

Simulation of Relaxation Processes by Monte Carlo

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A Monte Carlo procedure is presented which allows the investigation of the relaxation process of a many-particle system from nonequilibrium states to the (thermal) equilibrium state, including chemical reactions and internal degrees of freedom. As an application the time-dependent relaxation of (a) a 100-particle system from a nonequilibrium state towards thermal equilibrium (Maxwell distribution), and (b) a chemical reacting system from a nonequilibrium state towards the chemical *and* thermal equilibrium state, is reproduced with this method.

I. SIMULATION OF RELAXATION PROCESSES BY MONTE CARLO

The relaxation of a many particle system from a nonequilibrium state to the (thermal-) equilibrium state is described by the nonlinear Boltzmann equation. Small deviations from the thermal equilibrium state may be investigated by approximation methods. For the special case of a spatial homogeneous system it is possible to simulate the relaxation process for an arbitrary initial distribution on a computer. To construct the simulation mechanism we perform the following argumentation:

The mean number of collisions C' per unit volume and unit time is given by [1]:

$$C' = \int d\mathbf{v}_1 \int d\mathbf{v}_2 f(\mathbf{v}_1, t) f(\mathbf{v}_2, t) \sigma^{\text{tot}}(|\mathbf{v}_1 - \mathbf{v}_2|) |\mathbf{v}_1 - \mathbf{v}_2|, \quad (1)$$

where $f(\mathbf{v}, t) d\mathbf{v}$ is the density of particles with velocities in the range $\{\mathbf{v}, \mathbf{v} + d\mathbf{v}\}$ at time t , and $\sigma^{\text{tot}}(|\mathbf{v}_2 - \mathbf{v}_1|)$ is the total cross section for a collision between two particles of velocities \mathbf{v}_1 and \mathbf{v}_2 .

For the mean number of collisions per unit time in the spatial volume element v we can give expression (1) another form and may write

$$C = \frac{1}{V} \sum_{i,k} \sigma^{\text{tot}}(|\mathbf{v}_i - \mathbf{v}_k|) |\mathbf{v}_i - \mathbf{v}_k|, \quad (2)$$

where the summation indices i, k run over all particles in the volume element v . In this form the expression for C is even valid for a mixture of arbitrary particles.

The mean time interval Δt between two collisions in v is then

$$\Delta t = \frac{1}{C}, \tag{3}$$

and we have

$$1 = \Delta t \cdot C = \sum_{i,k} W_{i,k} \tag{4}$$

and

$$W_{i,k} = \frac{\sigma^{\text{tot}}(|\mathbf{v}_i - \mathbf{v}_k|) |\mathbf{v}_i - \mathbf{v}_k|}{\sum_{i,k} \sigma^{\text{tot}}(|\mathbf{v}_i - \mathbf{v}_k|) |\mathbf{v}_i - \mathbf{v}_k|}. \tag{5}$$

The quantity $W_{i,k}$ can be interpreted as the probability for a collision between the particles i and k .

Equations (2), (3), (4), and (5) dictate us now the following Monte Carlo game:

- (1) Take at time $t = 0$ for a set of N particles the initial conditions:

TABLE I

Particle	Velocity	Mass	Internal Energy
1	\mathbf{v}_1	m_1	E_1
2	\mathbf{v}_2	m_2	E_2
⋮	⋮	⋮	⋮
i	\mathbf{v}_i	m_i	E_i
⋮	⋮	⋮	⋮
k	\mathbf{v}_k	m_k	E_k
⋮	⋮	⋮	⋮
N	\mathbf{v}_N	m_N	E_N

- (2) Calculate out of this table the quantities $Z = \sum_{i,k} \sigma^{\text{tot}}(|\mathbf{v}_i - \mathbf{v}_k|) |\mathbf{v}_i - \mathbf{v}_k|$, $W_{i,k}$, and $\tau = 1/Z$, and increase the time t by τ . (Note that in this case we have to multiply τ by

$$\frac{\text{Total number of particles in the system}}{\text{Total density}} \cdot 10^{24}$$

to obtain the time in seconds, if we measure the cross sections in units of barn.)

