# Chaos in Many-Particle Systems

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13/06/18

# Molecular Dynamics: Definition

"...molecular dynamics simulation involves solving the classical many-body problem in contexts relevant to the study of matter at the atomistic level..."[1]

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"Computer simulation generates information at the microscopic level ... and the conversion of this very detailed information into macroscopic terms ... is the province of statistical mechanics."[2]

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# Interaction Potentials

- The Lennard-Jones potential is defined by

$$u(r_{j,k}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{j,k}}\right)^{12} - \left(\frac{\sigma}{r_{j,k}}\right)^{6}\right], & \text{for } r_{j,k} < r_c, \\ 0, & \text{for } r_{j,k} \geq r_c, \end{cases} \tag{1}$$

  where $r_{j,k} = |\vec{r}_j - \vec{r}_k|$, $\varepsilon$ is the interaction magnitude, and $\sigma$ defines a length scale.

- By removing the attractive part of the Lennard-Jones potential, we obtain the soft-sphere potential:

$$u(r_{j,k}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{j,k}}\right)^{12} - \left(\frac{\sigma}{r_{j,k}}\right)^{6}\right] + \varepsilon, & \text{for } r_{j,k} < r_c, \\ 0, & \text{for } r_{j,k} \geq r_c, \end{cases} \tag{2}$$

  for $r_c = 2^{\frac{1}{6}}\sigma$.

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# Potential Sketch

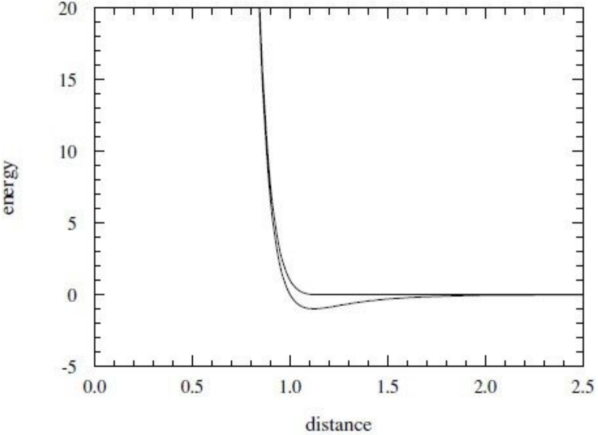


Figure 1: Lennard-Jones (lower curve) and soft-sphere (upper curve) potentials in dimensionless molecular dynamics units.[1]

[1] D. C. Rapaport, *The Art of Molecular Dynamics Simulation*.

# Perturbation

- Consider two identical simulations of $N$ two-dimensional particles. At a chosen time $t_p$, the following perturbation is applied on every particle in one of the systems:

$$\vec{v}_{2,j}(t_p) = \vec{v}_{1,j}(t_p) + \varepsilon \vec{w}_j, \tag{3}$$

where $\vec{v}_{1,j}$ is the velocity of the $j$-th particle in the original system, $\vec{v}_{2,j}$ is the corresponding velocity in the perturbed system, $\vec{w}_j$ is a random unit vector, and $\varepsilon$ is the perturbative parameter.

# Criteria for Chaos

- Mean-square position deviation:

$$\langle(\vec{r}_1 - \vec{r}_2)^2\rangle = \frac{1}{N}\sum_{j=1}^{N}(\vec{r}_{1,j} - \vec{r}_{2,j})^2, \quad (4)$$

where $\vec{r}_{1,j}$ is the position of the $j$-th particle in the original system and $\vec{r}_{2,j}$ is the corresponding position in the perturbed system.

