



ELSEVIER

Physica A 287 (2000) 100–104

PHYSICA A

www.elsevier.com/locate/physa

# Crystallization of hard spheres under gravity

Yan Levin\*

*Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051,  
CEP 91501-970, Porto Alegre, RS, Brazil*

Received 24 July 2000

---

## Abstract

We present a simple argument to account for crystallization of hard spheres under the action of a gravitational field. The paper attempts to bridge the gap between two communities of scientists, one working on granular materials and the other on inhomogeneous liquid state theory. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 64.60.-i; 68.45.-v; 05.20-y

---

## 1. Introduction

Sedimentation of colloidal particles in a gravitational field has been the subject of continued interest since the early work of Jean Perrin. The external gravitational field breaks the translational symmetry, producing an altitude-dependent density profile. For a dilute suspension in which the interactions between the colloidal particles can be neglected, the density profile takes a simple exponentially decreasing form. In fact, it was this observation which had first allowed Perrin in 1910 to obtain an estimate of the Avogadro number and the Boltzmann constant [1]. This early work has stimulated much of the modern development of inhomogeneous fluid theory.

A few years ago it was observed in Monte Carlo simulations that a system of hard spheres can become unstable under the action of a sufficiently strong gravitational field [2]. This instability appeared as a sudden crystallization of the bottom layers of the sample confined to a three-dimensional rectangular box. In order to understand this transition the authors appealed to the weighted density functional theory (WDF). Unfortunately, the WDF is quite computationally demanding and is not very physically

---

\* Fax: +55-51-319-1762.

E-mail address: levin@if.ufrgs.br (Y. Levin).

transparent. Perhaps it is for this reason that this work went unnoticed by the community of physicists studying granular materials [3,4]. Thus, the fluid–solid condensation under the gravitational field has been recently rediscovered in the context of granular materials. Here the instability appeared as the break down of the Enskog kinetic theory for elastic hard spheres [5], which Hong associated with the formation of a solid layer at the bottom of a sample [3,4]. However, we must stress that the identification of the break down point of the Enskog equation with crystallization is far from obvious. In particular, it is possible to show that at equilibrium the Enskog theory is equivalent to the local density approximation (LDA) [3,4]. Within the liquid state theory it is well known that the LDA cannot be used to obtain reliable information about the fluid–solid coexistence. The reason for this is that the LDA fails to account for strong density variations in a highly structured phase, such as the solid [6–8]. Furthermore, in the absence of an external field, the LDA for hard spheres is reduced to the usual Carnahan–Starling equation of state [9], which carries no information about the entropy driven crystallization of a homogeneous hard sphere fluid. Therefore, it is difficult to understand how a theory which knows absolutely nothing about the existence of an instability in a homogeneous system, suddenly develops this “knowledge” in the presence of a gravitational field. Thus, it is dubious that the break down of the LDA – and, therefore, of the Enskog theory – can be associated with a phase transition, and not with the failure of the approximations underlying the theory.

In view of all this, it seems worth while to present a simple argument to account for crystallization of hard spheres under the action of an external gravitational field.

## 2. Lattice gas in a gravitational field

Before entering into the discussion of a phase transition in the system of hard spheres, we shall explore a much simpler model of fluid and granular matter [10] in a gravitational field – a non-interacting lattice gas. Consider a three-dimensional rectangular volume  $V = L^2H$ , divided into cubic cells of volume  $a^3$ . Each cell can be occupied by at most one “cubic” particle of mass  $m$  and volume  $a^3$  equal to that of a unit cell. The constant gravitational field of strength  $g$  acts in the  $-z$  direction. Since the particles do not interact, in the thermodynamic limit, it is a simple matter to write an exact Helmholtz free energy functional,

$$\frac{\beta a^2 F[\sigma(z)]}{L^2} = \sum_{z=0}^{\infty} \{ [1 - \sigma(z)] \ln [1 - \sigma(z)] + \sigma(z) \ln \sigma(z) + \beta m a g z \sigma(z) \}, \quad (2.1)$$

where  $\beta = 1/k_B T$ , and  $\sigma(z)$  is the average occupation of the row  $z$ . The equilibrium density profile can be obtained by minimizing the functional (2.1), subject to the constraint of conservation of the total number of particles  $N$ ,

$$\sum_{z=0}^{\infty} \sigma(z) = N a^2 / L^2 \equiv n. \quad (2.2)$$

Performing a simple calculation we find

$$\sigma(z) = \frac{1}{1 + e^{\beta m g z + \beta \mu}}, \quad (2.3)$$

where the chemical potential  $\mu$  is the Lagrange multiplier associated with constraint (2.2). It is convenient to define the reduced parameters,  $\beta^* = \beta m g a$  and  $\mu^* = \mu / m g a$ . In the limit  $-\beta \mu \gg 1$  the reduced chemical potential is very well approximated by  $\mu^* = -n$ . The density profile now takes a particularly simple form

$$\rho(z) = \frac{m}{a^3} \frac{1}{1 + e^{\beta^*(z-n)}}. \quad (2.4)$$

On the other hand, the static pressure inside the lattice gas satisfies,

$$\frac{dP(z)}{dz} = -g a \rho(z), \quad (2.5)$$

where to simplify the calculations we have passed to the continuum limit. Eq. (2.5) can now be integrated yielding

$$P(z) = \frac{m g}{a^2} \left( n + \frac{\ln[1 + e^{\beta^*(z-n)}]}{\beta^*} - z \right). \quad (2.6)$$

We note that the pressure is a uniformly decreasing function of the height  $z$ . At high altitudes – where the average density is small and the excluded volume constraint is irrelevant – the density profile reduces to the exponentially decreasing form first obtained by Perrin.

