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Kinetics of a Finite One-Dimensional Mixture of Hard Rods with Different Masses

J. Masoliver[1] **and J. Marro**[1]

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A one-dimensional binary mixture of impenetrable (hard core) particles with different mass ratios, $m_2/m_1 = 1$, 1.05, 1.2, 2, 3, and 4, was simulated to evolve in a computer by the molecular dynamics method. The systems with $m_2 > m_1$ and initial velocity distribution $\pm v_0$ show a clear tendency to the equipartition of energy and relaxation toward a Maxwellian velocity distribution unlike the nonergodic system with $m_2 = m_1$. Several quantities have been monitored during the evolution to investigate its dependence on the mass ratio m_2/m_1.

KEY WORDS: One-dimensional mixture; computer simulation; ergodic theory, kinetic theory.

1. INTRODUCTION

One-dimensional systems are interesting as mathematical curiosities and, very often, because they provide physical insight into more complex problems. Moreover, those oversimplified models of reality present sometimes an intrinsic interest. The known exact solutions corresponding to one-dimensional systems of hard points,[1] equal hard rods,[2,3] and hard rods with different lengths,[4] together with other results on hard spheres systems in two and three dimensions, e.g., Ref. 5, have raised considerable expectation about the kinetic and ergodic properties of one-dimensional mixtures of particles with different masses whose exact solution is still lacking.

We present in this paper the results of a series of computer simulations on the evolution of a finite system with a "large" number of particles on a line with different masses. The computations clearly show that the system

[1] Departamentos de Física Teórica y de Ecuaciones Funcionales, Universidad de Barcelona, Diagonal 647, Barcelona-28, Spain.

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with a $\pm v_0$ initial velocity distribution relaxes toward a Maxwellian distribution and satisfies equipartition of energy. We have also computed the evolution of the velocity autocorrelation function and Boltzmann's H function, relaxation time, diffusion constant, and their dependence on the difference between the masses of the particles. The final equilibrium state is shown to be independent of that difference.

2. DESCRIPTION OF MODEL

The system consists of $N = 1000$ impenetrable (hard core) point particles, $N_1 = 500$ with masses m_1 and $N_2 = 500$ with masses m_2, on a line of length L_r with periodic boundary conditions. The initial location of each particle on the line was decided at random in order to simulate spatial uniformity in the distributions of the number of particles and mass. Each particle was initially assigned at random either a velocity $+v_0$ or $-v_0$ independently of its mass. Note that the sizes of the particles do not influence most of the system properties[4] and one may then reinterpret, when necessary, our original system of point particles as a system of rods with different lengths just by rescaling the length of the line to, say, $L = L_r + N_1 a_1 + N_2 a_2$, where a_1 and a_2 are the respective diameters of the two kinds of particles.

The evolution proceeds according to a scheme, based on the one first developed by Adler and Wainwright,[6] which slightly reduces the computation time required by the standard algorithm. Let $x_{ij} = x_i - x_j$ and $v_{ij} = v_i - v_j$ the relative position and velocity of particles i and j in the system. The relative position after a time interval t is given by $x'_{ij} = x_{ij} + v_{ij}t$ so that a collision ($x'_{ij} = 0$) occurs at time $t_{ij} = -x_{ij}/v_{ij}$. Given that the hard core potential only allows for collisions between initial neighboring particles, we compute the vector $t_i \equiv t_{i,i+1}$ ($i = 1, 2, \ldots, N$; $N + 1 \equiv 1$) of *virtual collision times*:

$$t_i = \begin{cases} -x_{i,i+1}/v_{i,i+1} & (x_{i,i+1} \leqslant 0) \\ (-x_{i,i+1} + L_r)/v_{i,i+1} & (x_{i,i+1} > 0) \end{cases} \tag{1}$$

The second value in Eq. (1) is computed when the first one happens to be negative (indicating that the particle at one end of the line will collide with the one at the other end because of periodic boundary conditions). The particles are then moved to the new positions

$$x'_i = x_i + v_i t_m, \qquad t_m = \min\{t_i\,;\, i = 1, 2, \ldots, N\} \tag{2}$$

and the velocities of the one (or more) pairs of colliding particles are

Table I. Mean Free Time, t_0, Equilibrium Values for the Standard Deviation σ and for the Mean Fluctuations Δ, as Defined in Eq. (6), of the Maxwellian Distribution of Velocities, Relaxation Times τ_1 and τ_2 as Measured from the Velocity Autocorrelation Function and Diffusion Constants D_1 and D_2 for the Two Species, Corresponding to Different Mass Relations.

