INSTITUTE OF PHYSICS PUBLISHING EUROPEAN JOURNAL OF PHYSICS

Eur. J. Phys. **26** (2005) S39–S46 doi:10.1088/0143-0807/26/5/S05

Tackling out-of-equilibrium systems by computer simulation: models of irreversible and reversible adsorption

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Received 23 May 2005
Published 4 July 2005
Online at stacks.iop.org/EJP/26/S39

Abstract

Although mainly devoted to the study of equilibrium systems, Monte Carlo simulations are also a helpful tool for investigating out-of-equilibrium dynamics. By studying simple adsorption models that may illustrate a numerical master's degree course, we show how computer simulations can handle some general features of non-equilibrium dynamics, in particular, the sensitivity to initial conditions and the emergence of long relaxation times.

1. Introduction

The interest of physicists in computers has a long history. Nicholas Metropolis, considered by some as the father of computational physics, built the first digital computer, MANIAC (Mathematical and Numerical Integrator and Computer) and elaborated with his coworkers [1] the celebrated Monte Carlo method in the early 1950s. Since then, the need for computations has contributed to the development of computers and supercomputers. It is now a common point of view that computer simulations, in a large sense, are the third approach of physics, complementing experiment and theory. Monte Carlo simulations have contributed to better understand the behaviour of N-body interacting systems [2].

Phase transitions can be investigated and universal quantities (such as critical exponents) and non-universal quantities (such as a critical temperature) can be obtained by an appropriate finite-size scaling analysis [3]. Even if the stochastic dynamics of a Monte Carlo algorithm does not reproduce a realistic microscopic dynamics, it captures the basic trends observed in physical systems at long enough times. For instance, close to the phase transition, the relaxation time for equilibrating a system increases drastically with a slight change in temperature, a tendency also observed in a Metropolis dynamics. The critical slowing down is closely associated with the existence of fluctuations whose size (correlation length) diverges at the approach of the critical temperature.

0143-0807/05/050039+08$30.00

For a computer study of a system at equilibrium, a Monte Carlo simulation is generally divided into two stages: starting from a random configuration, the Markov dynamics is performed until the system reaches equilibrium, and once this is obtained, averaging of the physical quantities is performed in the second stage. The first stage must be long enough to allow the system to reach equilibrium, independently of the initial state.

There exists many physical situations in which the experimental time exceeds the typical relaxation time of the system, which means that the system cannot in practice be studied in an equilibrium situation. For the last 20 years, there has been a development of out-of-equilibrium statistical mechanics [4] and, again, computer simulation is a very powerful means for obtaining quantitative information on the behaviour of the system. A generic feature of these out-of-equilibrium situations is that the evolution of the system depends on the initial state (and on the history) contrary to what occurs at equilibrium, which complicates, *a priori*, their study. Moreover, a large relaxation time is not always associated with a large length scale that can be clearly identified.

To illustrate these basic concepts, we consider in the following, simple adsorption models that involve ‘hard’ particles governed by a stochastic dynamics and can evolve either far from equilibrium or slowly to equilibrium. The equilibrium version of these systems—the hard-rod fluid—is a paradigm of equilibrium statistical mechanics [5]. The purpose of this paper is to show that computer simulation is an efficient tool for investigating the behaviour of non-equilibrium systems, whose properties are not always intuitive compared to equilibrium situations.

2. Random sequential adsorption model

2.1. Definition and physical motivation

The random sequential adsorption (RSA) model is a Markov stochastic process in which hard particles are added sequentially to a D-dimensional volume at random positions with the condition that no trial particles can overlap previously inserted ones.

In two dimensions, this model captures the physics of macromolecule adsorption on solid surfaces. The associated phenomenology is characterized by two main features: the adsorption is often irreversible on experimental time scales (once adsorbed, a macromolecule does not desorb and does not move on the surface) and the adsorption rate is limited by geometric blockage from previously adsorbed particles [6, 7]. The relevance of two-dimensional RSA for describing the adsorption of macromolecules at liquid–solid interfaces has been demonstrated in several experiments on proteins [8, 9].

