References

1) I. Prigogine, Cl. George and F. Henin, Physica **45** (1969) 418.
2) Cl. George, I. Prigogine and L. Rosenfeld, Dan. mat. fys. Med. **38** (1972) 12.
3) I. Prigogine, Non-Equilibrium Statistical Mechanics (Interscience, New York, 1962).
4) Cl. George, Physica **65** (1973) 277.
5) Cl. George, Bull. Acad. Roy. Belgique, Cl. Sci. **56** (1970) 505.
6) Cl. George, F. Mayné and I. Prigogine, Adv. Chem. Phys. **61** (1985) 223.
7) B. Misra, I. Prigogine and M. Courbage, Physica **98A** (1979) 1.
8) P.V. Coveney, Physica **143A** (1987) 123, to be referred to as I.
9) P.V. Coveney and Cl. George, Physica **141A** (1987) 403, to be referred to as II.
10) F. Henin, Physica **54** (1971) 385; Bull. Acad. Roy. Belgique, Cl. Sci. **56** (1970) 1113.
11) R. Balescu and J.H. Misguich, Report EUR-CEA-FC-691 (1973) (Fontenay-aux-Roses, France); J. Plasma Phys. **11** (1974) 357, 377, to be referred to as III.
12) P.V. Coveney, Bull, Acad. Roy. Belgique, Cl. Sci. (1987), in press.
13) B. Misra, I. Prigogine and M. Courbage, Proc. Natl. Acad. Sci. USA **76** (1979) 4768.
14) M. de Haan, Physica **132A** (1985) 375, 397.
15) J. Jeener and F. Henin, Phys. Rev. A (1986), preprint.
16) J. Wilcox, J. Math. Phys. **8** (1967) 962.

Physica 143A (1987) 535–546
North-Holland, Amsterdam

A MONTE CARLO SIMULATION OF COAGULATION

Alejandro L. GARCIA
Service de Chimie Physique II, Université de Bruxelles, Bvd. du Triomphe, Campus Pleine, B1050 Brussels, Belgium

Christian VAN DEN BROECK, Marc AERTSENS and Roger SERNEELS
Limburgs Universitair Centrum, Universitaire Campus, B3610 Diepenbeek, Belgium

Received 20 August 1986

A Monte Carlo simulation technique is described for the study of the coagulation of suspended particles. The method is computationally efficient since the particle trajectories are not used to determine coagulations. Instead, pairs of particles are assigned probabilities to coagulate and the evolution is computed as a stochastic Markov game. We also describe a simple analytic method to obtain the stationary distribution of sizes for the various mechanisms of relative particle motion. It is demonstrated that the simulation yields the correct stationary size distribution independent of initial condition.

1. Introduction

In recent years, Brownian dynamics has been employed in an increasing number of fields. The basic scenario of noninteracting Brownian particles in an infinite homogeneous medium can be modified in various ways. For example, the particles may move in an inhomogeneous medium (e.g. Taylor diffusion) or the particles may interact (e.g. charged suspensions). Coagulation systems are complicated further in that there is a distribution of particle sizes which is not fixed but is rather determined by the dynamics.

Computer simulations are often useful in studying complex physical systems. In studying Brownian systems, one typically integrates, with small time increments, the Langevin equations for a large set of particles. At each time increment any interparticle interactions (such as coagulations) can be evaluated. Such a stochastic simulation method for coagulation problems has been discussed by Pearson et al.[1]). They consider spherical particles initially distributed at random in a large volume. At each time step a Brownian displacement is chosen for each particle and a pair of particles coagulates when

they are within a given interaction distance. They demonstrate the method by measuring the stationary distribution of conglomerate sizes which results when there is a steady flux of small particles appearing at random within the volume (nucleation) and a steady flux of large particles disappearing due to sedimentation.