			equilibrium					
m_2/m_1	Steps	t_0	σ	$\Delta \times 10^{-3}$	τ_1/t_0	τ_2/t_0	D_1	D_2
1	160,000	2.00	—	—	0.25		0.49	
1.05	350,000	1.90	—	—	0.30	0.21	0.47	0.50
1.2	160,000	1.76	1.00	4.45	0.29	0.26	0.46	0.51
2	160,000	1.68	1.06	3.55	0.25	0.33	0.39	0.59
3	350,000	1.56	1.14	4.61	—	—	—	—
4	160,000	1.46	1.21	4.06	0.17	0.51	0.31	0.70

changed to

$$v_i' = \frac{2(m_i v_i + m_j v_j)}{m_i + m_j} - v_i \tag{3}$$

as implied by momentum and energy conservation. A new vector of virtual collision times is computed by subtracting t_m from t_i; when $t_i - t_m$ is zero, the new corresponding virtual collision time is computed according to (1).

The above basic *step* is repeated T times. At the end of each *run* (T steps) we computed the *mean free time* t_0 (the inverse of the collision frequency) which is taken as our unit of time.

The degree of "irreversibility" introduced by the computer during the evolution of the system because of round-off errors was monitored from time to time by computing the total momentum and energy; we never observed relative differences larger than 10^{-13} for the momentum or 10^{-12} for the energy. We have also checked by making independent short runs (i.e., short runs with the same mass relation m_2/m_1 but different initial velocity and spatial distributions) that our system evolution with $N = 1000$ is practically independent of the particular randomization of the initial state.

Table I gives some details of the runs reported in this paper[2]; they are for $m_2/m_1 = 1$, 1.05, 1.2, 2, 3, and 4. The choice $m_2 = m_1$ was included for comparison and as a previous test of our results which can then be compared with the known analytical results by Lebowitz *et al.*[2-4] The

[2] We have just learned about a computation by M. K. Phani and R. Bhargava on a system with $m_2/m_1 = 10$ which partially reproduces some of the results reported in this paper.

choice $m_2 = 3m_1$ satisfies (when $\theta = 2\pi/3$) the condition

$$\cos\theta = (m_1 - m_2)/(m_1 + m_2)$$
$$\theta = \text{rational multiple of } \pi \tag{4}$$

which was shown[7] to bring periodic behavior (thus avoiding ergodicity) into a system with *two* particles of masses m_1 and m_2.

3. DISCUSSION OF RESULTS

The velocity distribution and the ratio $e \equiv (E_2 - E_1)/(E_1 + E_2)$, where E_α represents the (kinetic) energy of species α, are two important quantities to conclude about the kinetic and ergodic properties of the system. We observe that $e \simeq (m_2 - m_1)/(m_2 + m_1)$ in the initial state (as implied by the initial random distribution of velocities $\pm v_0$, $v_0 = 1$) while $e \to 0$ when time increases revealing that there is a clear tendency to the equipartition of energy in the system with $m_1 \neq m_2$. Fluctuations prevent very definite conclusions but one observes that the time at which e starts to fluctuate around zero roughly increases with decreasing m_2/m_1. A better indication of the system relaxation toward equilibrium is given by the time evolution of the velocity distribution.

When $m_2 = m_1$ the initial distribution $\pm v_0$ is conserved during the evolution. When $m_2 > m_1$, however, we observe that the initial distribution degenerates into two Gaussians centered, respectively, at $\pm v_0$; these finally evolve into a unique Gaussian centered around $\bar{v} = 0$:

$$f(v) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[(v - \bar{v})^2/2\sigma^2\right] \tag{5}$$

This behavior is illustrated in Fig. 1b, corresponding to $m_2/m_1 = 1.2$, where the Maxwellian distribution (5) is clearly present in the system before 150,000 steps. Fig. 1a corresponds to $m_2/m_1 = 4$ where the distribution is already Maxwellian before 10,000 steps. The case $m_2/m_1 = 1.05$ never reached a Maxwellian distribution before 350,000 steps but one guesses from Fig. 1c a behavior similar to the one in Fig. 1b although with a much larger relaxation time (which will then diverge when $m_2/m_1 \to 1$).