2.2. The car parking problem

For the sake of simplicity, we consider in the following the one-dimensional version of the model. The model, known as the car parking problem, was first introduced by Rényi [10], a Hungarian mathematician. Consider an infinite line, assumed empty at $t = 0$. Hard rods of length σ (taken as the unit length in the following) are dropped randomly and sequentially at a rate k_a (chosen also as the inverse time unit) onto the line. They are adsorbed only if they do not overlap previously adsorbed rods; otherwise, they are rejected. If $\rho(t)$ denotes the number density of particles on the line at time t, the kinetics of this process is governed by the equation

$$\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = \Phi(t), \tag{1}$$

where $\Phi(t)$, the insertion probability at time t, is the fraction of the substrate (i.e. the line) that is available for the insertion of a new particle.

Because the adsorbed particles cannot move once inserted, the system keeps a 'memory' of the initial state.

The kinetics of the car parking problem can be derived analytically for an empty initial state, but not for an arbitrary initial configuration of particles. Details of the calculation are given in the appendix. For an arbitrary non-empty initial state, computer simulation provides numerical solutions; the algorithm being independent of the choice of the initial state, a simulation with an empty initial state can first validate a code, before performing a more complete study.

A first non-trivial property of the model is that the process reaches a 'jamming limit' (when $t \to \infty$) at which the density saturates at a non-trivial value $\rho_\infty = 0.7476\ldots$; this value is significantly lower than the closed-packed density ($\rho_\infty = 1$) that is expected for an equilibrium hard-rod system.

The long-time kinetics displays a power-law behaviour,

$$\rho_\infty - \rho(t) \simeq \frac{\mathrm{e}^{-2\gamma}}{t}, \tag{2}$$

where $\gamma \simeq 0.5772$ is the Euler constant; the slowing down of the kinetics comes from the small number of successful adsorption events. Indeed, close to saturation, holes that can fit a particle become small and scarce.

2.3. Simulation methods

The kinetics can be studied numerically by Monte Carlo. The basic iterative sequence is as follows: starting from a segment of size L (with periodic boundary conditions),

(i) the position of a trial particle of size 1 is chosen uniformly at random between 0 and L;
(ii) the time is incremented by $1/L$. If the trial particle does not overlap any previously adsorbed particle, the particle is definitively inserted; otherwise, it is rejected.

This algorithm, although correct, is very inefficient at long times. At each elementary step, the number of tests to perform goes as the number of previously adsorbed particles. Because of the finite range, hard-core interaction between particles, a grid construction avoids useless overlap tests. The size of the grid cell is chosen equal to the particle diameter, and each cell can accommodate only one particle. An array associated with the grid is created and initialized to zero at the beginning of the simulation (for an empty initial state). When a particle is inserted, the cell in which the centre of the particle is inserted becomes occupied and the corresponding array element is set to 1. For each new trial particle, one first determines the corresponding cell. If the cell is already occupied, the particle is rejected, otherwise, one considers the two nearest neighbour cells. If the neighbouring cells are also empty, the particle is immediately inserted. If the neighbouring cells are occupied (with a landing cell unoccupied), the overlap tests are then performed and the particle is inserted if there is no overlap. In summary, for a new trial particle, the maximum number of tests is now small.

Nevertheless, close to the jamming limit the process is dominated by very few successful events of adsorption, which means that computer time is wasted by rejecting a considerable amount of particles, because the available line for inserting new particles is very small.

A significantly accelerated procedure can be found by rewriting the dynamics of the process. Let us introduce the variable τ, such that $\mathrm{d}\tau = \Phi\,\mathrm{d}t$; because Φ is a positive function, τ can be interpreted as a new time (in fact, a variable associated with an event number). Therefore, the dynamics becomes a sequence of successful adsorption events,

$\rho = \tau$. It is necessary to calculate Φ along the process, and this can be easily done in one dimension. Indeed, $\Phi = A/L$, where A is the available line and is given by $A = \sum_{i=1}^{N} \mathrm{Max}(x_{i+1} - x_i - 2, 0)$, where x_i denote ordered abscissas of adsorbed particles, and with the convention that $x_{N+1} = x_1 + L$ for periodic boundary conditions.

