Computational statistical physics: The example of hard spheres

Lectures at the 16th Chris Engelbrecht Summer School in Theoretical Physics, Drakensberg, KwaZulu-Natal, South Africa
Second part: Statistical physics approach

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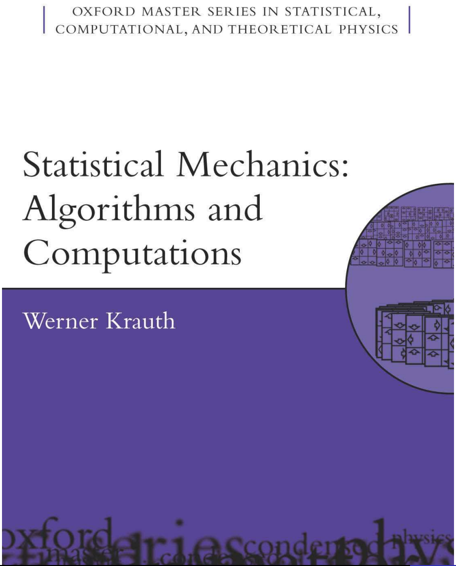
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Statistical Mechanics:
Algorithms and
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Werner Krauth

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Hard spheres (Boltzmann)

Let's forget about collision rules etc.

- Each configuration has same energy
- Each configuration has same probability (Boltzmann)

$$\pi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \begin{cases} \text{const} & \text{if } d(\mathbf{r}_k, \mathbf{r}_l) > 2\sigma \;\; \forall k \neq l \\ 0 & \text{otherwise} \end{cases}$$

Alg. `direct-disks` (≡ children's algorithm)

procedure `direct-disks`

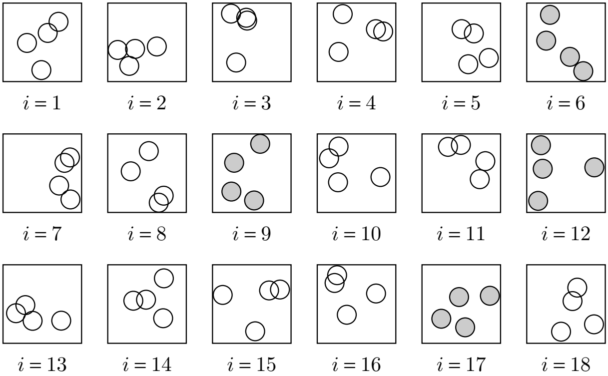
1 **for** $k = 1, \ldots, N$ **do**

$$\left\{ \begin{array}{l} x_k \leftarrow \texttt{ran}[x_{\min}, x_{\max}] \\ y_k \leftarrow \texttt{ran}[y_{\min}, y_{\max}] \\ \textbf{for } l = 1, \ldots, k-1 \textbf{ do} \\ \quad \left\{ \begin{array}{l} \text{compute distance } d_{kl} \\ \textbf{if } (d_{kl} < 2\sigma) \textbf{ goto } 1 \text{ (reject sample—tabula rasa)} \end{array} \right. \end{array} \right.$$

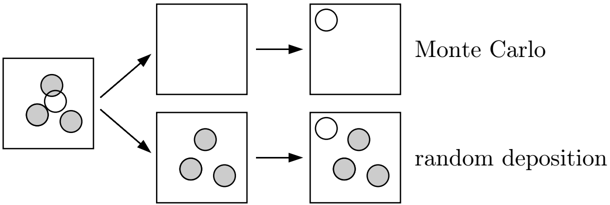
output $\{\mathbf{x}_1, \ldots, \mathbf{x}_N\}$ (direct sample, $\{x_k, y_k\} = \mathbf{x}_k$)

- Foundation of statistical physics.

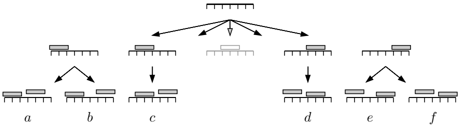
Movie of Alg. `direct-disks`



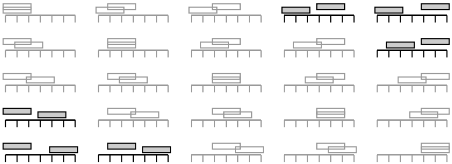
Direct sampling $\neq$ Random deposition I



Random deposition:

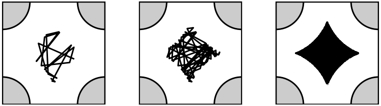


Monte Carlo:



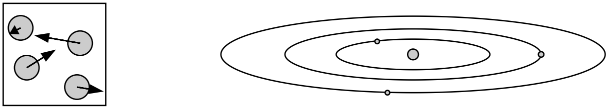
Alg.`direct-disks` ≡ Alg.`event-disks` etc

- The two-disk system with periodic boundaries considered earlier is ergodic (Sinai (1970,1973)).