The cases $m_2/m_1 = 2$, 3, and 4 are very similar to each other. The only differences present are a clear tendency of the velocity dispersion to increase with m_2/m_1. The fluctuations, on the other hand, seem to be larger for the case $m_2 = 3m_1$; if real, this would be the only distinctive characteristic of the system satisfying the condition (4). In order to be more definite

about this effect we have looked at

$$\Delta = \frac{1}{m}\left\{\sum_{i=1}^{m}\left[f_{\max}(v_i) - f_{\exp}(v_i)\right]^2\right\}^{1/2} \tag{6}$$

where $f_{\exp}$ is the actual distribution measured during the experiment and $f_{\max}$ is the function given by Eq. (5) with the standard deviation τ and mean $\bar{v}$ corresponding to $f_{\exp}$. Computing Δ from $v_1 = -3.90$ to $v_m = 3.80$ with

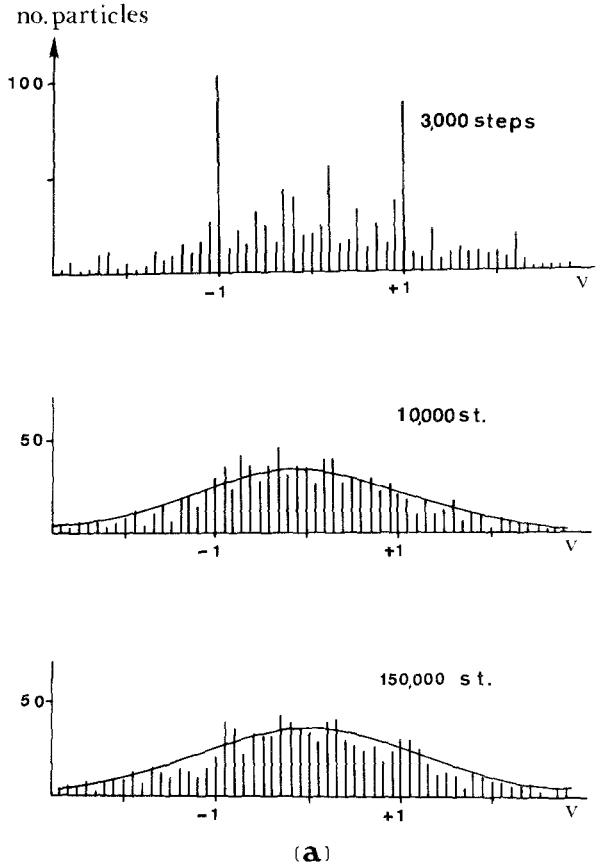


Fig. 1a. Evolution with time (at indicated number of steps) of the velocity distribution in a binary mixture of 1000 hard particles when one starts with velocities ± 1 randomly distributed among the particles. The relation between the masses of the species is $m_2/m_1 = 4$. The solid curves are Gaussian distributions (5) with the mean and standard deviation equal to the ones measured in the system at that time.

velocity increments of 0.1 (i.e., $m = 78$) we obtain for Δ (and τ) the values shown in Table I as an average over the stationary part of the evolution.

We have also looked at the velocity autocorrelation function $\psi(t) = \text{constant}\langle v(0)v(t)\rangle$, which is defined here as

$$\psi_\alpha(t) = \sum_{i=1}^{N_\alpha} v_i(0)v_i(t) \Big/ \sum_{i=1}^{N_\alpha} v_i(0)^2, \qquad \alpha = 1,2 \tag{7}$$

where ψ_α corresponds to particles with a mass m_α.