Each adsorption event corresponds to an increase of the number density by $1/L$. One must determine the 'waiting' time, which is defined as the time interval between two successive adsorption events. For a given configuration (or a given value of A), one introduces the probability $P(\Delta t)$ that the waiting time is greater than Δt. Since successive events are independent (Markovian property),

$$P(\Delta t + \mathrm{d}\Delta t) = P(\Delta t)(1 - A\,\mathrm{d}\Delta t) + O(\mathrm{d}\Delta t^2). \tag{3}$$

By using $P(0) = 1$, one obtains $P(\Delta t) = \mathrm{e}^{-A\Delta t}$.

A random number uniformly distributed between 0 and 1, ξ is chosen for sampling a random waiting time consistent with this distribution (recalling that $A = \Phi L$)

$$\Delta t = -\frac{\ln(\xi)}{\Phi L}. \tag{4}$$

The iterative sequence is as follows.

(i) The position of a trial particle of size 1 is chosen uniformly between 0 and A, and the particle is inserted.

(ii) The time t is incremented by a quantity Δt given by equation (4), the density number ρ by $1/L$ and the available line A is updated by adding the new particle in the sum.

The simulation then becomes very fast and is stopped when A becomes equal to zero, corresponding to the fact that no more particles can be inserted, i.e, to the jamming limit of the process (a GNU code is available in [11]).

It is worth noting that the accelerating procedure above allows us to investigate the adsorption model in situations for which no analytical solutions are known. For instance, starting from a given configuration of particles, the simulation shows that the jamming limit is sensitive to the initial state of the line, a feature absent in the equilibrium system. In particular, we let the reader check that starting with an RSA jammed configuration, removing randomly a finite fraction of particles on the line, and restarting an RSA dynamics leads to a jamming density higher than $\rho = 0.7476\ldots$. Theoretical explanations go beyond the scope of this paper, but interested readers can find details in [12].

3. Adsorption–desorption model

3.1. Definition and physical motivation

In the adsorption–desorption model, particles are placed in a D-dimensional space at randomly selected positions with a constant rate k_+. If the trial particle does not overlap any previously adsorbed particle, the new particle is accepted. In addition, all adsorbed particles are subject to removal (desorption) at random with a constant rate k_-. The properties of the adsorption–desorption model depend only on the ratio $K = k_+/k_-$.

A series of experiments [14] on the packing of granular materials has revived interest in the adsorption–desorption model. Let us start with a brief description of the experiments: by pouring glass beads into a column, and by tapping periodically the system with a given intensity, Knight *et al* [14] showed that the density increases monotonically with the number of taps for various intensities of tapping.

Let us consider the horizontal configuration of a given slice or layer of the material, perpendicular to the tapping force, during the compaction. As a result of a tapping event, particles leave the layer essentially at random. Densification proceeds when particles fall back into the layer under the influence of gravity and the system reaches a new state of mechanical stability in which particles are at rest. This is captured by the desorption/adsorption model, the ratio of desorption to adsorption rates being an increasing function of the tapping strength.

3.2. Parking lot model

We focus, in the following, on the one-dimensional version of the model. If time is expressed in units of k_+^{-1}, the densification kinetics is given by

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \Phi(t) - \frac{\rho}{K}, \tag{5}$$

where $\Phi(t)$, the insertion probability, is again the fraction of the line that is available for insertion of a new particle. The presence of a relaxation mechanism, i.e. competing desorption and adsorption with an equilibrium constant K, implies that the system eventually reaches a steady state that corresponds to an equilibrium configuration of hard particles with $\rho_{\mathrm{eq}} = K\Phi_{\mathrm{eq}}(\rho_{\mathrm{eq}})$, where ρ_{eq} denotes the equilibrium density. The equilibrium properties of the hard-rod system can be obtained exactly [5, 13]. Hence,

$$\Phi_{\mathrm{eq}}(\rho) = (1-\rho)\exp(-\rho/(1-\rho)). \tag{6}$$

Inserting equation (6) into equation (5) leads to the following expression for the equilibrium density:

$$\rho_{\mathrm{eq}} = \frac{L_w(K)}{1 + L_w(K)}, \tag{7}$$

where $L_w(x)$ (the Lambert-W function) is the solution of $x = y\,\mathrm{e}^y$. In the limit of small K, the isotherm takes the Langmuir form, $\rho_{\mathrm{eq}} \sim K/(1+K)$, while for large K, $\rho_{\mathrm{eq}} \sim 1 - 1/\ln(K)$. At small values of K, equilibrium is rapidly obtained, but at large values the densification process is dramatically slowed.

