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Microcanonical Monte Carlo simulation of lattice gas models

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We introduce a true microcanonical ensemble appropriate for Monte Carlo simulations of lattice gas models in which both the energy and the number of particles are held fixed. We also deduce formulas that allow us to do the calculation of the intensive quantities: temperature and chemical potential. The numerical results coming from Monte Carlo simulations defined according to this microcanonical ensemble compare well with results coming from the ordinary canonical ensemble.

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I. INTRODUCTION

The use of Monte Carlo simulations has become an important tool in the study of interacting systems in thermodynamic equilibrium [1]. The simulations are performed within the framework of a given specified ensemble. The lattice gas model, or Ising model, for instance, can be simulated in the grand-canonical [2–4], in the canonical [5,6], or in other ensembles [7–11]. If one is interested in the bulk properties, the use of one or other ensemble is a matter of mathematical or computational convenience since in the thermodynamic limit the ensembles are equivalent, at least for short range interactions [12–14]. If, on the other hand, one is interested in the study of small systems, one should keep in mind that results coming from distinct ensembles might be different. In this case the choice of which ensemble to use should be dictated by the physics one is interested in.

An important feature of any ensemble is that if a certain thermodynamic quantity is kept fixed then its conjugate is a fluctuating quantity. If the fixed variable is an intensive thermodynamical quantity, the ensemble calculation of its extensive conjugate quantity poses no problem since, usually, the conjugate quantity is simply the ensemble average of a fluctuating variable. When this is not the case, as happens with the entropy, it can be indirectly calculated from some function of a fluctuating variable [15]. However, if the extensive quantity is kept fixed the ensemble calculation of its intensive conjugate quantity is not a trivial task. For instance, to calculate the chemical potential in the canonical ensemble one has to use such schemes as the insertion or removal of particles [16,17].

Two problems concern us here. First, we wish to define a microcanonical ensemble appropriate for Monte Carlo simulations of lattice gas systems in which both the energy *and* the number of particles are conserved. This should be distinguished from simulations in which the energy is conserved but *not* the number of particles (or magnetization), as are the cases of the Monte Carlo simulation introduced by Creutz [7], the so called Q2R cellular automaton [8–10], or the lattice gas with kinetic energy of Ray and Frelechoz [11]. Actually, the ensemble used by Creutz [7] is such that the energy of the system is not strictly fixed but fluctuates above a fixed lower bound. In the case of the work of Ray and Frelechoz [11], kinetic energy is introduced so that potential energy fluctuates, with overall energy fixed.

Second, we wish to deduce formulas that can be used to calculate the intensive variables over an ensemble in which the conjugate extensive quantity is conserved. This is accomplished by the use of the following reasoning. Consider an ensemble in which a certain intensive variable h is held fixed. Suppose that we have obtained for this h-constant ensemble an equation of the type

$$h = f(\langle Q_1\rangle,\langle Q_2\rangle,\ldots), \tag{1}$$

where f is a function of the averages $\langle Q_1\rangle$, $\langle Q_2\rangle,\ldots$ and neither the function f nor the quantities $Q_1, Q_2,\ldots$ depend explicitly on h. Let us now consider the ensemble in which the variable M, conjugate to h, is held fixed. If the two ensembles are equivalent, Eq. (1) must also be valid for the M-constant ensemble. But the right-hand side of Eq. (1) does not depend on h, so that it can be used to calculate h.

In the following section, we deduce formulas such as Eq. (1) appropriate for generalized lattice gas models, or Ising model with general interactions, within the grand-canonical ensemble. Then, assuming the equivalence of ensembles, the formulas will be used within the canonical and microcanonical ensembles. The algorithm we use for the simulations of the lattice gas model is a generalization of the Kawasaki dynamics [5,6] and is defined as follows. At each time step two sites of the lattice, one occupied by a particle and the other vacant, are chosen at random. The particle is, then, transferred to the empty site if the total energy does not change. The total number of particles and the total energy is then strictly conserved. Note that the pair of empty-occupied sites is chosen among all possible pairs, not only nearest neighbor pairs as is the case in usual Kawasaki dynamics [6]. In this paper we apply the method to the lattice gas model with nearest neighbor interaction on a square lattice.