- ...same is true for N disks (or spheres) with almost all distributions of masses $\{m_1, \ldots, m_N\}$, if space of configurations is connected. (Simanyi, 2003)

Chaos in the hard-sphere system and others



- A finite number of hard spheres are ergodic,
- small planetary system usually not ergodic (Kolmogoroff-Arnold-Moser theorem).

Equipartition

- Other excellent reasons to believe in equipartition–ergodicity

$$\pi(\mathbf{x}) = \pi(E(\mathbf{x}))$$

  - Boltzmann equation
  - Jayne's principle (related to Bayes statistics)
  - Quantum mechanics

Ergodicity/Equipartition

NB: Two uses of the word 'ergodic'

- each configuration can be reached (Markov-chain)
- each configuration is visited with correct probabilities.

Random points on d–dimensional unit sphere

take d Gaussians $x_1, \dots, x_k, \dots, x_d$ with

$$\pi(x_k) = \frac{1}{\sqrt{2\pi}} \exp\left[-x_k^2/2\right]$$

we have

$$\pi(x_1, \dots, x_N) \propto \exp\left[-(x_1^2 + \dots + x_N^2)\right]$$

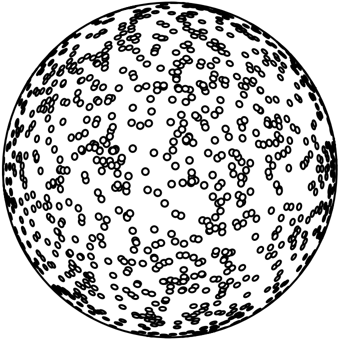
Clearly, $\pi(x_1, \dots, x_N)$ only depends on the radius $r = \sqrt{x_1^2 + \dots + x_N^2}$, not on the angle.

Random points on d–dimensional unit sphere (algorithm)

$$
\begin{array}{l}
\textbf{procedure } \texttt{direct-surface} \\
\sigma \leftarrow 1/\sqrt{d} \\
\Sigma \leftarrow 0 \\
\textbf{for } i = 1, \ldots, d \textbf{ do} \\
\quad \left\{ \begin{array}{l} x_i \leftarrow \texttt{gauss}[\sigma] \\ \Sigma \leftarrow \Sigma + x_i^2 \end{array} \right. \\
\textbf{for } i = 1, \ldots, d \textbf{ do} \\
\quad \left\{ \; x_i \leftarrow x_i/\sqrt{\Sigma} \right. \\
\textbf{output } \{x_1, \ldots, x_d\}
\end{array}
$$

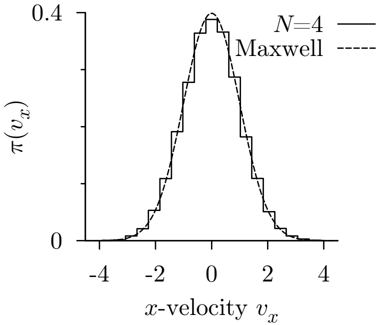
- One more direct-sampling algorithm.

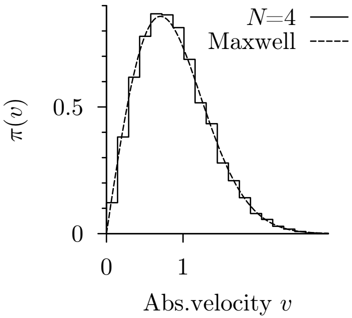
Picture of random points on a sphere



- each point: all velocities of N particles in a gas/liquid
- each component: velocity component of one particle

Maxwell distribution in 4–particle system

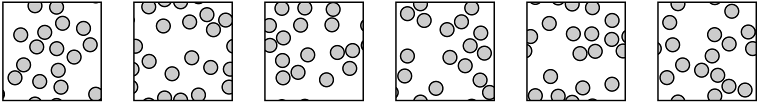




- $v = \sqrt{v_x^2 + v_y^2}$ in a two-dimensional gas or liquid.
- each component: velocity component of one particle.

- convergence in the $t \to \infty$ limit is not enough. We need convergence on a time-scale, the correlation time.

