

## Harmonic properties of hard-sphere crystals: a one-dimensional study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys. A: Math. Gen. 26 4819

(<http://iopscience.iop.org/0305-4470/26/19/015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.68

The article was downloaded on 01/06/2010 at 19:41

Please note that [terms and conditions apply](#).

# Harmonic properties of hard-sphere crystals: a one-dimensional study

J Piasecki† and L Peliti‡§

†Institute of Theoretical Physics, Warsaw University – Hoza 69, PL-00-681 Warsaw, Poland

‡Institut Curie – Section de Physique et Chimie, Laboratoire Curie – 11, rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France

Received 21 January 1993

**Abstract.** We show that the hard rod fluid in one dimension behaves like a harmonic crystal when the high density limit is suitably defined. We highlight analogies and differences with analogous results for hard-sphere solids in higher dimensions.

## 1. Introduction

We describe an interesting analogy in the behaviour of two apparently very different systems: a hard rod fluid in one dimension and a linear chain of harmonically coupled particles. The idea was sparked by the study of the results of D Young and B Alder on distribution functions for hard-sphere solids (Young and Alder 1974). They had indeed discovered that, in the high density limit, the singlet distribution acquired a Gaussian form, like the one for harmonic oscillators. The similarity between a hard-sphere crystal and a harmonic one appeared most clearly near the closest packing density. In this paper we show that this Gaussian property also holds in *one dimension*, if one considers a suitably defined high density limit.

Hard rods (one-dimensional hard spheres) are supposed to have length  $\sigma$  and to be enclosed in a volume  $L$  (figure 1). The particles cannot penetrate each other. Their linear order is preserved by the dynamics. The motion between hard elastic collisions is free. Hence, the probability density of a given configuration  $(x_1, x_2, \dots, x_N; L, N, \sigma)$  of  $N$  identical particles is given by

$$\rho_N(x_1, x_2, \dots, x_N; L, N, \sigma) = \theta(x_1 + \frac{1}{2}(L - \sigma)) \left[ \prod_{i=2}^N \theta(x_i - x_{i-1} - \sigma) \right] \theta(\frac{1}{2}(L - \sigma) - x_N) / \Omega(N, L) \quad (1)$$

where

$$\Omega(N, L) = (L - N\sigma)^N / N!. \quad (2)$$

Here  $\theta$  is the unit step function

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0. \end{cases} \quad (3)$$

§ Boursier Henri de Rothschild. On leave of absence from: Dipartimento di Scienze Fisiche and Unità INFN, Università “Federico II”, Mostra d’Oltremare, Pad. 19, I-80125 Napoli (Italy). Associato INFN, Sezione di Napoli.

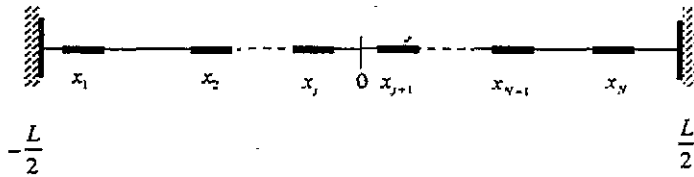


Figure 1. Hard-rod fluid.

It is well known that a one-dimensional hard-rod fluid does not crystallize. It is only when the particles are constrained in a finite volume  $L$  that they fluctuate around well defined mean positions. This situation is forced by the external field represented by the rigid walls defining the volume  $L$ . However, in the thermodynamic limit

$$\lim_{\infty} \equiv \begin{cases} N \rightarrow \infty ; L \rightarrow \infty \\ n = N/L = \text{constant} \end{cases} \tag{4}$$

the rods become entirely delocalized. In fact one can prove (Jepsen 1965, Lebowitz and Percus 1967) that a tagged particle starting from a prescribed initial position follows in the long time limit a Brownian motion. This motion reflects a global diffusive motion of the fluid: since particles cannot penetrate each other, their large-scale displacements involve the whole bulk of the fluid. No trace of localization is left.