Their method is computationally expensive since at each time step the relative separation between all pairs of particles must be computed. The efficiency is somewhat improved by the use of neighbor lists (a technique well known in Molecular Dynamics simulations) at the cost of additional bookkeeping. However, much of the information contained in this type of simulation is irrelevant for the physical process under consideration. It is then natural to seek another technique which yields the same results at reduced expense. This leads us to introduce a Monte Carlo technique which does not use the exact particle trajectories to evaluate coagulations but rather chooses coagulation partners via a stochastic game.

The specification of the physical model and the formulation of the Monte Carlo simulation follow in the next two sections. In section 4 we consider the problem of computing the steady state size distribution in a nucleation–sedimentation system and demonstrate that the simulation yields excellent agreement with the theory. Finally, in the conclusion we discuss analogous Monte Carlo methods which have been successful in other fields.

2. Physical properties

In a fluid of volume V, consider a suspension of N_v spherical particles with an initial distribution $n_0(a, \boldsymbol{r})$, the number of particles of radius a per unit volume at the point $\boldsymbol{r}$. As the system evolves, the particles undergo Brownian motion with an average square displacement $\langle \Delta r^2 \rangle = 2D(a)t$, where D is the diffusion coefficient[2]). When two particles with radii a_1 and a_2, respectively, approach within some critical distance $R(a_1, a_2)$, they coagulate into a single larger particle of radius $a = (a_1^3 + a_2^3)^{1/3}$. Typically, the critical distance is chosen to be $R(a_1, a_2) = a_1 + a_2$ so that particles coagulate when they physically touch. We assume that only binary coagulations occur in the suspension; this is reasonable provided the suspension is dilute. As such, the volume fraction $\varphi \equiv (4\pi/3)\langle a^3 \rangle N/V$ should be much less than unity.

Different types of boundary conditions may be considered at the walls of the system: periodic, reflecting, absorbing, etc. Periodic boundary conditions are the most appropriate for approximating systems of infinite extent. The system can be maintained at a nonequilibrium steady state by introducing particle fluxes. The walls can serve as sources or sinks of particles. Particles may also

be spontaneously created in (nucleation) or removed from (sedimentation) the bulk of the system.

3. Markov simulation

Any simulation of a physical process must specify the state of the system by some complete set of variables. We take the set $\{\boldsymbol{r}_i, a_i\}$, where $\boldsymbol{r}_i$ is the position of the ith particle and a_i is its radius. In addition, an evolution law by which the initial state will be propagated in time must be specified. A central assumption of our simulation method is that for a sufficiently small time step, Δt, the evolution may be decomposed into two distinct processes: free diffusion and coagulation. The free diffusion is computed exactly by choosing a Brownian displacement for each particle. The coagulations are represented as a stochastic game, each pair of particles being assigned a probability of coagulating. The simulation proceeds in this manner: all particles are displaced, a few are chosen to coagulate, and the process is repeated.

In a time step Δt, all pairs of particles are not equally likely to coagulate since the coagulation rate depends on their relative distances; so

$$P_{12} = P_{12}(a_1, a_2, |\boldsymbol{r}_1 - \boldsymbol{r}_2|)\,. \tag{1}$$

A coagulation simulation based on this result would require computing the relative distance between all pairs of particles and is thus expensive. On the other hand, dropping the spatial dependence of P_{12} entirely would be unrealistic. Instead, we divide the space into a set of N_c cells of volume $V_c = L_c^3 = V/N_c$. We assume that in a time step Δt, particles in a given cell will coagulate predominantly with particles in the same cell. Thus we write

$$P_{12} = P_{12}(a_1, a_2) \times \begin{cases} 1, & \text{if 1 and 2 are in the same cell,} \\ 0, & \text{otherwise.} \end{cases} \tag{2}$$

Within a time step, coagulations in a given cell are treated as a stochastic game independently of the evolution in the other cells. Of course, particles also move between the cells by free diffusion. This approximation scheme places some restrictions on Δt and L_c. The cell size should be a fraction of the coagulation mean free path and several times the mean displacement in a time step.