- The only 6 ‘survivors’ of a one-million trial direct sampling computation with Alg. `direct-disks` ($N = 16$, density $\eta = 0.3$ [1] (periodic boundary conditions).



$i = 84976$ 506125 664664 705344 906340 909040

- Why so many/few ($\sim 10^1$)?

[1] $\eta = \pi\sigma^2 \cdot \frac{N}{L_x L_y}$

Computing rejection probabilities (algorithm)

procedure `direct-disks-any`

$\sigma \leftarrow 0$

for $k = 1, \ldots, N$ **do**

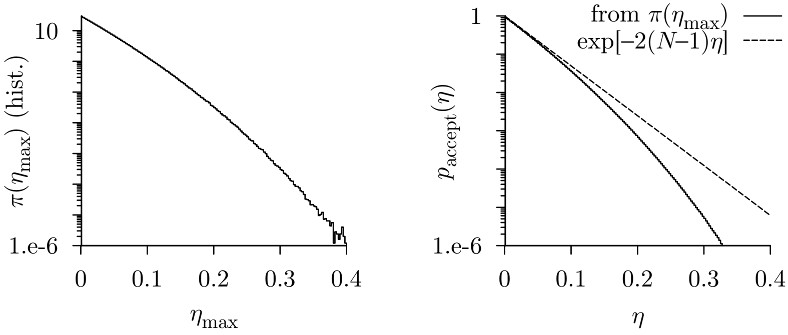
$$\left\{ \begin{array}{l} x_k \leftarrow \texttt{ran}[0, L_x] \\ y_k \leftarrow \texttt{ran}[0, L_y] \\ \textbf{for } l = 1, \ldots, k-1 \textbf{ do} \\ \quad \{ \ \sigma \leftarrow \texttt{max}[\sigma, \texttt{dist}[\mathbf{x}_k, \mathbf{x}_l]/2] \end{array} \right.$$

$\eta_{\text{max}} \leftarrow \pi \sigma^2 N / (L_x \cdot L_y)$ (limiting density, see eqn (**??**))

output η_{max}

- …computes smallest radius σ, $\equiv$ smallest density η of hard-sphere configuration.

Computing rejection probabilities II



$$\left\{ \begin{array}{c} \text{rejection rate of} \\ \text{Alg.}\texttt{direct-disks} \\ \text{at density } \eta \end{array} \right\} = 1 - p_{\text{accept}}(\eta) = \int_0^\eta d\eta_{\max}\ \pi(\eta_{\max})$$

Rejection rate and partition function

$$\left\{ \begin{array}{c} \text{Number of} \\ \text{configurations} \\ \text{with } \sigma = 0 \end{array} \right\} : \underbrace{Z(\eta = 0)}_{\text{partition function}} = \int d\mathbf{x}_1 \ \ldots \int d\mathbf{x}_N = V^N$$

$$Z(\eta) = \int \ldots \int d\mathbf{x}_1 \ldots d\mathbf{x}_N \quad \underbrace{\pi(\mathbf{x}_1, \ldots, \mathbf{x}_N)}_{\text{for disks of finite radius}}$$

$$= Z(0) \cdot p_{\text{accept}}(\eta)$$

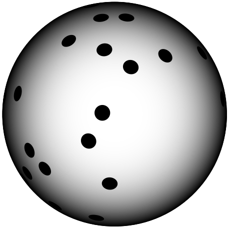
- The rejection probability of an *algorithm* is a *physical* parameter.

Velocities

- "Boltzmann = Newton", but where are the velocities?

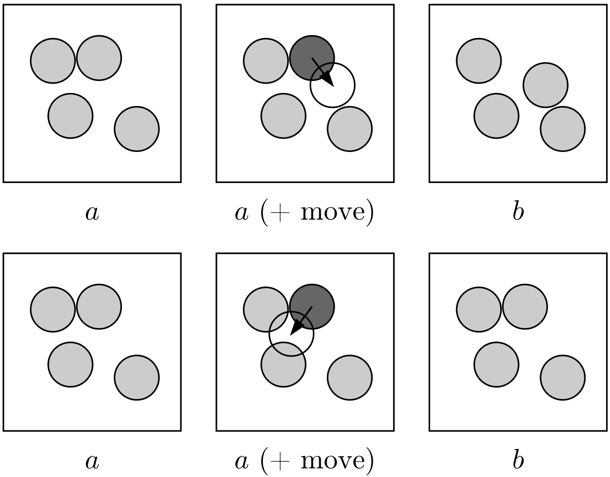
$$\pi(\mathbf{v}_1, \ldots, \mathbf{v}_{N_{\text{disk}}}) = \begin{cases} \text{const} & \text{if } \mathbf{v}_1^2 + \ldots + \mathbf{v}_{N_{\text{disk}}}^2 = \frac{2E_{\text{kin}}}{m} \\ 0 & \text{otherwise} \end{cases}$$

- random point on hypersphere of dimension $2 \times N_{\text{disk}}$ (for disks) or $3 \times N_{\text{disk}}$ (for spheres)



- Gaussians—Maxwell distribution.