II. GRAND-CANONICAL ENSEMBLE

Let us consider a lattice for which at each site we attach an occupation variable η_i that takes the value 0 or 1. In the grand-canonical ensemble the probability distribution $P(\eta)$ of the state $\eta=(\eta_1,\eta_2,\ldots,\eta_V)$, where V is the total number of sites of the lattice, is given by

$$P(\eta)=\frac{1}{\Xi}\exp\{-\beta\phi(\eta)+\beta\mu n(\eta)\}, \tag{2}$$

where

$$\phi(\eta)=\sum_{i<j}\varepsilon_{ij}\eta_i\eta_j \tag{3}$$

is the energy and

$$n(\eta)=\sum_i \eta_i \tag{4}$$

is the number of particles. The quantity β is the inverse of temperature and μ the chemical potential.

Next we consider the probability distribution $P(\eta^k)$ of the configuration η^k defined by $\eta^k=(\eta_1,\eta_2,\ldots,1-\eta_k,\ldots,\eta_N)$. The configuration η^k is the configuration obtained from η by removing or placing a particle at site k according to whether the site k is occupied or empty, respectively. From Eq. (2) it follows that

$$\frac{P(\eta)}{P(\eta^k)}=\exp\{-\beta(2\eta_k-1)[\phi_k(\eta)-\mu]\}, \tag{5}$$

or

$$P(\eta)=P(\eta^k)\exp\{-\beta(2\eta_k-1)[\phi_k(\eta)-\mu]\}, \tag{6}$$

where

$$\phi_k(\eta)=\sum_j \varepsilon_{kj}\eta_j \tag{7}$$

is the difference in energy between a state with a particle at site k and a state with no particle at the same site.

If we consider the average of any state function $f(\eta)$, defined by

$$\langle f(\eta)\rangle_{\mathrm{gc}}=\sum_\eta f(\eta)P(\eta), \tag{8}$$

we have

$$\langle f(\eta)\rangle_{\mathrm{gc}}=\langle f(\eta^k)\exp\{-\beta(1-2\eta_k)[\phi_k(\eta)-\mu]\}\rangle_{\mathrm{gc}}, \tag{9}$$

where $\langle\cdots\rangle_{\mathrm{gc}}$ denotes the average over the grand-canonical ensemble defined by Eq. (2).

If we choose $f(\eta)=\eta_k$ then $f(\eta^k)=1-\eta_k$ and we have

$$\langle\eta_k\rangle_{\mathrm{gc}}=\langle(1-\eta_k)\exp\{-\beta\phi_k(\eta)\}\rangle_{\mathrm{gc}}\exp\{\beta\mu\}, \tag{10}$$

where we have taken into account the obvious relations $\eta_k\eta_k=\eta_k$ and $\eta_k(1-\eta_k)=0$. From this we get

$$\exp\{-\beta\mu\}=\frac{\langle(1-\eta_k)\exp\{-\beta\phi_k(\eta)\}\rangle_{\mathrm{gc}}}{\langle\eta_k\rangle_{\mathrm{gc}}}. \tag{11}$$

Analogously, if we consider $f(\eta)=1-\eta_k$ then $f(\eta^k)=\eta_k$ and we get

$$\langle(1-\eta_k)\rangle_{\mathrm{gc}}=\langle\eta_k\exp\{\beta\phi_k(\eta)\}\rangle_{\mathrm{gc}}\exp\{-\beta\mu\}, \tag{12}$$

so that

$$\exp\{\beta\mu\}=\frac{\langle\eta_k\exp\{\beta\phi_k(\eta)\}\rangle_{\mathrm{gc}}}{\langle(1-\eta_k)\rangle_{\mathrm{gc}}}. \tag{13}$$

Next we consider $f(\eta)=\eta_k\delta(\phi_k(\eta),E)$ where δ is the Kroneker delta, and E is any of the possible values of $\phi_k(\eta)$. We have then

$$\langle\eta_k\delta(\phi_k(\eta),E)\rangle_{\mathrm{gc}}=\langle(1-\eta_k)\delta(\phi_k(\eta),E)\rangle_{\mathrm{gc}}\times\exp\{-\beta E+\beta\mu\}, \tag{14}$$

or

$$\exp\{\beta E-\beta\mu\}=\frac{\langle(1-\eta_k)\delta(\phi_k(\eta),E)\rangle_{\mathrm{gc}}}{\langle\eta_k\delta(\phi_k(\eta),E)\rangle_{\mathrm{gc}}}. \tag{15}$$