Let us consider in detail the Monte Carlo selection of a coagulation pair within a given cell. During a time step, a number of coagulations will take place. One needs to determine when the next coagulation will occur and

determine the pair of particles which coagulate. We use the standard simulation procedure for a Markov process. First, the waiting time τ between two events (i.e. coagulations) is an exponentially distributed random variable. If W_Σ is the total coagulation rate in a cell, then τ is distributed as

$$P(\tau) = W_\Sigma \exp(-W_\Sigma \tau) . \tag{3}$$

Note that $\langle \tau \rangle = 1/W_\Sigma$. Next, the two particles which are to coagulate must be chosen. Clearly the probability, P_{ij}, that a coagulation in cell c occurs between particles i and j is proportional to the rate $W(a_i, a_j)$ at which these particles coagulate; thus

$$P_{ij} = W(a_i, a_j)/W_\Sigma , \quad i, j \in c , \tag{4}$$

with the normalization property

$$W_\Sigma = \sum_{i=1}^{N} \sum_{j=i+1}^{N} W(a_i, a_j) , \quad i, j \in c , \tag{5}$$

where N is the total number of particles in cell c. The two probability distributions, $P(\tau)$ and P_{ij}, entirely specify the stochastic Markov process. The rate at which particles coagulate is given by the Smoluchowski formula

$$W(a_1, a_2) = 2\pi(D(a_1) + D(a_2))R(a_1, a_2)/V_c , \tag{6}$$

where $R(a_1, a_2)$ is the critical distance at which particles coagulate.

If the number of particles in a cell is not too large, we can directly use (3) and (4) to compute the coagulation evolution in a cell. First, W_Σ must be computed from the current state of the cell. The time till the next coagulation is chosen as

$$\tau = -\ln(R_u)/W_\Sigma , \tag{7}$$

where R_u is a random number uniformly distributed in the interval (0, 1]. We accumulate an elapsed cell time

$$t_c' = t_c + \tau . \tag{8}$$

Next, we need to use the probability distribution P_{ij} given by eq. (4) to select the next pair to coagulate. The most direct way is to construct the cumulative probability distribution F_{ij} from P_{ij}; the coagulation pair (i, j) is then determined from the condition

$$F_{i,j-1} < R_u' < F_{i,j} . \tag{9}$$

That is, one makes an ordered list of all pairs and computes an accumulating sum of P_{ij} (which is by definition F_{ij}) until the sum surpasses the random number R_u'; the last pair taken is then the coagulating pair. This procedure is known as the inverse method[3]) and it is exact for any probability distribution with a discrete set of states.

After the coagulation pair is chosen, one of the particles is removed and the size of the other is augmented. Note that W_Σ must be reset after each coagulation. One continues in this manner, selecting τ, i and j until the accumulated cell time exceeds the time step. The excess $t_c - \Delta t$ is stored as the initial value of t_c for the next time step. After computing all the coagulations in a cell, one proceeds to the next cell and so on through the system until all coagulations for the current time step have been evaluated.

Since the computation of W_Σ involves a sum over the $N(N-1)/2$ pairs, use of (3) and (4) directly is unwieldy if the number of particles in a cell is large. In the selection of the coagulation pair i, j we can use an exact procedure for sampling from a discrete distribution, namely, acceptance–rejection[3]), which does not require the computation of W_Σ. By this method, first a pair i, j is selected entirely at random. The pair is *accepted* as coagulating if

$$R_u < W(a_i, a_j)/\max\{W(a_k, a_l)\} , \tag{10}$$

where the maximum is computed over all particle pairs. If the pair is rejected, another pair is selected at random, a new value for R_u is generated and the pair is accepted or rejected in the same manner. Pairs are randomly selected and tested until inequality (10) is satisfied. In the appendix we demonstrate that this method exactly samples from P_{ij}. Note that the method is still exact, only less efficient, if the maximum of $W(a_1, a_2)$ is overestimated. It is typically more efficient to make, once and for all, an overestimating guess than to compute $\max\{W\}$ exactly all the time.