- Position correlation:

$$\mathrm{corr}(\vec{r}_1, \vec{r}_2) = \frac{\langle(\vec{r}_1 - \langle\vec{r}_1\rangle)(\vec{r}_2 - \langle\vec{r}_2\rangle)\rangle}{\sigma(\vec{r}_1)\sigma(\vec{r}_2)}, \quad (5)$$

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# Comparative Simulation

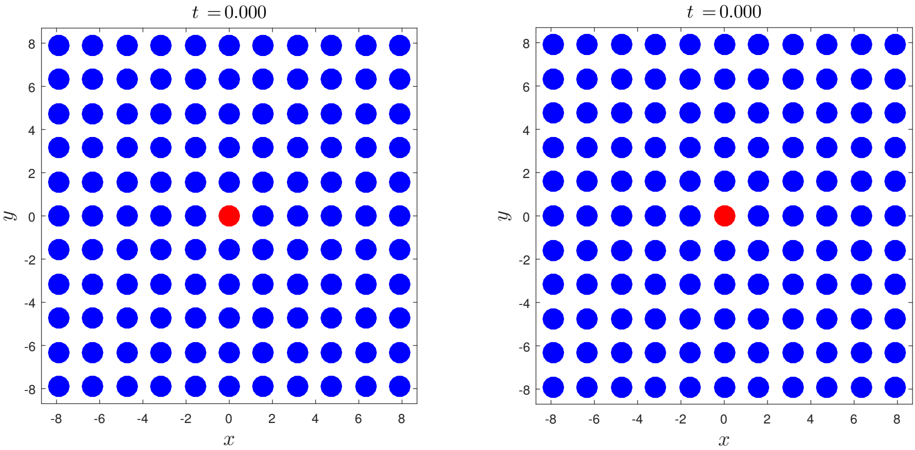


Figure 2: Comparative simulation of two-dimensional soft-sphere particles for $\rho = 0.4$, $T = 1$, $N = 121$, and $\varepsilon = 10^{-6}$.

# Root-Mean-Square Position Deviation and Correlation

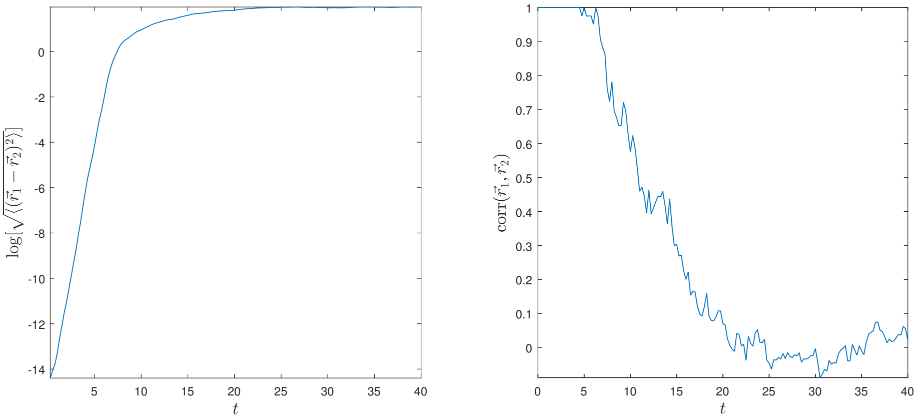


Figure 3: Root-mean-square deviation (left panel) and correlation (right panel) between particle positions and their perturbed versions. Simulation of soft-sphere particles for $d = 2$, $\rho = 0.4$, $T = 1$, and $N = 121$.

# Saturation

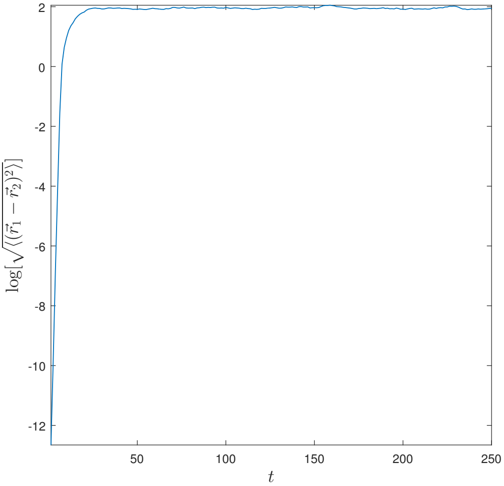


Figure 4: Root-mean-square deviation between particle positions and their perturbed versions. Simulation of soft-sphere particles for $d = 2$, $\rho = 0.4$, $T = 1$, and $N = 121$.

