HAL
open science

Distance Geometry: A Viewing Help for the Solid-Liquid Phase Transition in Small Systems

Pierre Labastie

To cite this version:

Pierre Labastie. Distance Geometry: A Viewing Help for the Solid-Liquid Phase Transition in Small Systems. 2009. hal-00365515

HAL Id: hal-00365515

https://hal.science/hal-00365515

Preprint submitted on 3 Mar 2009

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distance Geometry: A Viewing Help for the Solid–Liquid Phase Transition in Small Systems

P. Labastie

Université de Toulouse, CNRS, UPS,

Laboratoire Collisions Agrégats Réactivité,

*IRSAMC; F-31062 Toulouse, France**

(Dated: March 3, 2009)

Abstract

Distance geometry is the study of the arrangements of points in space using only the mutual distances between them. The basic idea in this letter is to use distance geometry for thermodynamics studies of small clusters in the microcanonical ensemble. There are constraints on these distances, which are shown to explain some characteristic features of the caloric curve in very small clusters containing 3 or 4 atoms. We anticipate that this approach could give a novel insight into the phase transitions in larger clusters as well. During these studies, we have established a very general and rather simple result for the Jacobian determinant of the change of variables from Cartesian coordinates to mutual distances, which is of wide applicability in the N–body problem.

PACS numbers: 36.40.Ei, 64.70.dm, 05.20.Gg, 82.60.Qr

It is well known that most of the tractable problems of physics are such because there exist a "good" choice of variables, which drastically simplifies equations to be solved. Such a good change of variable has not been found yet for the N–body problem. Actually, for computational purposes, it has been agreed that the Cartesian coordinates are the less expensive coordinates because of the simplicity of the equations of motions when written in terms of them, at least in classical mechanics. On the other hand, those coordinates introduce unnecessary invariance (the euclidean group), while physics describes mainly interactions between systems characterized by their relative position. In this respect, mutual distances should be enough to describe all physical processes. Another reason for considering mutual distances as variables is the simplicity of the potential energy when written in terms of them. It might thus be worth the try to go as far as possible with these variables in the studies of model systems described by pair potential. The work in this letter is a start in this direction and primarily of exploratory nature. It aims at bringing attention to some remarkable results (the simplicity of the Jacobian of the transformation from Cartesian coordinates to mutual distances) and to the ease of representation given by these variables.

Mutual distances have been considered by Lagrange in his study of the 3-body problem. Several formulas for expressing various quantities of the system as a function of distances alone are known. The basic reference for these is Blumenthal's book [1]. A more modern account is given in chapter 4 of [2]. Note that distance geometry is an invaluable tool in the study of protein conformation, where the problem is to determine all the distances between a set of atoms, knowing just a few of them, as given by NMR or X-ray studies [3, 4].

Several new directions can be explored and some results will be presented in forthcoming publications. In this letter, this change of variable is applied to the computation of the configurational density of states (CDOS) of a small cluster of N atoms interacting by a pair potential, in a D dimensional space for the special cases $N = D$ or $N = D + 1$. In both cases, the number of distances is equal to the number s of independent variables specifying a configuration: $s = DN - D(D+1)/2$. Note that for $N > D+1$, one has to choose a subset of the distances as internal variables, which introduces technical complexities not usefull for the purpose of this letter. The general case will be presented in a forthcoming publication[5]. The CDOS is the fundamental quantity in classical thermodynamics. Its computation involves an s-dimensional integral. We show below that, when mutual distances are used as variables for an $N = D$-atom clusters, this s-dimensional integral can be approximately reduced to s

convolution products. This reduction is even exact at low energy. In any case, it is much easier to compute than an s-dimensional integral.

The $N = D = 3$ case is especially interesting because it is possible to draw a representation of the constant energy surface in the distance space. The accidents of the density of states as a function of energy (or rather of its logarithm, the entropy $S(E)$) can be visualized and given a simple interpretation on this drawing. It is well known that accidents of $S(E)$ are related to so-called phase transitions in clusters [6, 7, 8, 9]. The solid–liquid transition (actually a phenomenon akin to this transition) has been observed both in simulations [6, 10, 11] and in experiments [12, 13, 14, 15, 16, 17]. We anticipate that the simple view given in this letter could be used in understanding the solid–liquid transition in larger clusters as well.