In order to choose the waiting time between events, τ, without computing W_Σ we use an approximation scheme developed by Bird[4]). An approximate waiting time, τ_a, is generated having the property

$$\langle \tau \rangle = \langle \tau_a \rangle = 1/W_\Sigma . \tag{11}$$

The construction is as follows: given that the pair (i, j) are accepted as coagulation partners, then a waiting time $\tau_a(i, j)$ is chosen as

$$\tau_a(i, j) = \frac{2}{N(N-1)W(a_i, a_j)} . \tag{12}$$

Note that

$$\langle \tau_a \rangle = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \tau_a(i, j) P_{ij}$$

$$= \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{2}{N(N-1)W(a_1, a_j)} \frac{W(a_i, a_j)}{W_\Sigma} = \frac{1}{W_\Sigma} . \tag{13}$$

In this approximate scheme, the time between coagulations is correlated with

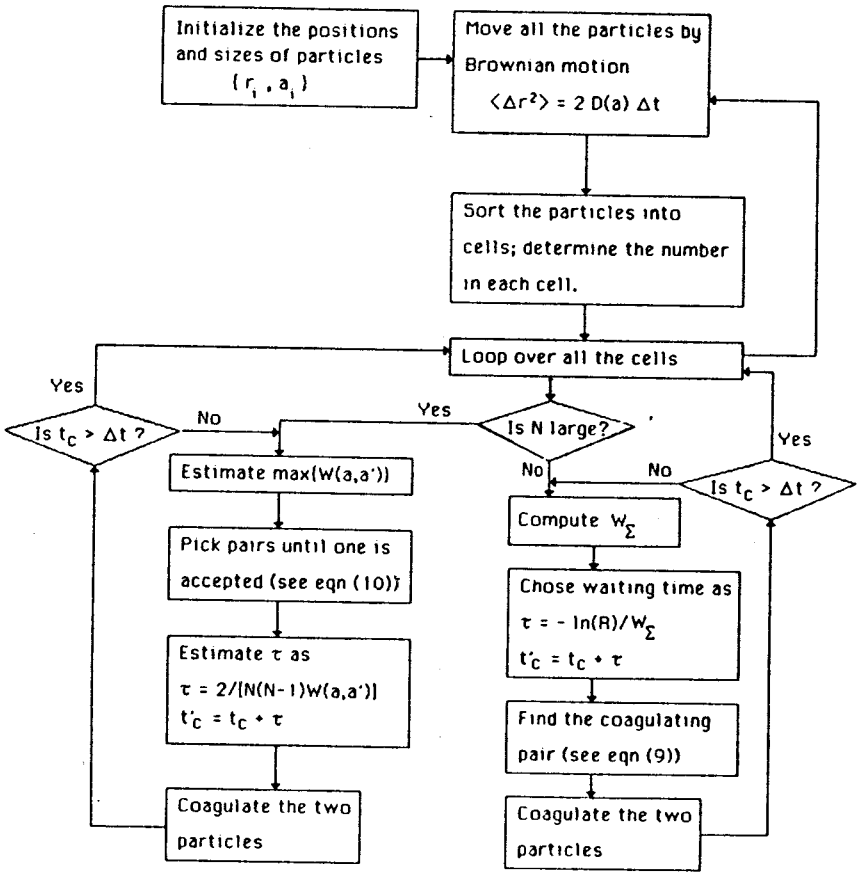

Fig. 1. Flow chart of the simulation algorithm.

the type of coagulation which occurs. This is not correct but, on average, the effect is generally negligible.

In fig. 1 we summarize the algorithm developed above. For more details on the technical aspects (e.g. how to efficiently sort particles into cells) see Bird[4]).

4. Stationary size distribution in a nucleation–sedimentation system

We consider the following physical model for a nucleation–sedimentation system. Small particles are introduced into the system at random locations at a steady rate and others are removed from the system when they reach a critical size. After some time it may be expected that some stationary state will appear with respect to the number of particles within a given volume. We obtain an expression for the stationary size distribution and show that the Monte Carlo simulation correctly reaches this distribution independent of initial distribution.