In the case $m_2 = m_1$ we find that $\psi(t)$ is practically indistinguishable from the exact solution,[3]

$$\psi(t) = v_0^2 \exp(-2nv_0 t) \tag{8}$$

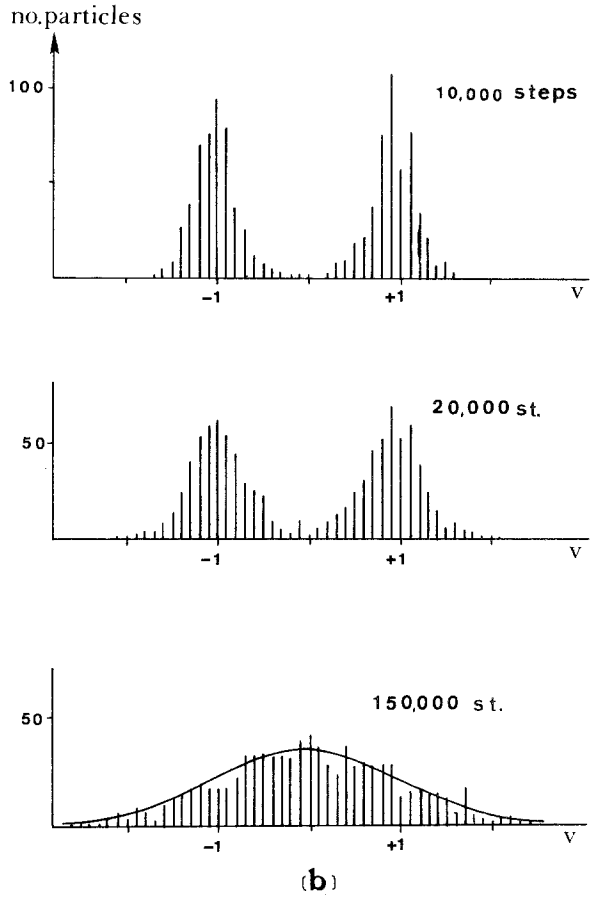
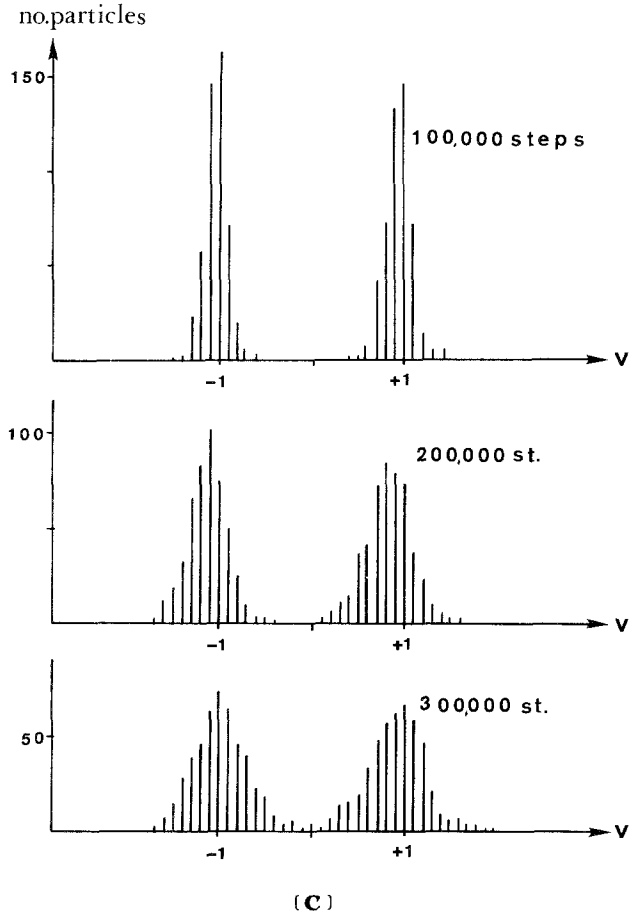


Fig. 1b. Same as Fig. 1a for $m_2/m_1 = 1.2$.

where $v_0 = 1$, $n = 1$ in our system, except for the fact that the experimental values present slight fluctuations around Eq. (8). Figure 2 shows the experimental $\psi_\alpha(t)$ when $m_2/m_1 = 2$ (dots) compared with the function (8) for equal masses; the other cases are qualitatively similar. We observe in general that $\psi_1(t)$ (smaller mass) presents more important fluctuations than $\psi_2(t)$. We also observe that $\psi_1(t)$ relaxes faster than $\psi(t)$ (equal masses), while $\psi_2(t)$ relaxes slower than $\psi(t)$. In order to be more precise about this fact, we have assumed

$$\psi_\alpha(t) \sim e^{-t/\tau_\alpha}, \qquad \alpha = 1, 2 \tag{9}$$

which happens to represent fairly well the data (the coefficient of linear



[C]

Fig. 1c. Same as Fig. 1a for $m_2/m_1 = 1.05$.