III. CANONICAL AND MICROCANONICAL ENSEMBLES

In the canonical ensemble the probability distribution $P_{\mathrm{c}}(\eta)$ is given by

$$P_{\mathrm{c}}(\eta)=\frac{1}{Z}\exp\{-\beta\phi(\eta)\}\delta(n(\eta),N), \tag{16}$$

where N is the total number of particles. Appealing to the equivalence of ensembles, we use Eqs. (11) and (13) to write

$$\exp\{-\beta\mu\}=\frac{\langle(1-\eta_k)\exp\{-\beta\phi_k(\eta)\}\rangle_{\mathrm{c}}}{\rho}, \tag{17}$$

and

$$\exp\{\beta\mu\}=\frac{\langle\eta_k\exp\{\beta\phi_k(\eta)\}\rangle_{\mathrm{c}}}{1-\rho}, \tag{18}$$

where $\langle\cdots\rangle_{\mathrm{c}}$ denotes the average over the canonical ensemble defined by Eq. (16). In this ensemble $\langle\eta_k\rangle_{\mathrm{c}}=\rho$, where $\rho=N/V$ is the density of particles. These two equations have been obtained previously by other methods [16,17] in which a particle is inserted or removed from the system.

In the microcanonical ensemble the probability distribution $P_{\mathrm{mc}}(\eta)$ is given by

$$P_{\mathrm{mc}}(\eta)=\frac{1}{W}\delta(\phi(\eta),U)\delta(n(\eta),N), \tag{19}$$

where U is the total energy, which is fixed. Taking into account the equivalence of ensembles we use Eq. (15) to write

$$\exp\{\beta E-\beta\mu\}=\frac{\langle(1-\eta_k)\delta(\phi_k(\eta),E)\rangle_{\mathrm{mc}}}{\langle\eta_k\delta(\phi_k(\eta),E)\rangle_{\mathrm{mc}}}, \tag{20}$$

where $\langle\cdots\rangle_{\mathrm{mc}}$ denotes the average over the microcanonical ensemble defined by Eq. (19). This formula shows that the local energies are canonically distributed and it allows us to calculate the temperature as well as the chemical potential with respect to the microcanonical ensemble. We remark that Creutz [7] and Lang and Stauffer [10] used distinct approaches to determine the temperature in their constant energy ensembles. Creutz [7] calculated the temperature by assuming a canonical distribution of the energies carried by the "demon" whereas Lang and Stauffer [10] used an empirical energy-temperature relationship determined by a canonical Monte Carlo Simulation. The numerator (denominator) on the right-hand side of Eq. (20) is interpreted as the probability that the energy cost of inserting (removing) a particle will be E.

IV. NUMERICAL SIMULATIONS

We have tested the efficiency of the present method on the lattice gas with nearest neighbor interactions defined on a square lattice with helical periodic boundary condition [18]. The system was simulated at fixed densities and energies. In order to prepare the system at each desired energy, we start the simulations from either ordered or disordered configurations and then particle-hole exchange at arbitrary distance [6] is attempted and accepted only if energy is lowered. Once the desired energy is achieved, we start the microcanonical simulation in which only random-distance particle-hole exchange that maintains energy unaltered is performed. After relaxation, measurement of the interesting variables is initiated. The system is assumed to be relaxed when variables measured from at least two independent simulations, started from ordered and disordered initial configuration, have merged. In our simulation, a Monte Carlo step is equal to N particle-hole exchange attempts where N is the number of particles.