One can imagine that the delocalization by diffusion can be compensated by the increase in density. In an arbitrarily large system, if the density is large enough, the rods will be bound to oscillate around well defined mean positions ('lattice sites'). Following this idea we propose to study the limit where the volume  $L$  and the particle number  $N$  tend to infinity in such a way that the number density  $n = N/L$  approaches its closest packing value  $\sigma^{-1}$ . More specifically, we define the high density limit  $\text{LIM}_{\infty \text{HD}}$

by

$$\text{LIM}_{\infty \text{HD}} \equiv \begin{cases} N \rightarrow \infty, L \rightarrow \infty \\ L/N - \sigma = n^{-1} - \sigma = 2\lambda\sqrt{N}. \end{cases} \tag{5}$$

Here  $\lambda$  is a fixed length scale. We let the specific volume approach the closest packing density as the inverse square root of  $N$ , in order to compensate exactly the delocalization induced by the diffusive motion.

In sections 2 and 3 we study the one- and two-particle distributions, respectively, in the asymptotic region (5). It turns out that they look like those characterizing a linear chain of harmonic oscillators. In order to analyse this analogy, we also evaluate the distributions for  $N$  point particles coupled to their nearest neighbours by springs with elastic constant  $k$  (figure 2).

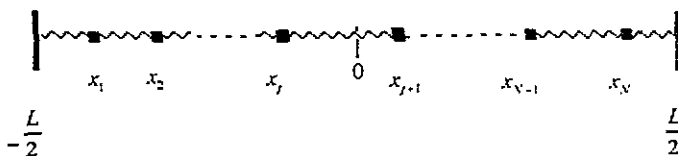


Figure 2. Linear harmonic chain.

The probability density to find the  $N$  oscillators, of elastic constant equal to  $k$ , in a configuration  $(x_1, x_2, \dots, x_N)$  is given, up to a normalizing factor, by the Boltzmann formula

$$\exp\{-\beta U(x_1, x_2, \dots, x_N)\} \quad (6)$$

where  $U$  is the potential energy,  $\beta = 1/k_B T$ ,  $k_B$  is the Boltzmann constant and  $T$  is the temperature. With our assumptions, we have

$$U(x_1, x_2, \dots, x_N) = \frac{k}{2} \left\{ \left( x_1 + \frac{L}{2} \right)^2 + \sum_{j=2}^N (x_j - x_{j-1})^2 + \left( \frac{L}{2} - x_N \right)^2 \right\}. \quad (7)$$

So, the extremities of the chain are attached to the points  $-L/2$  and  $L/2$ , defining the volume  $L$ . All configurations of the oscillating points are allowed:

- linear order is not preserved;
- the particles are free to move outside of the interval  $[-L/2, L/2]$ .

We have set to zero the rest length of the springs, since it would not appear anyway in the formulae defining the one- and two-particle distributions. The rest length would be important in calculations involving the stress acting on the fixed extremities. We shall see in the next section that the oscillators also become delocalized, unless the spring constant  $k$  is taken to diverge proportionally to  $N$ .

We are now ready to investigate the behaviour of both systems.

## 2. One-particle distributions

Let us calculate the probability density  $\rho(x; j)$  for finding the  $j$ th particle at the point  $x$ . Such an event is only possible if the intervals  $[-L/2, x - \sigma/2]$  and  $[x + \sigma/2, L/2]$  are long enough to contain  $(j-1)$  and  $(N-j)$  particles respectively. The formula for  $\rho(x; j)$  can be obtained by a straightforward calculation from equation (1). We find

$$\begin{aligned} \rho(x; j) &= \theta(1 - n\sigma) \theta\left(\frac{L-\sigma}{2} + x + (j-1)\sigma\right) \theta\left(\frac{L-\sigma}{2} - x - (N-j)\sigma\right) \\ &\quad \times \Omega\left(x + \frac{L-\sigma}{2}, j-1\right) \Omega\left(\frac{L-\sigma}{2} - x, N-j\right) / \Omega(N, L), \end{aligned} \quad (8)$$

where the volume  $\Omega$  has been defined in equation (2).