3.3. Algorithm

Introducing τ, such that $\mathrm{d}\tau = (\Phi + \rho/K)\,\mathrm{d}t$, the kinetics is given by

$$\frac{\mathrm{d}\rho}{\mathrm{d}\tau} = P_A - P_D, \tag{8}$$

where $P_A(t) = \Phi/(\Phi + \rho/K)$ denotes the adsorption probability and $P_D(t) = \rho/(K\Phi + \rho)$ the desorption probability. Obviously, $P_A + P_D = 1$.

The probability that the time interval between any two successive events (adsorption or desorption, assumed independent) is larger than Δt then reads

$$P(\Delta t) = \mathrm{e}^{-(\Phi+\rho/K)L\Delta t}. \tag{9}$$

The iterative sequence is then as follows.

(i) One generates a random number ξ uniformly distributed between 0 and 1, and the time t is incremented by $-\frac{\ln(\xi)}{(\Phi+\rho/K)L}$.

(ii) A second random number, $0 < \xi' < 1$, is chosen. If $\xi' < P_A$, an adsorption event is selected, the position of a trial particle of size 1 is chosen uniformly between 0 and $A = \Phi L$, the available line and the particle is inserted. If $\xi' > P_A$, an adsorbed particle is selected at random and removed from the substrate, i.e., a desorption event is performed.

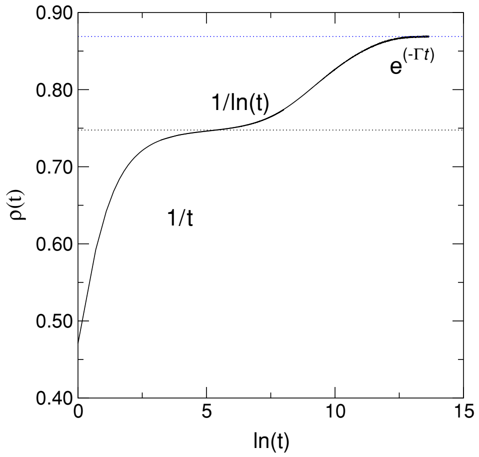

Figure 1. Linear-logarithmic plot of the adsorbed density as a function of time for the large value $K = 5000$. The process is characterized by three slow kinetic regimes: (i) RSA-like regime whose final stage is described by a $1/t$ behaviour, (ii) $1/\ln(t)$ regime and (iii) exponential approach towards equilibrium.

Only such an accelerating procedure provides an efficient way for investigating the very long time kinetics, and reach equilibrium. Note that the introduction of a desorption mechanism restores the detailed balance of the Monte Carlo algorithm, which can then be interpreted as a Monte Carlo simulation of hard particles in a grand canonical ensemble for which particles' displacements on the line are prohibited. The particle reservoir has a chemical potential $\mu = -k_B T \ln(K)$, where k_B is the Boltzmann constant and T is the temperature.

3.4. Simulation results and discussion

For small desorption rates ($1/K \ll 1$), the density evolves very slowly (see figure 1) and three successive regimes can be identified. After a rapid (partial) filling of the line, the first slow stage of the process remains dominated by adsorption events and the kinetics follow an RSA-like behaviour, i.e. an algebraic power-law $1/t$. Close to the jamming limit $\rho \simeq 0.74$, the frequency of desorption events increases, yielding particle rearrangements on the line and, sometimes, insertion of additional particles. The kinetics of this regime is well described by a $1/\ln(t)$ behaviour. Eventually, adsorption and desorption events occur with a comparable frequency, and the density can no longer increase significantly. This last regime is well described by an exponential approach (see figure 1) [15].