(3) Choose out of the distribution W_{ik} a pair (i, k) of colliding particles and perform the collision due to the possible reaction mechanism resulting in

$$\underbrace{(\mathbf{v}_i m_i E_i ; \mathbf{v}_k m_k E_k)}_{\text{before the collision}} \quad \underbrace{(\mathbf{v}'_i m'_i E'_i ; \mathbf{v}'_k m'_k E'_k)}_{\text{after the collision}}$$

(4) Replace the values for the particles i and k in Table I by their values after the collision and go back to step (2).

In this way we may follow the system over a large number of collisions and at prescribed timepoints we may scan the Table I for the quantities we are interested in (e.g., distribution of kinetic energies $\frac{1}{2}m_i v_i^2$ or internal energies E_i of the particles).

This procedure may work if we can deal with a system of a reasonable large number of particles. In practice however the available computer storage permits only to treat systems of about (in our case!) 100 particles. To compensate for this we sum over several (about 20–50) histories (each history starting from step (a)) and average over these histories at prescribed time points.

Note, that by following the time-behaviour of one system and averaging the energy-distribution of this system in the equilibrium state over some time interval, we obtain the time-average. If, on the other hand, we follow the time-behaviour of more systems and average over the systems (if they are in equilibrium), we obtain the ensemble average. So, in principle, this method allows the separate investigation of time- and ensemble averages of a many particle system.

II. APPLICATIONS

(A) In a first application we consider the relaxation of a gas from a non-equilibrium state to the Maxwell distribution.

As our system we take $N^{(0)} = 100$ particles all of the same type. The mass of a particle is $m = 1$ mass unit (10^{-24} g). As reactions we allow only elastic scattering, isotropic in the c.m. system with a constant scattering cross section of 1 b. In the initial nonequilibrium state we give each particle the same absolute value of velocity ($v^{(0)} = 10^6$ cm/sec) with an isotropic distribution of their directions.

30 system histories are constructed and the distribution of the kinetic energy at fixed time points is shown in Fig. 1a–c. The curves in Fig. 2 represent the time dependence of the number of particles $\Delta N(E, t)$ in an energy interval ΔE ($= 0.05$ [eV]) at some energy values. After $t \approx 40$ time units a stationary energy