It is more convenient to consider a size distribution in particle volume rather than radius. We define $n(v)\,dv$ as the number of particles with a volume between v and $v + dv$. If $j(v)$ is the volume flux through a volume v, then the continuity equation for volume is

$$\frac{\partial}{\partial v} j(v, t) + v \frac{\partial}{\partial t} n(v, t) = 0 . \tag{14}$$

There are two contributions to the volume flux. First, this volume flux occurs because particles of volume v_1 and v_2 (v_1 and $v_2 < v$) coagulate to form a particle of volume greater than v. The resulting contribution to the volume flux is

$$j_1(v) = \tfrac{1}{2} \int_{v_0}^{v} dv_1 \int_{v_0}^{v} dv_2\, n(v_1) n(v_2)(v_1 + v_2)\beta(v_1, v_2) H(v_1 + v_2 - v) , \tag{15}$$

where $H(v_1 + v_2 - v)$ is the Heaviside function which guarantees that $v_1 + v_2 > v$ and $\beta(v_1, v_2)$ describe the probability that a particle of volume v_1 will coagulate with a particle of volume v_2 per unit volume. A second contribution to $j(v)$ is due to coagulation of a particle of volume $v_1 < v$ with a particle of volume $v_2 > v$. The volume transport through v due to this mechanism is then

$$j_2(v) = \tfrac{1}{2} \int_{v_0}^{v} dv_1 \int_{v}^{v_m} dv_2\, n(v_1) n(v_2) v_1 \beta(v_1, v_2) . \tag{16}$$

The total volume current is the sum $j(v) = j_1(v) + j_2(v)$. In the integration

bounds, v_0 stands for the smallest volume (volume at which particles appear by nucleation) and v_m for the largest volume before sedimentation. We assume that these integrals converge and that v_0 is sufficiently small to be taken as zero and v_m sufficiently large to be taken as infinite.

In a stationary state, the volume flux is constant and independent of v. Different coagulation mechanisms yield different expressions for $\beta(v, v')$ but a common feature is that the function is a homogeneous function,

$$\beta(av, av') = a^p \beta(v, v') . \tag{17}$$

When the particles move with Brownian motion, then $p = 0$, with laminar shear $p = 1$, etc.[1]). Now let us assume that a stationary distribution exists in the form of a power law of the form $n(v) = Av^k$ with A and k constants. If we substitute this power law into (15) and (16) and define $x \equiv v_1/v$ and $y \equiv v_2/v$, we see that the volume flux $j(v)$ is independent of v provided