# Saturation Value

- According to figure 4, the saturation value of the root-mean-square position deviation is

$$\log\left[\sqrt{\langle(\vec{r}_1 - \vec{r}_2)^2\rangle}\right] \approx 1.947, \tag{6}$$

for $t = 250$.

- As a consequence of the derivation presented in the appendix, the predicted value of saturation is

$$\log\left[\sqrt{\langle(\vec{r}_1 - \vec{r}_2)^2\rangle}\right] = \log\left(\sqrt{\frac{d}{12}}\,L\right) \approx 1.960, \tag{7}$$

for $d = 2$ and $L \approx 17.39$.

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# Maxwell-Boltzmann Distribution

- Velocity distribution of two-dimensional classical particles in thermal equilibrium:

$$f(v) = \frac{v}{T} \exp\left(-\frac{v^2}{2T}\right). \tag{8}$$

- The Boltzmann $H$-function is defined as

$$\begin{aligned} H &= \int \tilde{f}(\vec{v}) \log\left[\tilde{f}(\vec{v})\right] \mathrm{d}^d v \\ &\propto \int f(v) \log\left[\frac{f(v)}{v^{d-1}}\right] \mathrm{d}v. \end{aligned} \tag{9}$$

- The $H$-function satisfies the following relation:

$$\left\langle \frac{\mathrm{d}H}{\mathrm{d}t} \right\rangle \leq 0, \tag{10}$$

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# *H*-Function

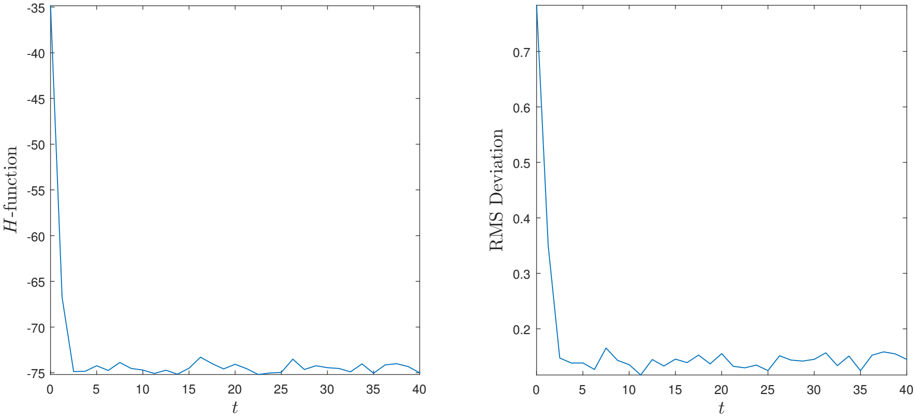


Figure 5: (Left panel) Boltzmann *H*-function. (Right panel) Root-mean-square deviation of the velocity histogram with respect to the Maxwell-Boltzmann distribution. Simulation of soft-sphere particles for $d = 2$, $\rho = 0.4$, $T = 1$, and $N = 121$.

# Thermalized Comparative Simulation

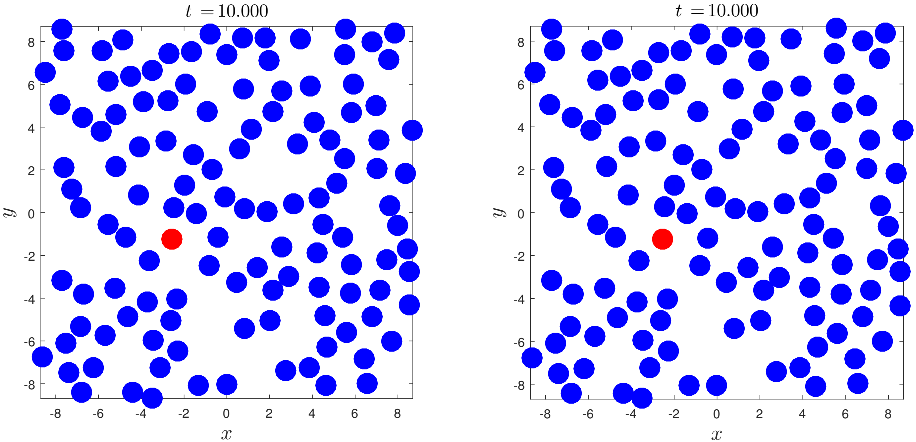


Figure 6: Comparative simulation of thermalized two-dimensional soft-sphere particles for $\rho = 0.4$, $T = 1$, $N = 121$, and $\varepsilon = 10^{-6}$.