Temperature-energy relations are obtained from relation (20). For the lattice gas on a square lattice with nearest neighbor interaction $\phi_k(\eta)=-\varepsilon\Sigma_\delta\eta_{k+\delta}$, thus the possible values of the nearest neighbor energy E are $-n\varepsilon$ where $n=0,1,2,3,$ and 4. The right-hand side of Eq. (20), which we denote by R_n, may be written as the ratio

$$R_n=\frac{\langle N_n\rangle_{\rm mc}}{\langle D_n\rangle_{\rm mc}} \qquad (21)$$

between the average of the number of particles N_n with n occupied nearest neighbor sites and the average of the number of holes D_n with n occupied nearest neighbor sites. According to Eq. (20), R_n can be written as

$$\ln R_n=-\beta\varepsilon n-\beta\mu, \qquad n=0,1,2,3,4. \qquad (22)$$

If we measure the temperature and the chemical potential in units of ϵ we may write

$$-\ln R_n=\frac{1}{T}n+\frac{\mu}{T}, \qquad n=0,1,2,3,4, \qquad (23)$$

and note that temperature and chemical potential can be obtained from the angular and linear coefficient of the linear relation. Figure 1 shows the quantities N_n and D_n as functions of Monte Carlo steps (mcs) for the total energy per site $u=-1.9$ and particle density ρ=0.5. From the averages of N_n and D_n we compute R_n. Results are shown in Fig. 2 for several values of u, both above and below the critical temperature T_c of the infinite system ($T_c=2/\ln(1+\sqrt{2})=2.269\ldots$ [19]) and for particle density ρ=0.5. We see that the linear fitting allows us to get the temperature with very good precision. Density ρ=0.5 corresponds to zero magnetization and zero magnetic field at all temperatures. Therefore, $\mu=-2\varepsilon$, from Ising-lattice gas equivalence [20], so that Eq. (23) becomes $\ln R_n=-\beta\varepsilon(n-2)$, a condition fulfilled by our data, as can be seen from Fig. 2.

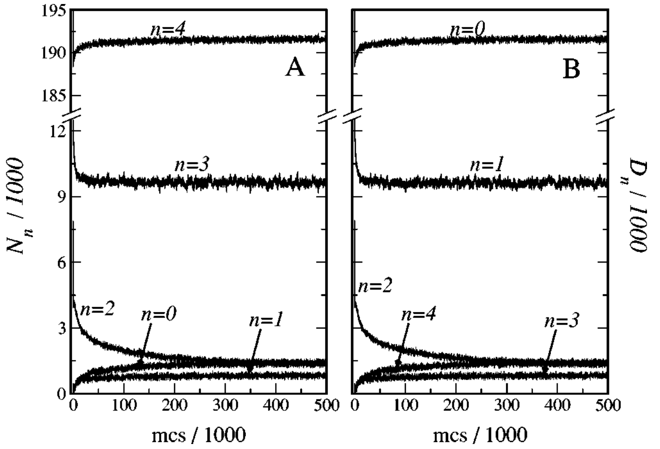

FIG. 1. Relaxation data for number of particles N_n (a) and number of holes D_n (b) with n occupied nearest neighbor sites. Data obtained from a simulation in a square lattice with linear size $L=640$, total energy per site $u=-1.9$, and particle density ρ=0.50, starting in a disordered initial condition.

We have compared our results both with exact results [19] (known for density ρ=0.5) and with previous results [21] of simulations in the canonical ensemble (for densities ρ=0.1, 0.2, and 0.5). Energy-temperature relations were obtained from the above linear fittings and specific heat was obtained from energy numerical differentiation. Figures 3 and 4 show our data for energy and specific heat as a function of temperature. Comparison with data from simulations in the canonical ensemble [21] shows that the two methods

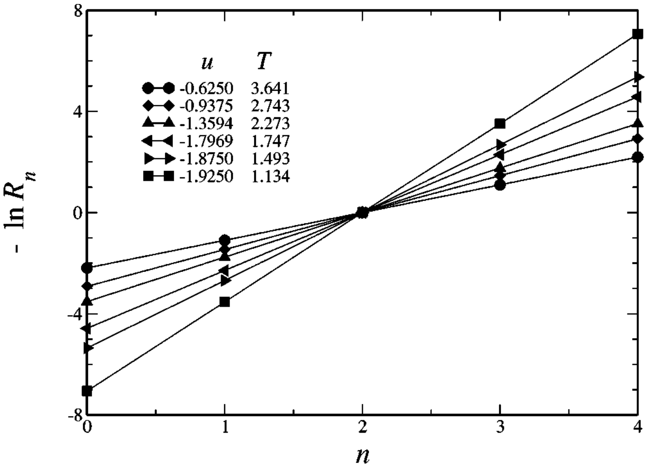

FIG. 2. Logarithm plot of R_n as a function of n for several values of the total energy per site u and its calculated temperature T according to Eq. (23), for a square lattice with linear size $L=80$ and particle density ρ=0.5.