This letter is organized as follows. First, we recall the formulas for the microcanonical thermodynamics of a set of atoms and the definition of the CDOS. Then, we make some considerations on the change of variables, and give the (very simple in our case) formula for the Jacobian determinant. We next give some properties of the space of distances. We then present drawings of the constant energy surface in this space in the case of $N = 3$ and explain the qualitative features of the entropy curve. Finally, we show how the CDOS can be expressed as a convolution product and present a comparison with more conventional calculations.

In the microcanonical ensemble, the system size (volume V, number of constituents N) and energy E are fixed. The fundamental function is the density of states $\Omega(E, V, N)$. It exists for any finite system with a classical Hamiltonian $H(\mathsf{P}, \mathsf{X})$. Here, the notation X represents the set of Cartesian coordinates of the constituents and P the corresponding momenta. The Hamiltonian H is the sum of the kinetic energy $T(\mathsf{P})$ and the potential energy $E_p(\mathsf{X})$, so that the density of states is actually the convolution of the kinetic density of states and the configurational density of states $\Omega_c(E, V, N)$

$$\Omega_c(E, V, N) = \frac{\partial}{\partial E} \int_{E_p(\mathsf{X}) \leq E} \mathrm{d}^{3N}\mathsf{X}. \tag{1}$$

Since the kinetic density of state can be computed analytically, the configurational density of state is the quantity we focus on. The configurational entropy $S_c(E)$ is defined by Boltzmann formula

$$S_c(E, V, N) = k_B \ln \Omega_c(E, V, N), \tag{2}$$

with k_B the Boltzmann constant. In the remaining of the paper, the configurational entropy will be called just entropy for short.

It can be shown [18] that, under mild conditions on the potential energy function $E_p(\mathsf{X})$, the entropy is extensive in the thermodynamic limit, and that in this limit, the second derivative of the entropy is always negative. This is not true in a finite system: the entropy is not extensive because surface effects are important, and furthermore it can show portions of positive curvature, which are the accidents of the CDOS we mentioned above.

We now describe shortly the change of variables from Cartesian coordinates to mutual distances. The Cartesian coordinates of an atom a, $(a = 1 \dots N)$, are noted x_{ia}, $(i = 1 \dots D)$. Rather than the distances, it is more convenient to define the variables y_{ab} by

$$y_{ab} = \sum_{i=1}^{D} \frac{(x_{ia} - x_{ib})^2}{2}. \tag{3}$$

When going from Cartesian coordinates to internal coordinates, one should define a "moving frame" (see for example Ref. 19). Amazingly enough, the Jacobian determinant for the transformation does not depend on this choice. We suppose that the cluster is contained in a (hyper)spherical volume of radius R, with the center of mass fixed at the center of the sphere. This eliminates the need to integrate on the translation degrees of freedom. The integration on the rotation coordinates gives a constant irrelevant multiplicative factor, the volume of the group $SO(D)$, noted $\mathcal{V}_{\text{rot}}$. Eventually, it can be shown that the configurational volume element can be written

$$\int_{\text{rotation}} \prod_{i,a} \mathrm{d}x_{ia} = \mathcal{V}_{\text{rot}}\, \mathcal{J} \prod_{1 \le a < b \le N} \mathrm{d}y_{ab}, \tag{4}$$

with $\mathcal{J} = 1$ if $N = D$ and $\mathcal{J} = 1/V$ if $N = D+1$, where V is the volume of the parallelotope built on the $D+1$ points. This volume can be computed as the square root of a determinant involving the y_{ab}'s only [1]:

$$V^2 = -\det \begin{vmatrix} 0 & 1 & 1 & 1 & \cdots & 1 \\ 1 & 0 & -y_{12} & -y_{13} & \cdots & -y_{1N} \\ 1 & -y_{12} & 0 & -y_{23} & \cdots & -y_{2N} \\ 1 & -y_{13} & -y_{23} & 0 & \cdots & -y_{3N} \\ \vdots & \vdots & \vdots & -\vdots & \ddots & \vdots \\ 1 & -y_{1N} & -y_{2N} & -y_{3N} & \cdots & 0 \end{vmatrix}. \tag{5}$$