Markov chain MC algorithm for hard spheres

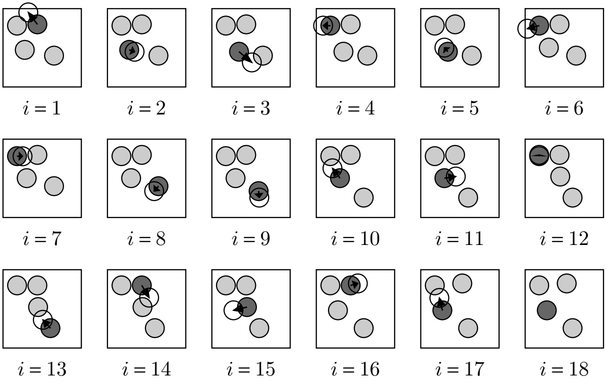


Markov chain algorithm for hard spheres (algorithm)

procedure `markov-disks`
input $\{\mathbf{r}_1, \ldots, \mathbf{r}_{N_{\text{disk}}}\}$ (initial configuration a)
$k \leftarrow \texttt{Nran}[1, N_{\text{disk}}]$
$\delta\mathbf{r}_k \leftarrow (\texttt{ran}[-\delta, \delta], \texttt{ran}[-\delta, \delta])$
for $\forall l \neq k$ **do**
$\left\{ \begin{array}{l} \text{compute distance } d_{kl} \\ \text{between } \mathbf{r}_k + \delta\mathbf{r}_k \text{ and } \mathbf{r}_l \end{array} \right.$
if ($\min_l d_{kl} > d$**)** $\mathbf{r}_k \leftarrow \mathbf{r}_k + \delta\mathbf{r}_k$
output $\{\mathbf{r}_1, \ldots, \mathbf{r}_{N_{\text{disk}}}\}$ (final configuration b)

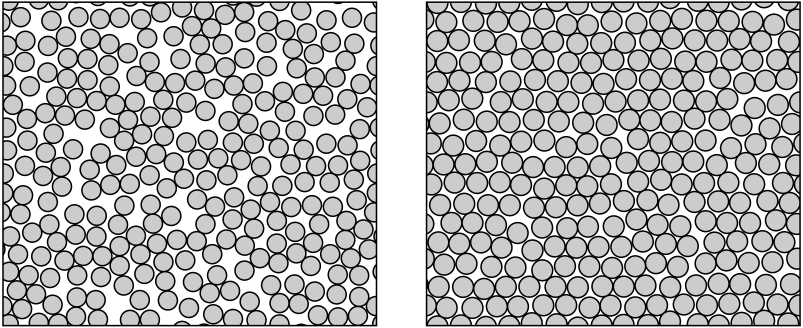
- + boundary effects

Markov-chain Monte Carlo algorithm



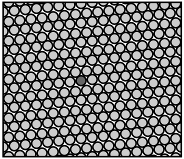
- Note Collisions

Large systems of hard spheres

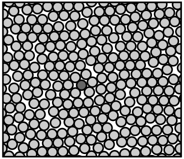


- Liquid–Solid phase transition in dimensions 2 or higher.

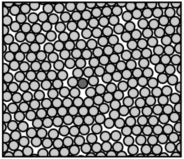
Convergence problems of the Monte Carlo algorithm



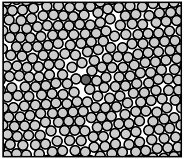
$i = 0$



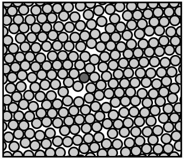
$i/N = 1000$



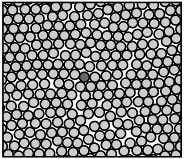
$i/N = 2000$



$i/N = 3000$

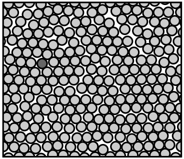


$i/N = 4000$



$i/N = 5000$

...



$i/N = 100000000$

Hydrodynamic behavior

- measuring the velocity-velocity autocorrelation function