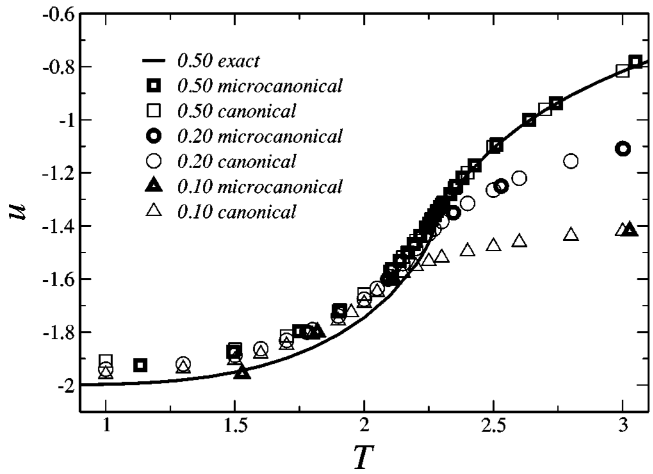

FIG. 3. Total energy per site u as a function of temperature T calculated from the microcanonical Monte Carlo simulation for several values of the density of particles. For comparison we show results coming from canonical Monte Carlo simulations [21]. For both cases the linear lattice size was $L = 80$. Also shown is the exact result for the infinite lattice.

give very similar results for different densities, for energy as well as for specific heat in accordance with the equivalence of ensembles assumed by our method. Data also compare very favorably with exact results for energy above T_c and for specific heat at all temperatures.

Deviation of energy from the exact result below T_c, seen in Fig. 3, can be attributed in both cases (canonical and microcanonical) to interface finite-size effects. In this range of temperatures, energy per particles is almost independent of density, in the case of the infinite lattice, and has -2 as a lower limit. However, the minimum total energy per site $u_{\min}$ for an L lattice of density ρ is given by

$$u_{\min} = -2 + \min\left\{\frac{4}{L}, \frac{\sqrt{\pi\rho}}{L}\right\}, \tag{24}$$

which gives $u_{\min}=-1.95$, ~ -1.99, and ~ -1.99 for densities $\rho=0.5$, 0.2, and 0.1, respectively. These lower limits for energy are in good agreement with the results shown in Fig. 3. This finite-size effect below T_c can also be seen in Fig. 5, which shows that the deviation of the temperature from its asymptotic value decays as $1/L$. Above T_c the deviation does not decay as $1/L$ anymore and becomes proportional to $1/L^2$ as can be seen in Fig. 5.

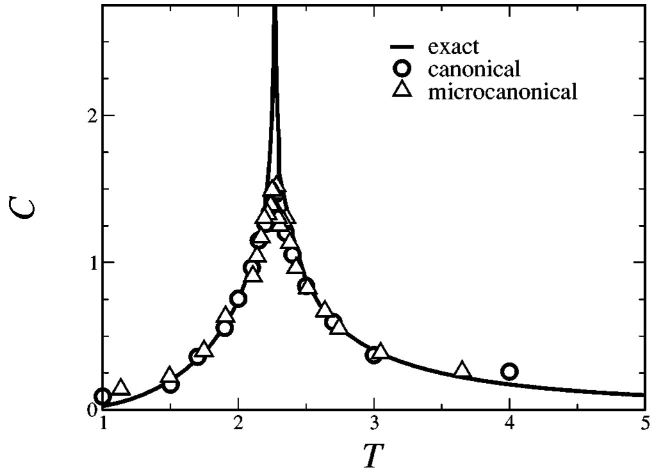

FIG. 4. Specific heat C as a function of temperature T from the microcanonical Monte Carlo simulation calculated by numerical differentiation of data in Fig. 3. For comparison we show also results coming from canonical Monte Carlo simulations [21]. For both cases the linear lattice size was $L = 80$. Also shown is the exact result for the infinite lattice.