### 3. The hard sphere fluid in the gravitational field

It is evident from the analytic expressions derived above that the lattice gas – in spite of its hard core repulsion expressed through the constraint of one particle per lattice site – is completely stable for all temperatures. It is reasonable to suppose that to zeroth order the density profile of a hard sphere fluid in a gravitational field should also be well approximated by Eq. (2.4). In fact, it has been found that the Fermi-like distribution (2.4), provides an excellent fit for various granular materials including the hard spheres [11,12].

Unlike the non-interacting lattice gas, the homogeneous system of hard spheres is known to undergo a structural fluid–solid transition [13] when the bulk pressure reaches  $P_b \approx 12k_B T/a^3$ . This entropic transition was first observed in Monte Carlo simulations almost half a century ago [14], and has since been confirmed by various theoretical methods [7,8,15,16]. In the presence of a gravitational field the pressure inside the suspension varies uniformly with maximum value located at  $z=0$ . In the limit  $\beta^* n \gg 1$ , the pressure at the bottom is well approximated by  $P(0) = m g n / a^2$ . Therefore, the first layer will crystallize when

$$P(0) = \frac{m g n}{a^2} \approx \frac{12 k_B T}{a^3} \quad (3.1)$$

or when

$$T < T_c = \frac{m g a n}{12 k_B}. \quad (3.2)$$

This is a discontinuous first-order transition. If the temperature is lowered further, additional fluid layers will solidify and a growing crystal will coexist with a diminishing fluid phase. The number of layers in the crystal can be determined by comparing  $P(z)$  with  $P_b$ . We note that in the region of phase transition,

$$\beta^* n \approx -\beta^* \mu^* \approx 12 \gg 1, \quad (3.3)$$

so that all the approximations adopted above are indeed justified.

We have presented a simple argument for crystallization of hard spheres in a gravitational field. This transition is nothing more than a realization of the well-known entropically driven liquid–solid phase separation of a homogeneous hard sphere fluid. The presence of a gravitational field leads to an altitude-dependent pressure, which increases with the depth of suspension. If the temperature is reduced below the critical value  $T_c$ , the pressure on the bottom layers becomes so large as to lead to their crystallization.

A comment should be made about the real granular materials. For macroscopic particles, temperature is an irrelevant parameter. Thus, in order to study dynamic equilibrium or steady-state, kinetic energy must be supplied to the system through, say, a vibrating bed [12]. If the collisions between the particles are elastic, in the disordered (fluid) state, then we can think of the kinetic energy as a form of “temperature”. Appealing to the same argument as above, we reach the conclusion that the granular materials also undergo phase separation under the action of a gravitational field. However, some care must be taken with this argument. It is well known that unlike for fluids, the pressure inside a container filled with packed granular matter saturates at some value [17]. The excess pressure is transferred to the walls and is equilibrated by friction forces. At high packing fractions, where the solidification takes place, the stress is not uniform but is concentrated along force lines. This unusual characteristics can significantly affect the location of the phase transition in real granular materials.

## Acknowledgements

I would like to acknowledge many interesting conversations with J. Arenzon. This work was supported in part by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Financiadora de Estudos e Projetos (FINEP).

## References

- [1] J. Perrin, *J. Phys.* 9 (1910) 5.
- [2] T. Biben, R. Ohnesorge, H. Löwen, *Europhys. Lett.* 71 (1993) 665.
- [3] D.C. Hong, *Physica A* 271 (1999) 192.

- [4] P.V. Quinn, D.C. Hong, cond-mat/0005196.
- [5] D. Enskog, K. Sven, Vetenskapsakad Handl. 63 (1922) 5.
- [6] S. Nordholm, M. Johnson, B.C. Freasier, Aust. J. Chem. 33 (1980) 2139.
- [7] P. Tarazona, Phys. Rev. A 31 (1985) 2672.
- [8] P. Tarazona, Mol. Phys. 52 (1984) 81.
- [9] N.F. Carnahan, K.E. Starling, J. Chem. Phys. 51 (1969) 635.
- [10] M. Sellitto, J.J. Arenzon, unpublished.
- [11] H. Hayakawa, D.C. Hong, Phys. Rev. Lett. 78 (1997) 2764.
- [12] E. Clement, J. Rajchenbach, Europhys. Lett. 16 (1991) 133.
- [13] D. Chandler, unpublished.
- [14] B.J. Alder, Wainwright, J. Chem. Phys. 27 (1957) 1208.
- [15] T.V. Ramakrishnan, M. Yussouff, Phys. Rev. B 19 (1979) 2775.
- [16] M. Baus, J.L. Colot, Molecular Phys. 55 (1985) 653.
- [17] D.E. Wolf, P. Grassberger (Eds.), Friction, Arching, Contact Dynamics, World Scientific, Singapore, 1997.