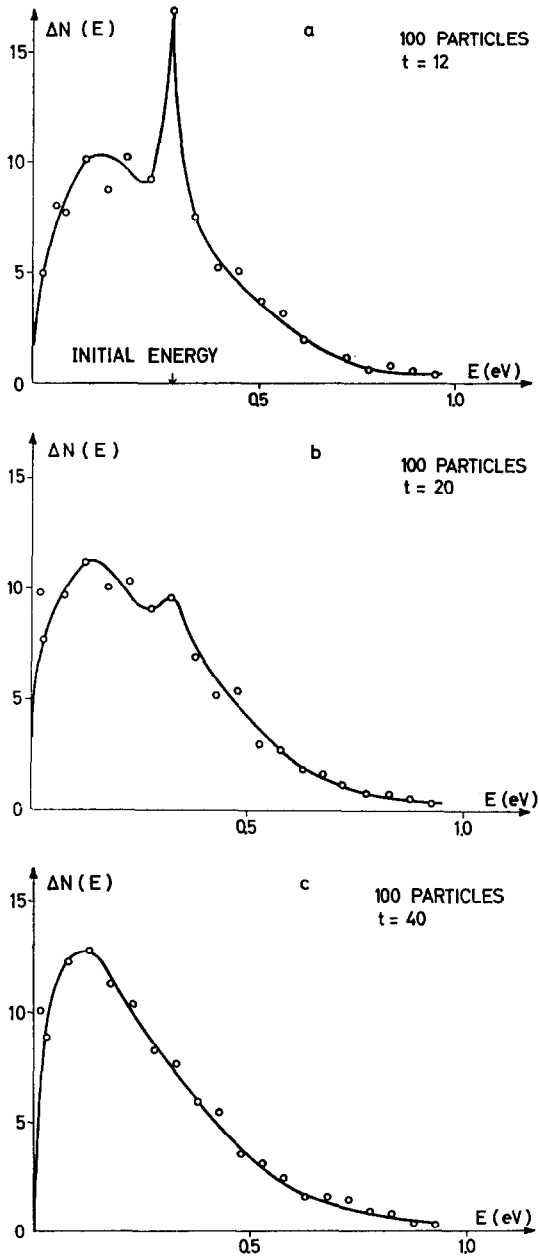


FIG. 1. Distribution of the kinetic energy in a system of 100 particles at the time points $t = 12$ (a), 20 (b), and 40 (c) time units. To obtain the time in seconds one has to multiply t by $(7.6 \times 10^{19})/\text{Density} \cdot \Delta N(E)$ is the number of particles in an energy interval $\Delta E (= 0.05 \text{ [eV]})$ around the energy value E .

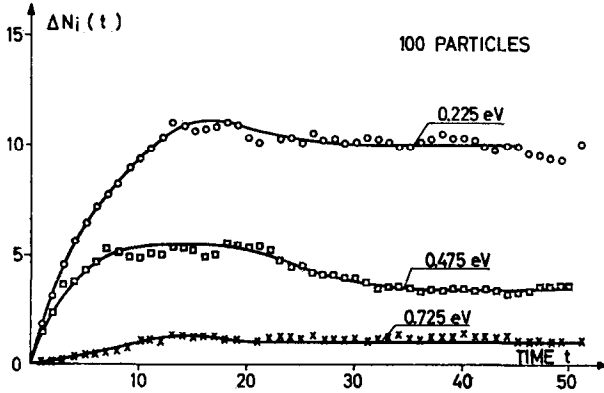


FIG. 2. Time dependence of the number $\Delta N(E_i, t)$ of particles in an energy interval ΔE ($= 0.05$ [eV]) around the energy values $E_1 = 0.225$ [eV], $E_2 = 0.478$ [eV], and $E_3 = 0.728$ [eV]. To obtain the time in seconds one has to multiply t by $(7.6 \times 10^{18})/\text{Density}$.

distribution is established. This distribution should correspond to a Maxwell distribution for temperature kT determined by

$$\text{Average energy} = \frac{3}{2} kT = \frac{\text{Total energy}}{\text{number of particles}} = \frac{E_t}{N}.$$

As the energy is conserved through the history, the total energy is equal to the total energy of the system in the initial state and is given by

$$N^{(0)} \cdot \frac{1}{2} m v^{(0)2}.$$

This leads us, therefore, to a temperature of $kT = 0.208$ [eV].

The calculated equilibrium distribution (for $t = 50$) and the Maxwell distribution for $kT = [0.208]$ eV are plotted in Fig. 3. It may be noted, that the calculated equilibrium distribution fits however well to a Maxwell distribution of $kT = 0.18$. The reason for this discrepancy might be due to the fact, that when constructing with the computer (using random number generator) the isotropic initial velocity distribution of the 100 particles, the sum of the velocities may not add up to zero but to a finite value v_0 . This means a nonzero translational velocity of the center-of-mass. But the kT -value of the Maxwell energy distribution for a particle system with $v_0 \neq 0$ is smaller than for a system with $v_0 = 0$ and has to be calculated out of $3kT/2 = (E_t/N) - mv_0^2/2$. This effect ($v_0 \neq 0$) will certainly increase if the number of particles decreases. However, we made no numerical investigation of this effect. The total calculation time for the 30 system histories,

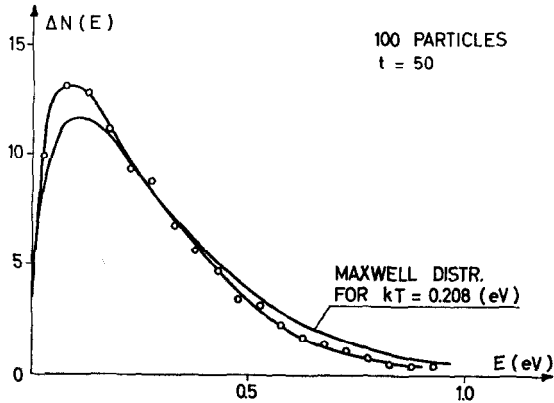
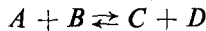


FIG. 3. (a) Equilibrium distribution of the kinetic energy in the system of 100 particles (at time $t = 50$). (b) Maxwell distribution for $kT = 0.208$ [eV].

each history 50 time units with about 10 collisions per time unit, needed 12' on an IBM 360/65.