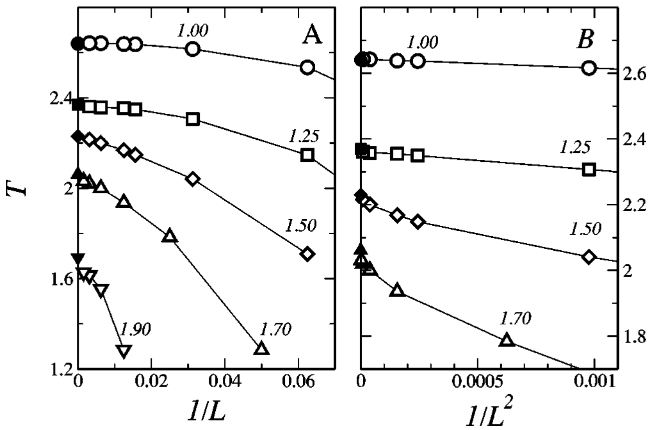

FIG. 5. Dependence of temperature with the linear size L for several values of the total energy per site u. The data for temperature are shown as a function of $1/L$ (a) and $1/L^2$ (b). The values approach the exact value (filled symbols) as $L \to \infty$. Absolute values of the energy are given.

V. CONCLUSION

We have defined a true microcanonical ensemble appropriate for lattice gas models in which both the energy and the number of particles are held fixed which has not been done previously for lattice gas systems. We have also deduced formulas that allow us the calculation of the intensive quantities: temperature and chemical potential. The microcanonical algorithm is of easy implementation and the temperature and chemical potenial can be calculated easily. The application of this scheme to the Ising model gives results that compare very well with results coming from the canonical ensemble. In contrast with other Monte Carlo ensembles used in equilibrium statistical mechanics, in which the states are drawn with the desired Gibbs probability distribution only in the long time regime, in the present microcanonical Monte Carlo ensemble the states are being chosen with the correct distribution at any time of the simulation even in the initial stages. However, the states generated in the initial stages of the microcanonical simulation should be discarded because the fabricated initial configuration is not a typical one, a fact reflected in the relaxation shown in Fig. 1.

[1] *Monte Carlo Methods in Statistical Physics*, edited by K. Binder, 2nd ed. (Springer-Verlag, Berlin, 1986).

[2] R.J. Glauber, J. Math. Phys. **4**, 294 (1963).

[3] L.D. Fosdick, Phys. Rev. **116**, 565 (1959).

[4] J.R. Ehrman, L.D. Fosdick, and D.C. Handscomb, J. Math. Phys. **1**, 547 (1960).

[5] K. Kawasaki, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic Press, London, 1972), Vol. 2, p. 443.

[6] C.S. Shida and V.B. Henriques, Int. J. Mod. Phys. C **11**, 1033 (2000).

[7] M. Creutz, Phys. Rev. Lett. **50**, 1411 (1983).

[8] Y. Pomeau, J. Phys. A **17**, L415 (1984).

[9] G.Y. Vichniac, Physica D **10**, 96 (1984).

[10] W.M. Lang and D. Stauffer, J. Phys. A **20**, 5413 (1987).

[11] J.R. Ray and C. Frelechoz, Phys. Rev. E **53**, 3402 (1996).

[12] L.D. Landau and E.M. Lifshitz, *Statistical Mechanics* (Pergamon Press, Oxford, 1958).

[13] D. Ruelle, *Statistical Mechanics: Rigorous Results* (Benjamin, Reading, MA, 1969).

[14] R.B. Griffiths, in *Phase Transitions and Critical Phenomena* (Ref. [5]), Vol. 1, p. 7.

[15] R.A. Sauerwein and M.J. de Oliveira, Mod. Phys. Lett. B **11**, 571 (1997).

[16] B. Widom, J. Chem. Phys. **39**, 2808 (1963).

[17] M.J. de Oliveira, Phys. Lett. A **91**, 234 (1982).

[18] K. Binder and D.W. Heermann, *Monte Carlo Simulations in Statistical Physics* (Springer-Verlag, Berlin, 1988).

[19] L. Onsager, Phys. Rev. **65**, 117 (1944).

[20] K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1987).

[21] C.S. Shida and V.B. Henriques, J. Chem. Phys. **115**, 8655 (2001).