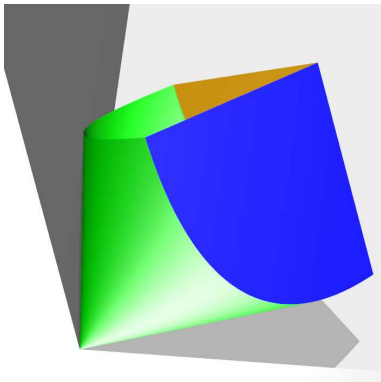

FIG. 1: (color on line) The distance space for $N = 3$ atoms. The axes for the coordinates (y_{12}, y_{13}, y_{23}) are shown by the intersection of two planes. An acceptable point can only be inside the cone. Furthermore, if the cluster is contained in a sphere, the accessible space is further limited by 3 planes, which interset on the $(1, 1, 1)$ direction. On the figure, one of the planes has been made transparent in order to show the cone interior.

Let us now think of the set of distances y_{ab} as defining the Cartesian coordinates of a point in an abstract space $\mathcal{D}$, which we call the 'Distance Space'. There are several conditions to be verified by this point. They amount to ensure that all the determinants similar to that of Eq. (5), for any subset of the N atoms, are positive. It can be shown (see e.g. Ref. 2) that these conditions restricts the representative point in the distance space to be inside a convex cone. In other words, $\mathcal{D}$ is a space with a frontier.

We have not yet included the condition that the atoms are confined inside a sphere of radius R. Actually, the distance r_a^2 from atom a to the center of mass can be expressed in terms of the y variables alone:

$$r_a^2 = \frac{2}{N^2}\left[(N-1)\sum_{b\neq a} y_{ab} - \sum_{\substack{b<c \\ b,c\neq a}} y_{bc}\right]. \tag{6}$$

Imposing that $r_a^2 \leq R^2$ amounts to adding the further constraints that the distance space is limited by a set of N (hyper)planes. Those planes, together with the cone defined above define a finite volume in the distance space. Figure 1 shows a view of the cone and the planes in the case $N = 3$.

Now, What is the shape of the constant energy surface (CES) in distance space? We suppose that the potential is $E_p = \sum_{a\neq b} v(y_{ab})$, where $v(y)$ has the usual shape of a pair potential: one minimum at $y = 1$ with value -1, the limit when $y \to \infty$ is 0 (that is the

dissociation energy is 1) and the limit when $y \to 0$ is $+\infty$. The CES in the case $N = 3$ is shown in the insets of Fig. (2). At low energy (inset (a), $E_p = 0.2$), the surface is close to a spheroid around the absolute minimum of the potential energy, which is $y_{12} = y_{13} = y_{23} = 1/2$. Notice that this surface is far from the limiting cone. At higher energy (inset(b), $E_p = 0.5$), the surface becomes elongated in the direction parallel to the (distance) axes. More precisely, it is easy to see that the intersection of the surface with the axis $y_{12} = y_{13} = 1/2$ for example, occurs for y_{23} such that $v(y_{23}) = E_p$. This value of y_{23} increases rapidly with increasing E_p. There is of course a symmetry between the three axes. On the other hand, at direction 45° from the axes, the maximum value of the y's is such that $v(y) = E_p/2$, which is much closer to the point $(1/2, 1/2, 1/2)$. At an energy close to 1, the shape is that of 3 "tentacles" along the directions parallel to the axis, and the surface reaches the enclosing cone for $E_p \simeq 0.969$ (inset (c)). This last value is specific of the Lennard-Jones potential; it is always very close to one for any potential. For $E > 1$ (inset (d)), the CES is open. However, the volume inside the cone is still finite. The configurational entropy is shown on the same figure. At low energy, $S_c(E) \propto \ln(E)$, which is the usual behavior. At higher energy, the entropy departs from the logarithm, and would even diverge when $E \to 1$ (the dashed curve). However, the limitation imposed by the cone results in a discontinuity of the slope when the CES meets the cone. It is important to understand that there is a balance between the tendency of the pair potential to allow a distance to become large, which results in a positive curvature of $S_c(E)$, and the limitation of pure geometric nature due to the limiting cone, which bends in the negative direction. Such "bumps" of the entropy curve are characteristic of a phase transition in a finite system. We give here a new geometric view of what happens, at least in this simple system.