(B) In a second application we take a gas-mixture of particles of type A , B , C , and D and allow for the reactions:



All collisions between particles other than (AB) or (CD) result in elastic scattering only isotropic in the c.m. system and with constant elastic scattering cross section of 1 b.

For the collisions (AB) and (CD) we take also an energy independent total cross section σ^{tot} of 1 b and separate

$$\sigma^{\text{tot}} = \sigma_r + \sigma_s.$$

σ_r is the cross section for the reaction $AB \rightarrow CD$ or $CD \rightarrow AB$ ($\sigma_r/\sigma^{\text{tot}} = 0.5$) and σ_s is the cross section for elastic scattering ($\sigma_s/\sigma^{\text{tot}} = 0.5$).

The initial condition of the system is fixed by the following values:

Type of Particles	Number of Particles	Mass in Mass Units 10^{-24} g m_I	Absolute Value of Initial Velocity $v_I^{(0)}$ [cm/sec]
I	$N_I^{(0)}$		
A	50	1	10^6
B	50	4	10^3
C	0	2	0
D	0	3	0

The build-up of the reaction product C and the decay of the number of type A particles is shown in Fig. 4a and b. The time dependence of the kinetic-energy distribution for the different species A , B , C , and D shows a similar behaviour as that shown in Fig. 1a-c. The equilibrium distribution of the kinetic energies (which is the same for all particle types) is plotted in Fig. 5 and should correspond to a Maxwell distribution of temperature kT defined by

$$\frac{3}{2} kT = \frac{N_A^{(0)} \left(\frac{1}{2} m_A v_A^{(0)2} \right) + N_B^{(0)} \left(\frac{1}{2} m_B v_B^{(0)2} \right)}{N_A^{(0)} + N_B^{(0)}},$$

which results in $kT = 0.104$ [eV].

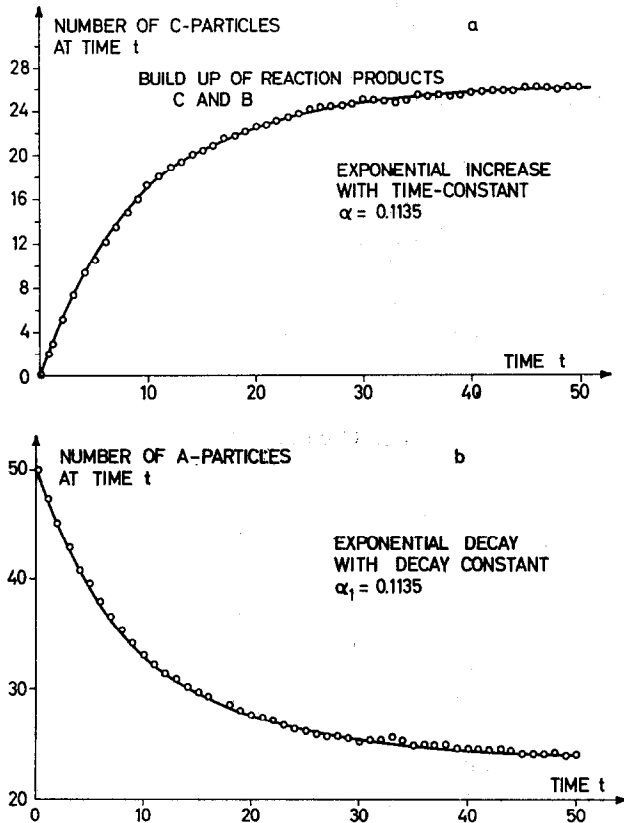


FIG. 4. (a) Number of C -particles at time produced in the reaction $A + B \rightleftharpoons C + D$ when the system started with 50A-particles and 50B-particles at time $t = 0$. To obtain the time in sec one has to multiply t by $(1.2 \times 10^{17})/\text{Density}$. (b) Decay of the number of A -particles as a function of time in the reaction $A + B \rightleftharpoons C + D$ when the system started with 50A-particles and 50B-particles at time $t = 0$. Time in sec is obtained by multiplying t by $(1.2 \times 10^{17})/\text{Density}$.