$$2k + p + 3 = 0 , \tag{18}$$

from which it follows that for the case of Brownian motion $k = -3/2$ as was

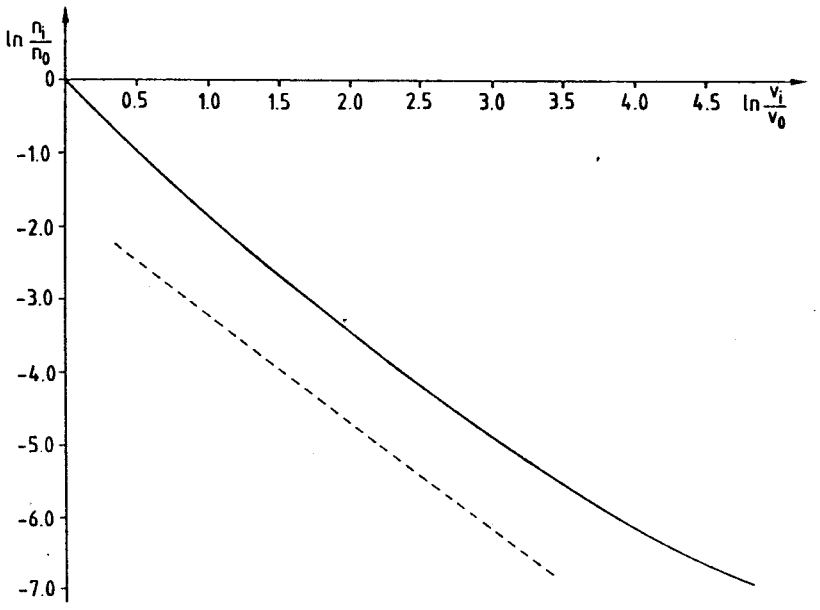

Fig. 2. The stationary size distribution $n(v)$ of coagulating particles as obtained from the simulation (full line) fits well the $v^{-3/2}$ power law predicted by the theory (dashed line).

found by Friedlander[5]) and Hunt[6]). The coefficients for the other mechanisms are also easily derived. If we substitute the integral expressions for the volume flux in the continuity equation (14) then we retrieve the well-known coagulation equation. The above relation (18) may also be obtained from the coagulation equation although the derivation is a bit more tedious.

A Monte Carlo simulation of 600 particles was run for 10 000 time steps to obtain the stationary size distribution. Initially, all the particles were of unit size. Particles of unit size were introduced at random within the system at a rate of 40 per time step. Particles with radii greater than 5 times the unit radius (125 times the unit mass) were removed. All spatial boundaries were periodic. The accumulation of statistics began after 50 particles had sedimented. The results in fig. 2 demonstrate the good agreement with the 3/2 power law. Similar results were obtained with various other initial conditions. The program was sufficiently fast so that meaningful results could be obtained running interactively.

5. Conclusions and discussion

In this paper, we demonstrated how the complex mechanism of coagulation may be modeled by a simple stochastic game. Note that the immediate underlying dynamics which the stochastic model replaces is itself a stochastic process. The philosophy of this approach is not new but does not appear to have been used to study coagulation problems. Similar Master Equation approaches have been used in two other fields: theory of chemical reactions and kinetic theory. The analogy with the coagulation problem becomes clear by comparing the following processes:

(1) a coagulation between two particles of radii a_1 and a_2,

$$a_1 + a_2 \rightarrow a' ;$$

(2) a chemical reaction between species A and B forming either C,

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} ,$$

or forming D and E,

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} + \mathrm{E} ;$$

and (3) a binary collision between particles with velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$,

$$\boldsymbol{v}_1 + \boldsymbol{v}_2 \rightarrow \boldsymbol{v}_1' + \boldsymbol{v}_2' .$$

From this analogy, it is clear that the particle size distribution for the coagulation problem is the analog of the Maxwell–Boltzmann velocity distribution.

In order to discuss the advantages and limitations of the method, we feel that it is useful to review the developments in stochastic modeling in the two other fields. The discovery of nonequilibrium chemical phase transitions in nonlinear reaction schemes attracted considerable attention to the role of fluctuations in chemical systems[7]). The theoretical formulation of a master equation in particle number led to the development of Monte Carlo simulations[8,9]). The transition rates between the states is given naturally by the chemical reaction rates. Inhomogeneous systems can also be modeled by allowing the particles to perform a random walk between cells[10–12]). Particles can interact (undergo chemical reaction) only if they are in the same cell. The validity of the stochastic model was confirmed by comparison with reactive molecular dynamics simulation[13,14]).

In kinetic theory, a formal master equation can be formulated by projection operator techniques[15]). Kac proposed a model master equation with a two-body Markovian collision operator[16]). There are in fact strong analogies between Kac's master equation and the chemical reaction master equation[17]). The collision probability for a pair of hard spheres can be shown to be simply proportional to their relative speed. A number of authors[18–20]) proposed simulation methods based (often unknowingly) on Kac's model. The most successful was developed by Bird[4]) to study intermediate Knudsen number ($0.1 < \mathrm{Kn} < 1$) flows encountered in high atmospheric aerodynamics. The validity of Bird's approach is well conformed by both experimental data and molecular dynamics results. It was in fact this method that stimulated the development of our coagulation simulation.