Let us now compute the CDOS. The simplest case is $N = D$. When $\epsilon < 1$, the equation $v(y) = \epsilon$ has two solutions, which we denote $y_{\max}(\epsilon)$ and $y_{\min}(\epsilon)$. When $\epsilon \to 1$, $y_{\max} \to \infty$ and disappears for $\epsilon > 1$, while $y_{\min}$ exists for any value of epsilon. To begin with, we forget about any constraint on the distances, and we suppose that $N = D$. It is easy to see that the CDOS can be written in this case

$$\Omega_c(E) = \int_{\sum_{i=1}^{s} \epsilon_i = E} \left[\prod_{i=1}^{s} \omega(\epsilon_i)\, \mathrm{d}\epsilon_i \right], \tag{7}$$

$$\text{with} \qquad \omega(\epsilon) = \frac{\mathrm{d}}{\mathrm{d}\epsilon}[y_{\max}(\epsilon) - y_{\min}(\epsilon)]. \tag{8}$$

Such an integral amounts to $s - 1$ convolutions. If the function ω is given on n points,

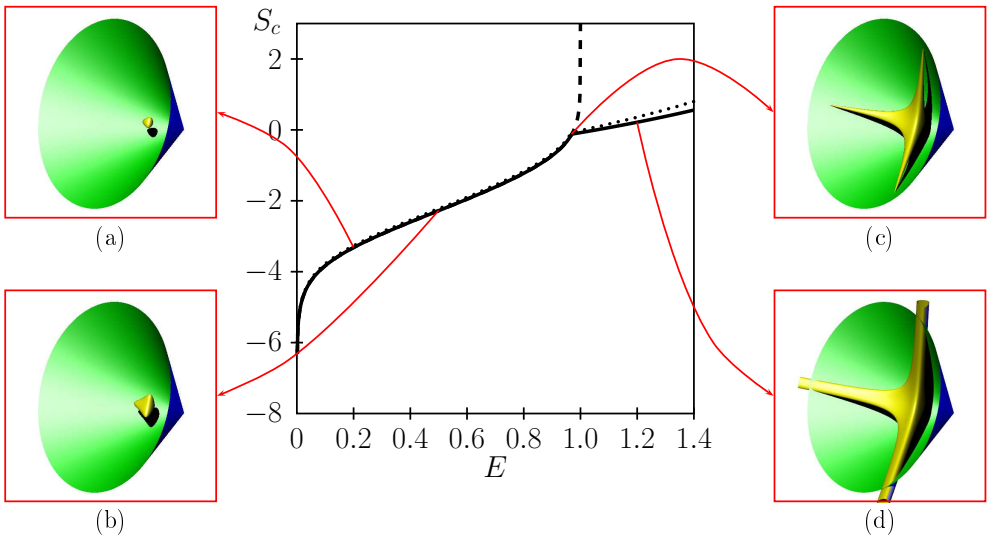

FIG. 2: Configurational Entropy S as a function of energy E for a 3 atom cluster interacting via Lennard-Jones potential. The insets represent the CES in distance space (see text): (a) $E = 0.2$, (b) $E = 0.5$, (c) $E = 0.969$, (d) $E = 1.2$. The dashed curve is the entropy without constraint, the dotted curve is the result of a Monte-Carlo calculation, the plain curve is the approximation by a convolution product (see text).

the integral can be computed in $O(n^2 s)$ time, to be compared to the $O(n^s)$ necessary for a general s-dimensional integral. Equation (7) is valid as long as the energy is low enough for the CES to not intersect the limiting cone. Above that, an approximate density of states can be computed if one supersedes Eq. (8) by

$$\omega(\epsilon) = \frac{\mathrm{d}}{\mathrm{d}\epsilon}[y_{\max}(\epsilon) - y_{\min}(\epsilon)] \quad \text{if } y_{\max}(\epsilon) \leq Y, \tag{9}$$

$$= \frac{\mathrm{d}}{\mathrm{d}\epsilon}[\qquad - y_{\min}(\epsilon)] \quad \text{if } y_{\max}(\epsilon) > Y. \tag{10}$$

$Y = (N-1)/N-2)$ is the value that zeroes the determinant (5) with all the y's equal to $1/2$ except one, which is equal to Y. The result of this approximation is shown on Fig. 2 for $N = 3$ and Fig. 3 for $N = 8$. Notice that the good agreement with the exact CDOS extends far beyond the expected range, which is $E < 1$.