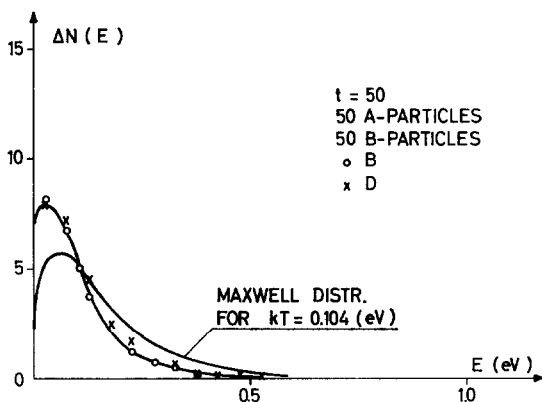


FIG. 5. (a) Equilibrium distribution of the kinetic energy of B- and D-particles (at $t = 50$). (b) Maxwell distribution for $kT = 0.104$ [eV].

Again a discrepancy exists between the calculated equilibrium distribution and the corresponding Maxwell distribution as shown in Fig. 5. A better fit is obtained for a temperature $kT = 0.08$ [eV].

The calculation was again done for 30 system histories, each history 50 time units with about 10 collisions per time unit, and needed 10' on an IBM 360/65.

III. CONCLUSIONS

A Monte Carlo procedure is presented which allows the investigation of the relaxation process of many-particle systems from nonequilibrium states to the (thermal) equilibrium state, including chemical reactions and internal degrees of freedom. The interaction between the particles occurs via two particle collisions and the physics of a single collision is put into the reaction cross sections.

Working only with the concept of the cross sections and the classical collision mechanics (momentum and energy conservation law, to perform a collision) it was possible to reproduce the time-dependent relaxation of (a) a 100-particle system from a nonequilibrium state towards thermal equilibrium (Maxwell distribution), and (b) a chemical reacting system from a nonequilibrium state towards the chemical *and* thermal equilibrium state.

The programme as such is rather simple. The main problem consists in compiling the (energy dependent) cross sections for the different chemical reactions or inelastic scattering processes for the investigation of the relaxation of internal degrees of freedom.

APPENDIX: COLLISION ROUTINE

We consider the following reactions:

Before the Collision	After the Collision
$m_1 v_1 E_1$	$m_A v_A E_A$
$m_2 v_2 E_2$	$m_B v_B E_B$

The energy available for the reaction before the collision in the c.m. system is given by

$$E_R = E_1 + E_2 + \frac{p_0^2}{2\mu} \quad (1)$$

with

$$p_0 = \mu |v_1 - v_2| \quad \text{and} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (2)$$

The total kinetic energy available for the reaction products after the collision in the c.m. system:

$$\epsilon = E_R - E_A - E_B = \frac{p_0'^2}{2\mu'} \quad (3)$$

with

$$\mu' = \frac{m_A m_B}{m_A + m_B}, \quad (4)$$

and p_0' is the absolute value of the momentum of the particles after the collision in the c.m. system.

The absolute values of the velocities v_{0A} and v_{0B} of the reaction products after the reaction in the c.m. system are then given by

$$v_{0A} = \frac{p_0'}{m_A} \quad \text{and} \quad v_{0B} = \frac{p_0'}{m_B}. \quad (5)$$

If \mathbf{n} is the direction of the relative velocity of the reaction products after the reaction in the c.m. system (determined out of the scattering law), we have for their velocities

$$\mathbf{v}_{0A} = v_{0B} \mathbf{n} \quad (6)$$

and

$$\mathbf{v}_{0B} = -v_{0B} \mathbf{n},$$

and for their velocities \mathbf{v}_A and \mathbf{v}_B in the Laboratory system,

$$\mathbf{v}_A = \mathbf{v}_{0A} + \mathbf{c}$$

and

$$\mathbf{v}_B = \mathbf{v}_{0B} + \mathbf{c}, \tag{7}$$

where

$$\mathbf{c} = \frac{m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2}{m_1 + m_2} \tag{8}$$

is the velocity of the center-of-mass (c.m.) in the Laboratory system.