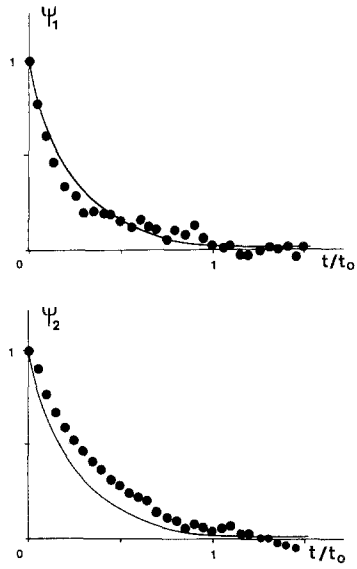


Fig. 2. Velocity autocorrelation functions $\psi_1(t)$ and $\psi_2(t)$ for the two species, computed according to Eq. (7), in the case $m_2/m_1 = 2$, as a function of the time. The solid curve represents the corresponding exact function computed by Lebowitz, Percus, and Sykes when $m_2 = m_1$.[3]

regression for $\ln\psi_\alpha$ versus t is always larger than 0.996), and computed the "relaxation time" τ_α for each species and mass relation. The result is shown in Table I: τ_2/t_0 increases with m_2/m_1; while τ_1/t_0 decreases with m_2/m_1 (and $m_2 = m_1$ is also singular from this point of view). (See Fig. 3.)

Another quantity of interest is the diffusion constant defined here as

$$D_\alpha = \int_0^{1.5t_0} \psi_\alpha(t)\, dt, \qquad \alpha = 1,2 \tag{10}$$

given that $\psi_\alpha(t) \simeq 0$ for $t \gtrsim 1.5t_0$. This gives the values reported in Table I; that is, like τ_α, D_1 decreases, while D_2 increases with m_2/m_1. The computed value when $m_2 = m_1$ (0.49) is comfortably close to the exact value 0.5, which follows from Eq. (8). Interesting enough the data fit very well (with coefficients of regression larger than 0.999) linear relations:

$$D_1 = -0.58\mu + 0.77, \qquad D_2 = 0.69\mu + 0.14$$

with $\mu = m_1m_2/(m_1 + m_2)$ the reduced mass, which intersects at $\mu = 0.496 \simeq 1/2$ ($m_1 = m_2$) with $D_1 = D_2 = 0.482 \simeq 0.49$ as one should expect for consistency.

The evolution of the system has also been monitored by computing the Boltzmann H function:

$$H(t) = \int dv\, f(v,t) \ln f(v,t) \tag{11}$$

This function is observed to decrease monotonically with time as shown by Table II, which collects some representative values of $-H(t)$ as a function of t/t_0 and m_2/m_1. Every run (with the exception of $m_2/m_1 = 1.05$) reached a stationary regime, $dH/dt = 0$. The time at which the system reaches this regime (with a common value $H_{eq} \simeq -0.37$) is approximately $t/t_0 \simeq 3.5$ at $m_2/m_1 = 2$, 3, and 4, $t/t_0 \simeq 50$ at $m_2/m_1 = 1.2$, and the extrapolation of the values at $m_2/m_1 = 1.05$ gives $t/t_0 \simeq 450$ in order to have $H \simeq -0.37$.

We have finally computed the equilibrium radial distribution function $g(r)$ corresponding to different systems. This should be independent of the mass relation m_2/m_1, thus allowing us to check that our systems relaxed to the true, common equilibrium state.

In this case we have also allowed for different lengths, a_2 and a_1, for the two kinds of particles. The function $g(r)$ was then computed as

$$g(r) = \frac{1}{2\rho N \Delta r} \left\{ \sum_{i=1}^{N} \left[\Delta n_i(+r) + \Delta n_i(-r) \right] \right\} \tag{12}$$

where $\rho = N/L$ and Δr is the r increment which was taken, $\Delta r = 0.05\, a_1$ with $a_1 < a_2$. The quantity $\Delta n_i(r)$ represents the portion (note $\Delta r < a_1 < a_2$) of a particle lying inside Δr a distance r apart from particle i.