The characteristic time of the exponential approach, $1/\Gamma$ (see figure 1) can be identified as the typical relaxation time for reaching equilibrium. One can show that the order of magnitude of this time is $K^2/\ln^3 K$ [15], a very large time when the desorption rate is small ($1/K \ll 1$). The relaxation time is then much larger than any typical microscopic time (adsorption and desorption times); however, contrary to what occurs near critical points, there is no obvious signature of a large correlation length associated with this relaxation time. This feature seems to be quite general in many 'glassy' systems.

4. Conclusion

In many physical situations, the relaxation time of the system is much larger than the experimental time. The analysis of simple adsorption models has shown that computer simulation is the method of choice for a detailed investigation. By using the kinetic equations describing the evolution of the models, we have derived event-driven methods, which give better algorithms for investigating the long-time behaviour. For irreversible adsorption models, we have shown that the dynamics keeps a 'memory' of the initial conditions, contrary to what occurs in equilibrium situations. For adsorption–desorption models, which eventually reach equilibrium, we have shown that the non-equilibrium kinetics exhibits a succession of regimes before reaching equilibrium. This illustrates the complexity of non-equilibrium physics, even for systems defined by simple rules. More generally, the results obtained by computer simulation can help develop theoretical methods for a better understanding of out-of-equilibrium systems.

Appendix A. RSA kinetics

The kinetics of the car parking problem can be obtained by introducing the gap distribution function $G(h,t)$. This quantity is defined so that $G(h,t)\,\mathrm{d}h$ denotes the density of voids of length between h and $h+\mathrm{d}h$ at time t. For a given void of length h, the available length for inserting a new particle is $h-1$. The available line function $\Phi(t)$ is obtained by summing over the number density of available intervals, i.e. $G(h,t)$:

$$\Phi(t) = \int_1^\infty \mathrm{d}h(h-1)G(h,t). \tag{A.1}$$

Since each interval corresponds to one particle, the number density $\rho(t)$ is equal to

$$\rho(t) = \int_0^\infty \mathrm{d}h\, G(h,t), \tag{A.2}$$

whereas the remaining empty fraction of the line is related to $G(h,t)$ by

$$1-\rho(t)\sigma = \int_0^\infty \mathrm{d}h\, hG(h,t). \tag{A.3}$$

Equations ((A.2)–(A.3)) represent the sum rules for the gap distribution function. The time evolution of $G(h,t)$ obeys

$$\frac{\mathrm{d}G(h,t)}{\mathrm{d}t} = -H(h-1)(h-1)G(h,t) + 2\int_{h+1}^\infty \mathrm{d}h'\, G(h',t), \tag{A.4}$$

where $H(x)$ is the unit step function. The first term on the right-hand side of equation (A.4) (loss term) comes from the insertion of a particle within a gap of length h (for $h \geqslant 1$). The second term (gain term) results from the insertion of particle in a gap of length $h' > h+1$. The factor 2 accounts for the two possibilities of creating a length h from a larger interval h'.

Equation (A.4) forms a closed set of equations (resulting from the property that the adsorption of a particle in one gap has no effect on other gaps). For an initial empty state, the above equations can be solved by introducing the ansatz

$$G(h,t) = F(t)\exp(-(h-1)t), \tag{A.5}$$

which leads to

$$F(t) = t^2 \exp\left(-2\int_0^t \mathrm{d}u \frac{1-\mathrm{e}^{-u}}{u}\right). \tag{A.6}$$

Inserting equations (A.5) and (A.6), one obtains $G(h,t)$ for $h > 1$ and integrating equation (A.4) with the solution of $G(h,t)$ for $h > 1$ finally gives $G(h,t)$ for $0 < h < 1$,

$$G(h,t) = 2\int_0^t \mathrm{d}u \exp(-uh)\frac{F(u)}{u}. \tag{A.7}$$

The three equations, (1), (A.2) or (A.3), combined with equation (A.1), all lead to the same result for the number density, $\rho(t)$, first derived by Rényi [10]:

$$\rho(t) = \int_0^t \mathrm{d}u \exp\left(-2\int_0^u \mathrm{d}v \frac{1-\mathrm{e}^{-v}}{v}\right). \tag{A.8}$$

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