The reaction cross sections determine the type of reaction and give us the quantities: $m_A E_A$, $m_B E_B$, and \mathbf{n} . The velocities \mathbf{v}_A and \mathbf{v}_B of the reaction products after the collision in the L -system have to be found out of expressions (7).

Note that the unit vector \mathbf{n} for the relative velocity refers to the c.m. system and has to be transformed into the Laboratory system to obtain \mathbf{v}_A and \mathbf{v}_B .

The transformation formulae are found with the help of Fig. 6 (laboratory system $\{\mathbf{i}_1, \mathbf{i}_2, \mathbf{i}_3\}$).

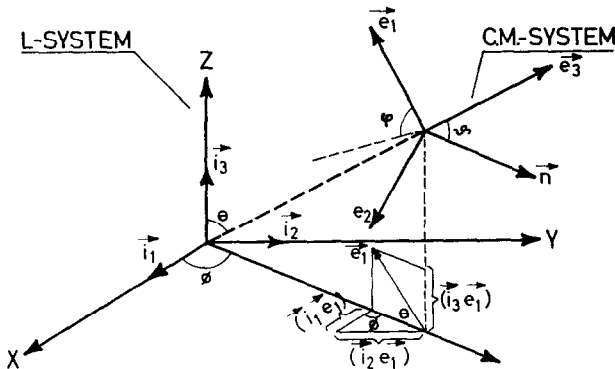


FIG. 6. Choice of coordinate systems (L = Laboratory system, c.m. = center-of-mass system) for the derivation of the transformation formula for the components of \mathbf{n} from the c.m. system to the L system.

$\mathbf{e}_3(\theta, \phi)$: Direction of relative velocity of the colliding particles before the collision. The unit vectors $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ form the base of an orthogonal coordinate system with \mathbf{e}_2 // to the $(\mathbf{i}_1, \mathbf{i}_2)$ plane.

The direction $\mathbf{n}(\vartheta, \varphi)$ for the relative velocity after the collision in the system $\{\mathbf{e}_k\}$ is found out of the scattering law. Then we have

$$\begin{aligned} (\mathbf{i}_1 \mathbf{e}_3) &= \cos \phi \sin \theta, & (\mathbf{i}_1 \mathbf{e}_1) &= -\cos \phi \cos \theta, & (\mathbf{i}_1 \mathbf{e}_2) &= \sin \phi, \\ (\mathbf{i}_2 \mathbf{e}_3) &= \sin \phi \sin \theta, & (\mathbf{i}_2 \mathbf{e}_1) &= -\sin \phi \cos \theta, & (\mathbf{i}_2 \mathbf{e}_2) &= -\cos \phi, \\ (\mathbf{i}_3 \mathbf{e}_3) &= \cos \theta, & (\mathbf{i}_3 \mathbf{e}_1) &= \sin \theta, & (\mathbf{i}_3 \mathbf{e}_2) &= 0. \end{aligned}$$

The components n_v' of \mathbf{n} in the $\{\mathbf{e}_v\}$ system are given by:

$$\left. \begin{aligned} n_1' &= \cos \varphi \sin \vartheta \\ n_2' &= \sin \varphi \sin \vartheta \\ n_3' &= \cos \vartheta \end{aligned} \right\} \mathbf{n} = \sum_{i=1}^3 n_i' \mathbf{e}_i$$

and the components n_k of \mathbf{n} in the Laboratory system are finally given by:

$$n_k = (\mathbf{n} \mathbf{i}_k) = \sum_{i=1}^3 n_i' (\mathbf{i}_k \mathbf{e}_i).$$

REFERENCE

1. K. HUANG, "Statistical Mechanics," John Wiley and Sons, Inc., New York, 1963.