Any simulation method has strengths and limitations in comparison with other approaches. The stochastic model proposed is between a strictly macroscopic formulation in partial differential equations (Smoluchowski equation) and a microscopic formulation such as discussed in the introduction. As already mentioned, the microscopic approach is computationally slower. A comparison of the Bird algorithm for a dilute gas with a good hard sphere molecular dynamics program (with bookkeeping) indicates a difference of speed of nearly two orders of magnitude. The time step in a microscopic simulation is of the order of $a^2/D(a)$. In the Monte Carlo simulation the time step may be a fraction of the mean time between coagulations. If the suspension is dilute, the latter will be several orders of magnitude greater than the former. The microscopic simulations have the advantage of being valid down to length scales of the order of a particle radius while our stochastic model is restricted to scales down to the order of a mean free path. If, for example, we were interested in the structure factor for large wavenumbers, a strictly microscopic method would be required.

The Monte Carlo method can be superior to the numerical solution of the macroscopic Partial Differential Equations (PDEs) or integral equations for a number of reasons. First, these equations can be difficult to formulate or solve numerically for some scenarios (peculiar boundary conditions, spatial inhomogeneities, source terms, etc.). Second, if one is interested in studying fluctuations a stochastic approach is necessary. Finally, a continuum formulation may be inappropriate in some cases, for example if the characteristic length in the problem (system size, boundary layer thickness) is of the order of the mean free path between coagulations.

Finally, we should point out that there are some similarities between our simulation method and the Particle Coalescence Model (PCM) introduced by Kang et al.[21]). The stochastic element in the PCM, however, represents the complicated geometrical effects of aggregating macromolecules when such clusters approach their interaction distance. Other than this, the PCM is essentially a microscopic-type simulation in which the particles move on a discrete lattice.

Acknowledgments

We wish to thank Professors M. Bouten, G. Nicolis, M. Malek Mansour and M. Mareschal and Drs. F. Baras and C. Penland for stimulating discussions. One of us (A.L.G.) would like to thank Professor I. Prigogine for his support and encouragement towards the development of new simulation methods.

Appendix

Proof of the acceptance–rejection method

In this appendix we wish to demonstrate that the acceptance–rejection method described in the text (see eq. (10)) exactly chooses coagulation pairs by the distribution P_{ij} given in eq. (4). The probability that, in any given try, the pair i and j are selected as candidates is $P_{ij}^{s} = 1/N_p$ where N_p is the total number of pairs in the cell, $N_p = N(N-1)/2$. The probability that, given their selection, they are accepted is $P_{ij}^{A} = W(a_i, a_j)/\max\{W(a_i, a_j)\}$ while the probability that no pair at all is accepted reads:

$$P_R = \frac{N_p \max\{W(a_i, a_j)\} - W_s}{N_p \max\{W(a_i, a_j)\}} \,. \tag{A.1}$$

The probability that the pair i and j is chosen is equal to the probability that this pair is selected and accepted right away plus the probability that a number of rejections occur before and finally the particular pair i and j is selected and accepted:

$$\begin{aligned} P_{ij} &= P_{ij}^{s} P_{ij}^{A} + P_{R} P_{ij}^{s} P_{ij}^{A} + P_{R}^{2} P_{ij}^{s} P_{ij}^{A} + \cdots \\ &= P_{ij}^{s} P_{ij}^{A} / (1 - P_{R}) \\ &= W(a_i, a_j) / W_{\Sigma} . \end{aligned} \tag{A.2}$$

We see immediately that this result is in agreement with eq. (4).

