/P_a) \simeq N_{b,i}^{-1} \sum \prod_j \tilde{\rho}(\mathbf{r}_{j,i}^b, \mathbf{r}_{j-1,i}^b;\beta/P_aP_b) \ .$$

The first summation is over the total number of a-chain configurations generated, N_a. Similarly, the second summation is over the $N_{b,i}$ b-chain configurations, generated for each link i in the a chain. The quantity $\bar{\rho}$ can be considered as a weight, which renormalizes the propagator between a-chain vertices. In the most primitive algorithm $\tilde{\rho}$, the short-time approximation to ρ is zero when one of the end points is located inside the excluded volume of a hard sphere, and unity otherwise. However, we employ a more efficient algorithm, known as the image approximation.[12,14]

An advantage of the two-stage method over the straight-forward (one-stage) approach is that the average displacement of neighboring a-chain vertices can be made comparable to the average separation between the hard spheres. Furthermore, in the direct-sampling scheme the high attrition rate for chain configurations is greatly reduced, since the probability of overlap with a hard sphere, for a chain with P_a (or P_b) vertices, is much smaller than for a chain
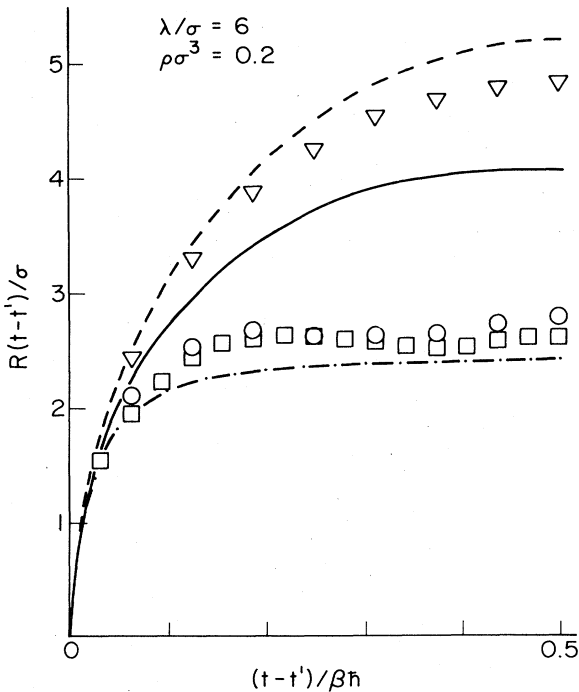

FIG. 1. Square root of the second moment of the response function R for a quantum particle in various hard-sphere systems at $\rho\sigma^3 = 0.2$. Direct sampling was used for the disordered array (circles) and the bcc lattice (triangles), while importance sampling was used for the fluid (squares). The solid line is the theoretical result from Ref. 10, and the dashed line is the free particle limit. The dash-dot line is the theoretical result at $\rho\sigma^3 = 0.39$ (the density at which the theoretical excess chemical potential reproduces the PIMC value).
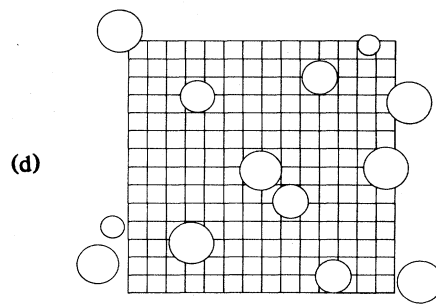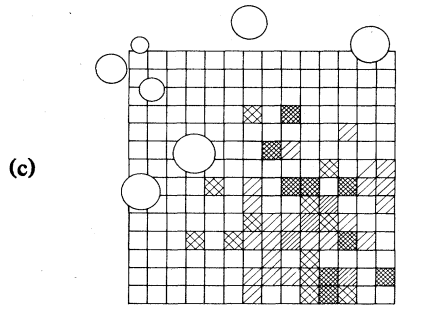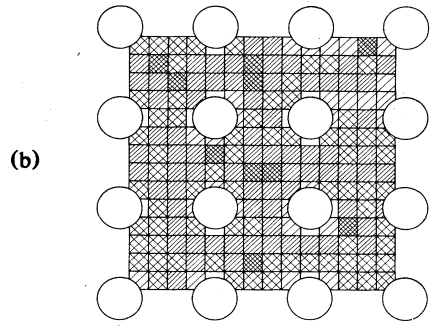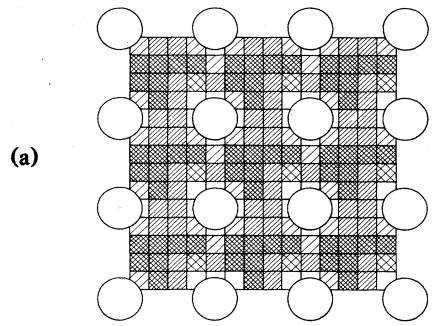

FIG. 2. Distribution f of the quantum particle as determined by direct sampling in a cube of $14 \times 14 \times 14$ bins at the center of the rigid hard-sphere systems for $\lambda = 6\sigma$ and $\rho\sigma^3 = 0.2$. Bin occupation is normalized to $f_{\max}$ and 5 levels of shading are used. The $[\frac{1}{2}00]$ plane of a bcc lattice is shown in (a) and (b). In (a) the values of f from 27 unit cells have been averaged and unfolded again, while in (b) $\ln f$ is shown unaveraged; (c) and (d) show $\ln f$ for low- and high-density regions in the disordered system.

with $P_a \times P_b$ vertices. The direct-sampling procedure also yields an estimate of the free energy (or excess chemical potential)

$$\beta(F - F_0) = -\ln \int d\mathbf{r}\, \rho(\mathbf{r},\mathbf{r};\beta)/V \ ,$$

where F_0 is the chemical potential of an unperturbed thermally equilibrated particle.