Table II. Values for the Negative of the Boltzmann H Function (9) at Different Values of t/t_0 and m_2/m_1 Showing That $dH(t)/dt \leqslant 0$ and a Common Equilibrium Value, $H_{eq} = -0.37$.

t/t_0 \ m_2/m_1	1.05	1.2	2	3	4
1	—	0.21	0.25	0.23	0.22
2	—	0.23	0.33	0.32	0.31
3	—	0.25	0.35	0.35	0.35
5	—	0.27	0.37	0.37	0.37
10	0.15	0.29	0.37	0.37	0.37
20	0.16	0.33	0.37	0.37	0.38
50	0.20	0.36	0.37	0.37	0.37
70	0.22	0.37	0.37	0.37	0.37
100	0.24	0.36	0.37	0.37	0.37
150	0.28	0.37	0.37	0.37	0.37
300	0.33	—	—	—	—

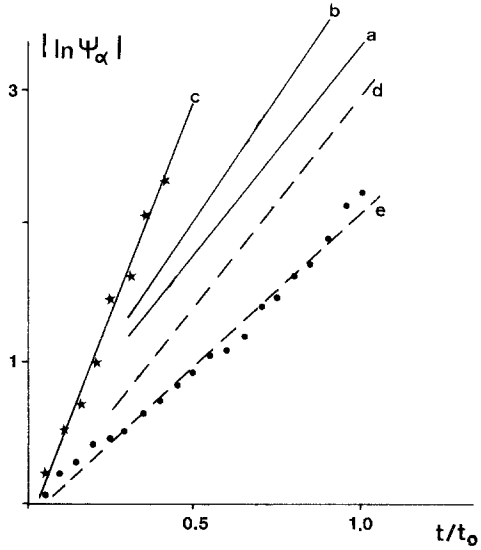


Fig. 3. Linear fits to the data $|\ln \psi_\alpha|$ versus t/t_0 in the cases: (a) $\alpha = 1$, $m_2/m_1 = 1.2$; (b) $\alpha = 1$, $m_2/m_1 = 2$; (c) $\alpha = 1$, $m_2/m_1 = 4$; (d) $\alpha = 2$, $m_2/m_1 = 2$; and (e) $\alpha = 2$, $m_2/m_1 = 4$. The experimental points are shown for (c) and (e).

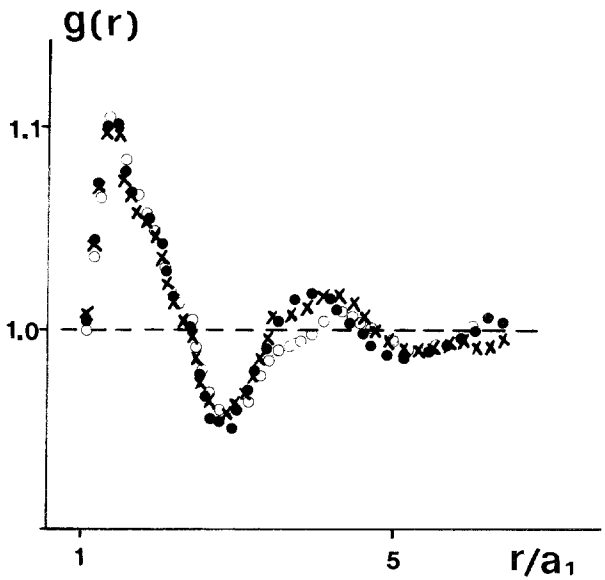


Fig. 4. The equilibrium radial distribution function $g(r)$, as defined in Eq. (10), versus r/a_1 in the cases $m_2/m_1 = 1.2$ (empty circles), 2 (full circles) and 4 (crosses).

The quantity (10) was also averaged over time during the stationary part of the evolution in order to reduce fluctuations. We find that indeed $g(r)$ at equilibrium is independent of m_2/m_1; in fact, assuming $a_2 = a_1$ for $m_2 = m_1$ and $a_2 = 2a_1$ for $m_2 > m_1$, $g(r)$ presents always two distinct maxima which for $a_2 = 2a_1$ have very approximately the same high and location, being 1.5 a_1 the location of the first maximum and 4.2 a_1 the location of the second one, as shown by Fig. 4.

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