In order to investigate bulk properties we set

$$j = J + (N+1)/2 \quad (9)$$

where we have assumed for convenience that  $N$  is odd. We now focus our attention on the  $J$ th particle counting from the centre (which corresponds to  $J=0$ ).  $J$  is negative on

the left of the centre, and positive on its right. We thus let  $N$  go to infinity, while we keep  $J$  fixed. Combining equations (2), (8), (9), we eventually get

$$\rho(x; J) = \theta \left( \frac{L - N\sigma}{2} - |x - J\sigma| \right) \times \frac{N! [x - J\sigma + (L - N\sigma)/2]^{J + (N-1)/2} [J\sigma - x + (L - N\sigma)/2]^{-J + (N-1)/2}}{[J + (N+1)/2]! [-J + (N+1)/2]! (L - N\sigma)^N}. \quad (10)$$

The evaluation of the limit (5) yields the simple result

$$\lim_{\infty} \rho_{\text{HD}}(x; J) = \frac{1}{\lambda\sqrt{2\pi}} \exp\{- (x - J\sigma)^2 / 2\lambda^2\}. \quad (11)$$

Equation (11) shows that in the asymptotic region (5) the particles remain localized even in the infinite volume limit. The limit (5) has thus properly compensated the effect of diffusion. It is remarkable that we here obtain a Gaussian distribution, despite the fact that the motion of hard rods between collisions is free. If one tries to introduce an effective potential one has to choose the harmonic one. As has already been mentioned in the introduction, the appearance of a Gaussian distribution could be expected on the basis of molecular dynamics calculations (Young and Alder 1974). The limit (5) allows one to derive analytically this interesting property in one dimension.

In order to develop the analogy with the harmonic chain let us now evaluate the probability density  $P(x; j)$  for finding the  $j$ th oscillator in position  $x$ . The calculation is straightforward, since it involves only Gaussian integrals (see equations (6), (7)). We obtain

$$P(x; j) = \left( \frac{\beta k(N+1)}{2\pi j(N+1-j)} \right)^{1/2} \exp\left\{ -\frac{\beta k}{2} \frac{(N+1)}{j(N+1-j)} (x - \bar{x}_j)^2 \right\} \quad (12)$$

where

$$\bar{x}_j = \left( \frac{2j}{N+1} - 1 \right) \frac{L}{2} \quad (13)$$

is the equilibrium position of point  $j$ , for which one has

$$\left. \frac{\partial U}{\partial x_j} \right|_{(\bar{x}_1, \bar{x}_2, \dots, \bar{x}_N)} = 0 \quad j = 1, 2, \dots$$

Letting again  $j = J + (N+1)/2$  (see equation (9)), we find for the oscillator in the bulk the law

$$P(x; J) = \left[ \frac{\beta k}{2\pi} \frac{N+1}{((N+1)/2)^2 - J^2} \right]^{1/2} \exp\left\{ -\frac{\beta k}{2} \frac{N+1}{((N+1)/2)^2 - J^2} (x - \bar{x}_J)^2 \right\} \quad (14)$$

where  $\bar{x}_J = JL/(N+1)$ .

Let us first remark that the oscillators become delocalized in the thermodynamic limit (4). This happens because the effective spring constant determining the amplitude of the forces which act on a given particle decreases as  $N^{-1}$  (see equation (12)). Particles are thus more and more weakly bound and can fluctuate over larger and

larger distances. In order to maintain the localization we must then combine the thermodynamic limit with a suitable rescaling of the elastic constant:  $k = N\kappa$ . We can thus define the strong coupling limit

$$\text{LIM}_{\infty}^{\text{SC}} = \begin{cases} N \rightarrow \infty, L \rightarrow \infty \\ n = N/L = \text{constant}, k = N\kappa. \end{cases} \quad (15)$$

We thus obtain the asymptotic form of equation (14):

$$\text{LIM}_{\infty}^{\text{SC}} P(x; J) = \sqrt{\frac{2\beta\kappa}{\pi}} \exp\{-2\beta\kappa(x - J/n)^2\}. \quad (16)$$

Equations (16) and (11) establish the analogy in the behaviour of hard rods and harmonic oscillators in the high density and strong coupling limits respectively. (Notice that  $\sigma$  in equation (11) can be replaced by  $n^{-1}$  for  $N \rightarrow \infty$ , since  $n^{-1} - \sigma = 2\lambda/\sqrt{N}$ .)