The behavior of the second moment of the response function[16]

$$R^2(t - t') = \langle |\mathbf{r}(t) - \mathbf{r}(t')|^2 \rangle \ ,$$

was examined for a quantum particle with $\lambda = 6\sigma$ in a bcc lattice, a rigid disordered array, and a fluid, at the same density $\rho\sigma^3 = 0.2$. The distance of closest approach of the quantum particle to a hard sphere is the radius of the hard sphere $\sigma/2$. In the disordered array of 2197 hard spheres, R was obtained from an average of 10^5 independent accepted a-chain configurations ($N_a = 5 \times 10^5$), using a chain with $P_a \times P_b = 16 \times 16$ vertices and $N_{b,i} = 100$. This amounts, effectively, to a sampling of 10^{37} chain configurations! For the fluid system, importance sampling was applied to a primary chain of $P_a = 32$ vertices, which interacted with 1458 hard spheres through the weight $\bar{p}$, taking $P_b = 8$ and $N_{b,i} = 100$. Averages were collected over about 10^4 moves per hard sphere, the latter each being moved three times for every attempted move of an a-chain vertex.

Figure 1 demonstrates that in both the disordered system and the fluid, the thermal wave function is considerably smaller than in the lattice. Moreover, R exhibits the ground-state dominance characteristic of a bound state.[10] Further evidence for localization is provided in Fig. 2, where the (quantum) particle density in the disordered array is compared with that found in the lattice. In the latter, the quantum particle is uniformly distributed, whereas in the former it favors regions with relatively few hard spheres. In fact, Fig. 2(c) suggests that at $\rho\sigma^3 = 0.2$, a Lifshitz trap is simply a cavity surrounded by hard spheres. Actually, in the direct-sampling scheme, many chain configurations are inserted into regions with high local density [such as shown in Fig. 2(d)] but are found to be of negligible weight.

The PIMC free energy in the bcc lattice (Fig. 3) is in excellent agreement with the Wigner-Seitz estimate of the band-edge energy.[16] This result, taken together with Fig. 2(a), suggests that the PIMC method provides a reliable representation of extended states. Moreover, the agreement between the values for R for the fluid and the disordered array (Fig. 1) confirms our algorithm for localized states. The comparison between our PIMC results and those of ap-
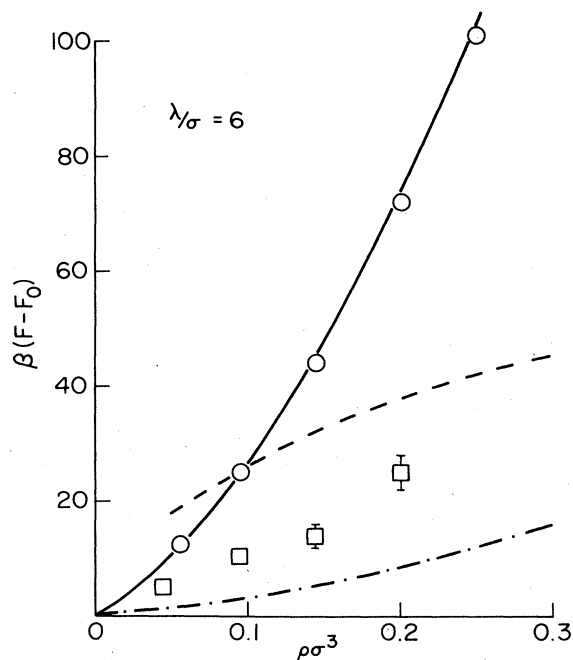

FIG. 3. Free energy difference with respect to the free particle limit for a quantum particle in a bcc lattice of hard spheres (circles) and in a quenched disordered system (squares) as a function of density. The solid curve is the Wigner-Seitz approximation to the band-edge energy of extended states, the dashed curve is the result for the localized states in a disordered system taken from Ref. 9, and the dash-dot curve is the excess chemical potential from Ref. 10.

proximate theory[9,10] shows that at a given density of scatterers, Ref. 10 underestimates the tendency for localization, whereas Ref. 9 overestimates it. Moreover, the free energy of the quantum particle (Fig. 3) is lower than found in Ref. 9 but higher than calculated in Ref. 10.

In conclusion, with the aid of a new sampling algorithm, we have demonstrated that numerical PIMC methods provide a useful compliment to existing methods for studying localization phenomena in disordered systems, and our numerical results should serve as a benchmark for necessary improvements on the existing approximate theories.

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