References

1) H.J. Pearson, I.A. Valioulis and E.J. List, J. Fluid Mech. **143** (1984) 367.
I.A. Valioulis, E.J. List and H.J. Pearson, J. Fluid Mech. **143** (1984) 387.
2) S. Chandrasekhar, in: Selected Papers on Noise and Stochastic Processes, N. Wax, ed. (Dover, New York, 1954).
3) M. Abramowitz and I. Stegun, Handbook of Mathematical Functions (Dover, New York, 1972).
4) G. Bird, Molecular Gas Dynamics (Clarendon Press, Oxford, 1976).
5) S.K. Friedlander, J. Meteor. **17** (1960) 373, 479.
6) J.R. Hunt, J. Fluid Mech. **122** (1982) 169.
7) G. Nicolis and I. Prigogine, Self-Organisation in Nonequilibrium Systems (Wiley, New York, 1977).
8) D. Gillespie, J. Phys. Chem. **81** (1977) 2340; Physica **95A** (1979) 69; J. Stat. Phys. **16** (1977) 311.
9) P. Hanusse and A. Blanché, J. Chem. Phys. **74** (1981) 6148.
10) H. Haken, Z. Physik **B20** (1975) 413.
11) H. Lemarchand and G. Nicolis, Physica **82A** (1976) 251.
12) C.W. Gardiner, K.J. McNeil, D.F. Walls and I.S. Matheson, J. Stat. Phys. **14** (1976) 307.
13) J. Boissonade, Phys. Lett. A **74** (1979) 285.
14) J. Boissonade and W. Horsthemke, Phys. Lett. A **68** (1978) 283.
15) I. Prigogine, Non-Equilibrium Statistical Mechanics (Wiley, New York, 1963).
16) M. Kac, in: Probability Theory and Related Topics in Physical Science (Wiley–Interscience, New York, 1959); Acta Phys. Austr. Suppl. **X** (1973) 379.
17) L. Brenig and C. Van den Broeck, Phys. Rev. A **21** (1980) 1039.
18) K. Koura, Phys. Fluids **13** (1970) 1457; J. Chem. Phys. **59** (1973) 691; **63** (1975) 3302.
19) W. Matthes, J. Comp. Phys. **6** (1970) 157.
20) K. Nanbu, J. Phys. Soc. Jap. **49** (1980) 2042, 2050, 2055.
21) K. Kang, S. Redner, P. Meakin and F. Leyvraz, Phys. Rev. A **33** (1986) 1171.

Physica 143A (1987) 547–567
North-Holland, Amsterdam

THE CORRELATION FUNCTION FOR A QUANTUM OSCILLATOR IN A LOW-TEMPERATURE HEAT BATH

E. BRAUN*
Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Apdo. Postal 55-534, México D.F., 09340 México

P.A. MELLO**
Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000 México D.F., México

Received 17 March 1986
Revised manuscript received 23 July 1986

The momentum autocorrelation function $c(t)$ for a quantum oscillator coupled with harmonic forces to a heat bath of oscillators is calculated at low temperatures. It is found that $c(t)$ contains two distinct terms: one, the zero-point contribution $c_0(t)$, is temperature independent, and the other, $c_1(t)$, does depend on temperature. We concentrate our attention on the low-temperature case. An expression for $c_1(t)$ is obtained, which is valid for arbitrary strengths of the coupling and for arbitrary times. It is shown that $c_1(t)$ is governed by the low-frequency behaviour of $F(\lambda) = A^2(\lambda)\rho(\lambda)$, where $\rho(\lambda)$ is the density of normal modes and $A(\lambda)$ is the central-oscillator component of the λth normal mode; other details of the problem are irrelevant. It is found that $c_1(t)$ decays in time as an inverse-power law, with a relaxation time $t_q \sim \hbar/kT$.

1. Introduction

The quantum description of the relaxation to thermal equilibrium of a system interacting with a heat bath has recently been of certain interest[1-3]). The work reported in ref. 3 calculates correlation functions by means of a fluctuation dissipation relation. These authors do not start with a Hamilitonian formulation of the system, but with an averaged Langevin equation. On the other hand, other authors do start with a Hamiltonian formulation. One of the models which has extensively been studied is a set of coupled harmonic

* Also at Facultad de Ciencias, U.N.A.M.
** Also at Departamento de Física, U.A.M.-I and fellow of the Sistema Nacional de Investigadores, México.