### 3. Two-particle distributions

Although the hard rod fluid performs a Brownian motion as a whole, the fluctuations of the distance between a pair of particles are governed by a well defined distribution in the thermodynamic limit. This reflects the fact that, owing to the impenetrability of the rods, the fluid formed from them is a strongly bound system.

We begin by calculating the conditional probability density  $\rho_{11}(y; l|x; j)$  to find particle  $l = j + r$ ,  $r = 1, 2, \dots$  at point  $y$  provided that particle  $j$  stands at point  $x$ . Fixing the position of particles  $j$  and  $l = j + r$  divides the volume  $L$  into three subvolumes  $[x + (L - \sigma)/2]$ ,  $[y - x - \sigma]$ , and  $[(L - \sigma)/2 - y]$ , respectively containing  $(j - 1)$ ,  $(r - 1)$ , and  $(N - j - r)$  particles. Therefore, the joint probability density for finding particle  $(j + r)$  at point  $y$  and particle  $j$  at point  $x$  will be given by the product of the three  $\theta$  functions for the intervals:

$$\theta\left(x + \frac{L - \sigma}{2} - (j - 1)\sigma\right) \theta(y - x - r\sigma) \theta\left(\frac{L - \sigma}{2} - y - (N - j - r)\sigma\right)$$

times the statistical weight

$$\Omega\left(j - 1, x + \frac{L - \sigma}{2}\right) \Omega(r - 1, y - x - \sigma) \Omega\left(N - j - r, \frac{L - \sigma}{2} - y\right) / \Omega(N, L). \quad (17)$$

We again situate particle  $j$  in the bulk by introducing  $J$  (equation (9)), and dividing by the one-particle density (8) we obtain the conditional probability density:

$$\begin{aligned} \rho_{11}(y; J+r|x; J) &= \theta\left(\frac{L-N\sigma}{2} + x - J\sigma\right) \theta(y-x-r\sigma) \theta\left(\frac{L-N\sigma}{2} + (J+r)\sigma - y\right) \\ &\times \frac{(y-x-r\sigma)^{r-1} \left[\frac{L-N\sigma}{2} + (J+r)\sigma - y\right]^{-J-r+(N-1)/2}}{(r-1)! \left(-J-r+\frac{N-1}{2}\right)!} \\ &\times \frac{\left(-J+\frac{N-1}{2}\right)!}{\left[\frac{L-N\sigma}{2} - x + J\sigma\right]^{-J+(N-1)/2}}. \end{aligned} \quad (18)$$

The thermodynamic limit can be readily calculated, yielding

$$\begin{aligned} \lim_{\infty} \rho_{11}(y; J+r|x; J) &= \theta(y-x-r\sigma) \\ &\times \frac{1}{(r-1)!} \left[\frac{n}{1-n\sigma}(y-x-r\sigma)\right]^{r-1} \exp\left\{-\frac{n}{1-n\sigma}(y-x-r\sigma)\right\}. \end{aligned} \quad (19)$$

The distribution of  $(y-x-r\sigma)$  follows therefore a  $\chi^2$  law with  $r$  degrees of freedom, and approaches a Gaussian when  $r$  becomes large (Abramowitz and Stegun 1964). Equation (19) could be derived in fact by considering the distribution of hard rods close to the boundary. Indeed, when calculating the conditional probability density  $\rho_{11}(y; J+r|x; J)$  we fix the position of particle  $J$  which plays the role of an impenetrable wall of particle  $(J+r)$ . In the high density limit we simply find

$$\text{LIM}_{\text{HD}} \rho_{11}(y; J+r|x; J) = \delta(y-x-r\sigma), \quad (20)$$

where  $\delta$  is Dirac's distribution. Therefore, in the limit (5), hard rods behave like a rigid body, subject however to Gaussian fluctuations (11). The asymptotic form of the joint probability density for finding particle  $J$  at  $x$  and particle  $(J+r)$  at  $y$  is thus given by

$$\frac{1}{\lambda\sqrt{2\pi}} \exp\left\{-\frac{(x-J\sigma)^2}{2\lambda^2}\right\} \delta(y-x-r\sigma). \quad (21)$$

