# Computational statistical physics: The example of hard spheres

## Lectures at the 16th Chris Engelbrecht Summer School in Theoretical Physics, Drakensberg, KwaZulu-Natal, South Africa

## Fourth part: Entropic phase transitions

Werner Krauth

Laboratoire de Physique Statistique
Ecole Normale Supérieure, Paris, France

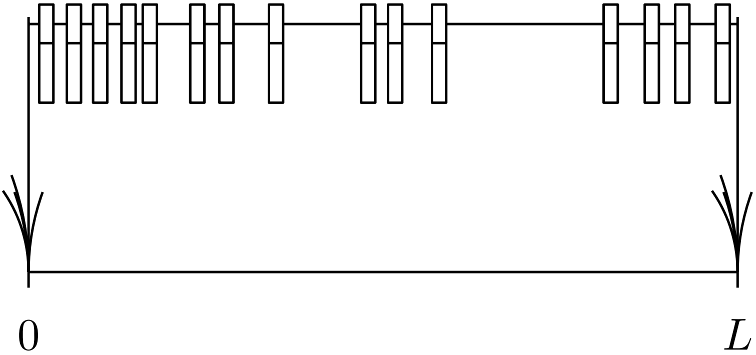
27 January 2005

# Paris, France, June 4th, 2004, Nº 4

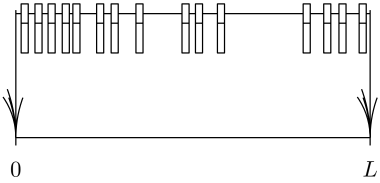
# Goal of lecture

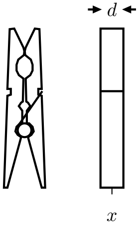
- Origin of ‘forces’ in systems without interactions

# Random clothes-pin model



# Random clothes-pin model




- $N$ pins, width $d = 2\sigma$, length $L$.
- simplest entropic system ($\equiv$ one-dimensional hard disks)

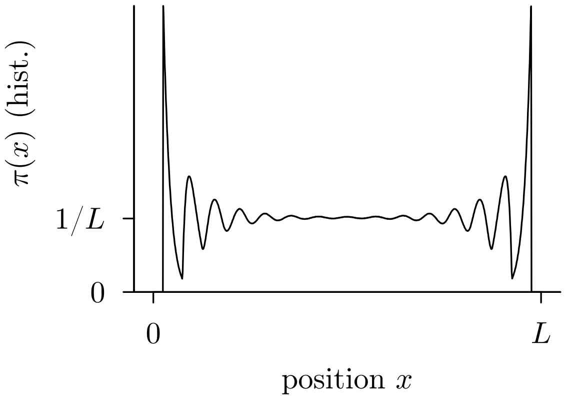
$$\pi(x_1, \ldots, x_N) = \begin{cases} 1 \text{ if no overlap} \\ 0 \text{ otherwise} \end{cases}$$

# Alg. `naive-pins`

```
    procedure naive-pins
1   for k = 1, ..., N do
      { x_k ← ran[d/2, L − d/2]
      { for l = 1, ..., k − 1 do
      {     { if (|x_k − x_l| < d) goto 1 (reject sample—tabula rasa)
    output {x_1, ..., x_N}
```

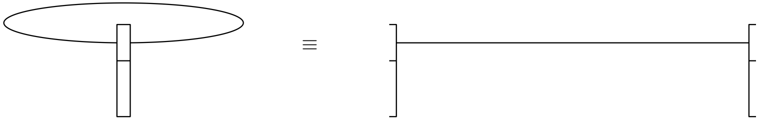
- What is the density $\pi(x)$ of clothes-pins for $0 < x < L$?
- NB: $\pi(x)$: probability to have a pin-center at $x$.

# Output of Alg. `naive-pins`




- Just a boundary effect?

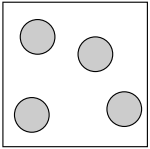
# Not a boundary effect

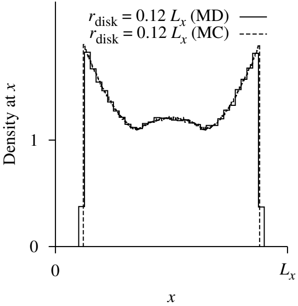


$$\underbrace{\pi(x_k, x_l) = \pi_2(x_k - x_l)}_{\substack{\text{pair correlation}\\ \text{periodic system}}} = \underbrace{\pi(x_k - d/2)}_{\substack{\text{density}\\ \text{segment}}}$$

- density of periodic system is constant (translation symmetry)