# Position Root-Mean-Square Deviation and Correlation

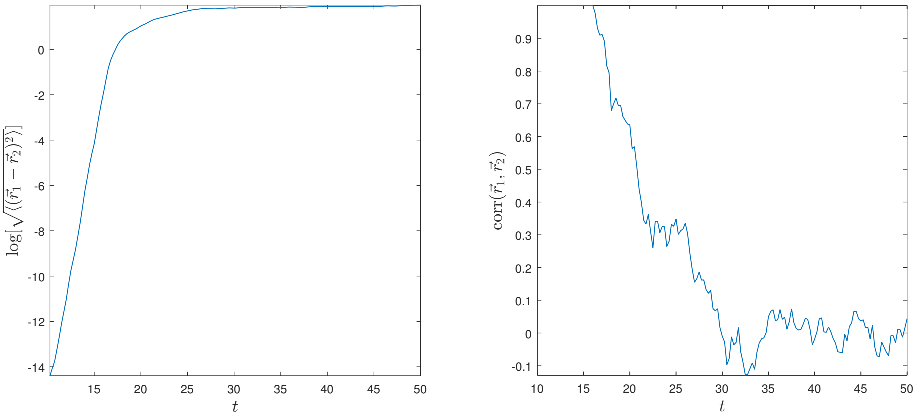


Figure 7: Root-mean-square deviation (left panel) and correlation (right panel) between particle positions and their perturbed versions. Simulation of thermalized soft-sphere particles for $d = 2$, $\rho = 0.4$, $T = 1$, and $N = 121$.

# Behaviour Invariance

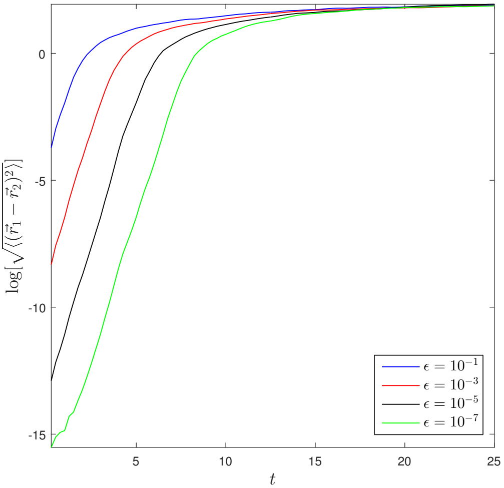


Figure 8: Root-mean-square deviation between particle positions and their perturbed versions. Simulation of soft-sphere particles for $\rho = 0.4$, $T = 1$, and $N = 121$.

# References


- D. C. Rapaport. *The Art of Molecular Dynamics Simulation*. Cambridge University Press, 2004.

# Saturation Value of Mean-Square Position Deviation

- As a first step, equation (4) is rewritten in terms of Cartesian coordinates:

$$\begin{aligned}\langle(\vec{r}_1 - \vec{r}_2)^2\rangle &= \sum_{j=1}^{d}\langle(r_{1,j} - r_{2,j})^2\rangle \\ &= \sum_{j=1}^{d}\langle(\Delta r_j)^2\rangle,\end{aligned} \tag{11}$$

  where $r_{1,j}$ and $r_{1,j}$ are the $j$-th Cartesian coordinates of a particle in the original and perturbed systems, respectively. Notice that $d$ dimensions are considered.

- Assuming that $\Delta r_j$ is a uniformly distributed random variable over the interval $[0, L_j/2]$, the following result is obtained:

$$\langle(\Delta r_j)^2\rangle = \frac{1}{12}L_j^2, \tag{12}$$

  where $L_j$ is the length of a $d$-dimensional box in the $j$-th direction, considering periodic boundary conditions.

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# Result

- Upon substitution of the assumption (12) into equation (11):

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