In the case of the harmonic chain the calculation of the conditional probability density  $\rho_{11}(y; J+r|x; J)$  is straightforward. We thus give directly the result after the thermodynamic limit has been taken:

$$\lim_{\infty} \rho_{11}(y; J+r|x; J) = \sqrt{\frac{\beta k}{2\pi r}} \exp\left\{-\frac{\beta k}{2r}\left(y-x-\frac{r}{n}\right)^2\right\}. \quad (22)$$

The result is finite because the spring coupling particles  $J$  and  $(J+r)$  does not weaken

in the thermodynamic limit, maintaining a constant effective elastic coefficient ( $k/r$ ). Again, the strong coupling limit (15) leads to a rigid-body-like behaviour:

$$\text{LIM}_{\text{SC}} \rho_{11}(y; J+r|x; J) = \delta(y-x-r/n). \quad (23)$$

The system keeps however oscillating as a whole according to the distribution (16).

Equations (11), (16), (20), and (23) show a complete analogy in the behaviour of a hard rod fluid in the high density limit (5), and of a linear oscillator chain in the strong coupling limit (15).

#### 4. Concluding remarks

The most interesting result presented in this note is contained in equation (11). Considering the *high density limit* (5), we found a Gaussian distribution of hard rods around their mean positions. Molecular dynamics simulations (Young and Alder 1974) indicate that the same phenomenon should be observed in the *thermodynamic limit* at high solid state densities. In the same limit, the two-point correlation function acquires a  $\chi^2$  form, which becomes practically indistinguishable from a Gaussian (by the central limit theorem) when  $r$  is of the order of 30 (Abramowitz and Stegun 1964). Even at smaller values of  $r$ , the low moments of the distribution are close to the corresponding Gaussian values. There is therefore a whole range of densities where the pure excluded volume effect leads to harmonic-like behaviour. It is likely that this phenomenon may be traced back to the numerous collisions experienced by any particle with its neighbours at high densities, which make its position become the sum of a great number of small displacements. A somewhat analogous property pertains to concentrated polymer solutions. When the concentration of polymers increases the distribution of the conformation becomes Gaussian (Flory 1949, see also de Gennes 1979, p. 54ff). The ingredients leading to this behaviour are the Brownian motion of the chains and the excluded volume interactions among the monomers. The chains turn out to be Gaussian since each monomer evolves in the effective field created by the monomers belonging to all *different* chains. Thus the appearance of Gaussian distributions is due to the same mechanism which is responsible for the central limit theorem.

#### Acknowledgment

J P thanks professor D Levi for his hospitality at the Dipartimento di Fisica, Università 'La Sapienza', Rome, where part of this work was done.

#### References

- Abramowitz M and Stegun I E *Handbook of Mathematical Functions*, Applied Mathematics Series, vol. 55 (Washington: National Bureau of Standards) § 26.4, p. 940ff
- de Gennes P-G 1979 *Scaling Concepts in Polymer Physics* (Ithaca and London: Cornell University Press)
- Flory P 1949 *J. Chem. Phys.* **17** 303
- Jepsen D W 1965 Dynamics of a simple many-body system of hard rods *J. Math. Phys.* **6** 405-13
- Lebowitz J L and Percus J K 1967 Kinetic equations and density expansions: Exactly solvable one-dimensional systems *Phys. Rev.* **155** 122-38
- Young D A and Alder B J 1974 Studies in molecular dynamics. XIII. Singlet and pair distribution functions for hard-disk and hard-sphere solids *J. Chem. Phys.* **60** 1254-67