# Boundary effects in two dimensions






- *exact* correspondence between correlation functions in 1D

# Clothes-pin partition function

$$Z_{\text{pin}}(N,L) = \int_0^L \mathrm{d}x_1 \ldots \int_0^L \mathrm{d}x_N \overbrace{\pi(x_1,\ldots,x_N)}^{\text{totally symmetric in } x_1,\ldots,x_N}$$

$$= N! \int_0^L \mathrm{d}x_1 \ldots \int_0^L \mathrm{d}x_N \underbrace{\pi(x_1,\ldots,x_N)}_{x_1<x_2<\cdots<x_N}$$

$$= N! \int_{d/2}^{L+\frac{d}{2}-Nd} \mathrm{d}x_1 \int_{x_1+d}^{L+\frac{d}{2}-(N-1)d} \mathrm{d}x_2 \ldots \int_{x_{N-1}+d}^{L-d/2} \mathrm{d}x_N$$

transformation $y_k = x_k - x_{k-1} - d$ with $\partial y_k / \partial x_k = 1$

$$= N! \int_0^{L-Nd} \mathrm{d}y_1 \ldots \int_0^{L-Nd} \mathrm{d}y_N \,\{y_1 < \ldots < y_N\}$$

$$= \ldots$$

# Clothes-pin partition function

$$
\begin{aligned}
Z_{\text{pin}}(N, L) &= \\
&= N! \int_0^{L-Nd} \mathrm{d}y_1 \; \ldots \int_0^{L-Nd} \mathrm{d}y_N \, \{y_1 < \ldots < y_N\} \\
&= \ldots
\end{aligned}
$$

# Clothes-pin partition function II

$$Z(N, L) = \begin{cases} (L - d \cdot N)^N & \text{if } L > d \cdot N \\ 0 & \text{otherwise} \end{cases}$$

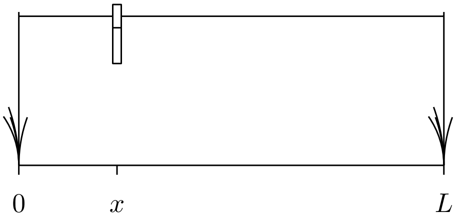
...

# Alg. `direct-pin`

**procedure** `direct-pin`
$\Delta \leftarrow L - d \cdot N$
**for** $k = 1, \ldots, N$ **do**
  $\{ \; \tilde{y}_k \leftarrow \texttt{ran}[0, \Delta]$
$\{y_1, \ldots, y_N\} \leftarrow \texttt{sort}[\{\tilde{y}_1, \ldots, \tilde{y}_N\}]$
**for** $k = 1, \ldots, N$ **do**
  $\{ \; x_k \leftarrow y_k + d/2 + d \cdot (k - 1)$
**output** $\{x_1, \ldots, x_N\}$

- works at any density, without rejections, unlike Alg. `direct-disks`

# computing $\pi(x)$ from partition function $Z(k, x)$

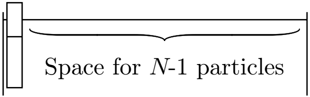


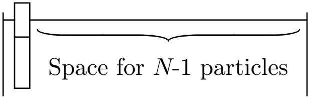

$$\pi(x) = \sum_{k=0}^{N-1} \pi_k(x) =$$

$$= \sum_{k=0}^{N} \frac{1}{Z(N, L)} \binom{N-1}{k} Z(k, x - \frac{d}{2}) Z(N - 1 - k, L - x - \frac{d}{2})$$

- $\pi(x)$ has a strictly constant piece, if $N \cdot d < L/2$!!

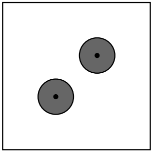
# Depletion interaction

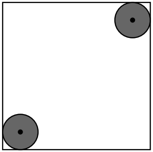


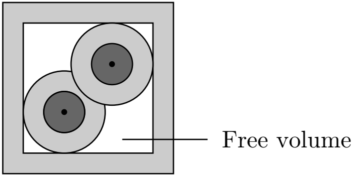

- attractive and repulsive
- two-body interaction only in one dimension

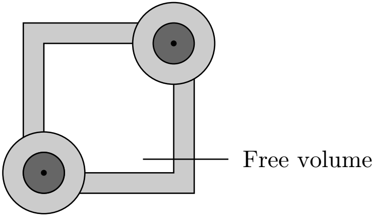
# Analysis of spatial repartition





# Entropic Attraction



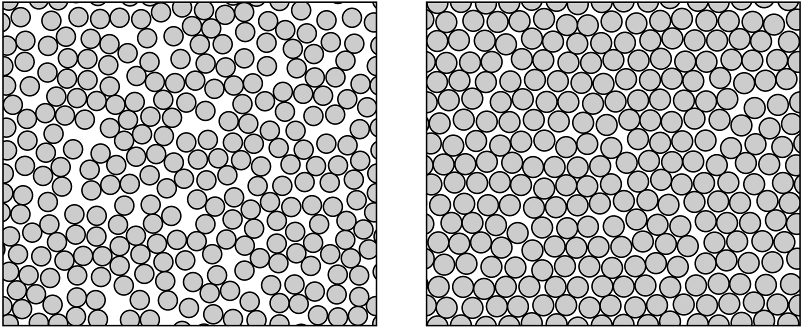
# Depletion interaction

- Asakura-Oosawa ‘depletion’ interaction
- of fundamental importance in soft condensed matter (polymers, colloids etc)
- underlies liquid-solid phase transition in hard spheres
- ... and phase-separation transition in binary mixtures

**The hard sphere paradox**

Hard spheres are not inpenetrable ?!?!?!?

# Large systems of hard spheres



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

# Binary mixtures