When $N = D+1$, the integral in Eq. (7) contains one more factor, the Jacobian determinant, so that it is no more a convolution. On the other hand, the CES develops essentially along directions parallel to the axes, hence all the y's are close to $1/2$. It can thus be included

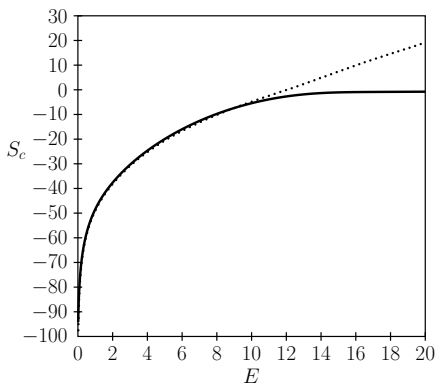

FIG. 3: Configurational Entropy S as a function of energy E for an 8 atom cluster interacting via Lennard-Jones potential. The dotted curve is the result of a Monte-Carlo calculation, the plain curve is the approximation by a convolution product.

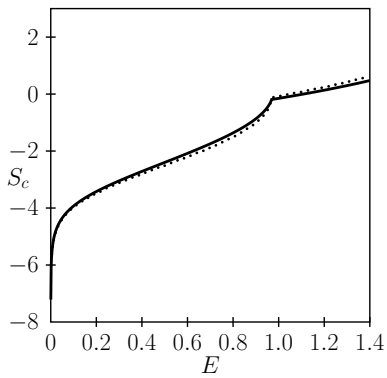

FIG. 4: Configurational Entropy S as a function of energy E for a 3 atom cluster interacting via Lennard-Jones potential in dimension 2.The dotted curve is the result of a Monte-Carlo calculation, the plain curve is the approximation from Eq. (11).

in the integral by changing one of the ω's with

$$\omega'(\epsilon) = \frac{1}{V[y_{\max}(\epsilon)]}\frac{\mathrm{d}y_{\max}}{\mathrm{d}\epsilon} - \frac{1}{V[y_{\min}(\epsilon)]}\frac{\mathrm{d}y_{\min}}{\mathrm{d}\epsilon}, \tag{11}$$

where $V(y)$ is the volume of Eq. (5) with all the y_{ab}'s equal to 1/2, save for one, which is y. Of course, when $y_{\max} > Y$, only the term containing $y_{\min}$ is retained as above. This approximation together with the exact Monte-Carlo result is shown on Fig. 4 for 3 atoms in dimension 2. The agreement is still very good, although the approximation is somewhat crude.

As a conclusion, mutual distances have been used as variables for the study of some N-

body problems. It has been shown that it is possible to make efficient approximations for the calculation of classical densities of states and that considering the space of distances is a good help for viewing what happens at phase transitions in small systems.

I thank Ms. Ch. Lauzeral for help on the initial stages of this project. Many calculations have been done or checked with the help of the Maple software from Maplesoft, a division of Waterloo Maple Inc.

---

* pierre.labastie@irsamc.ups-tlse.fr

[1] L. M. Blumenthal, *Theory and Applications of Distance Geometry* (Oxford at the Clarenton Press, 1953).

[2] J. Dattorro, *Convex Optimization & Euclidean Distance Geometry* (Meboo Publishing USA, 2005), URL `http://www.convexoptimization.com/TOOLS/0976401304.pdf`.

[3] G. M. Crippen, J. Comp. Chem. **25**, 1305 (2004).

[4] T. F. Havel, in *Encylopedia of Computational Chemistry*, edited by P. von Ragué, P. R. Schreiner, N. L.Allinger, T. Clark, J. Gasteiger, P. A.Kollman, and H. F. Schaefer III (J. Wiley & Sons, 1998), pp. 723–742, URL `http://web.mit.edu/tfhavel/www/Public/dg-review.ps.gz`.

[5] P. Labastie, Phys. Rev. E (2009), to be submitted.

[6] P. Labastie and R. Whetten, Phys. Rev. Lett. **65**, 1567 (1990).

[7] D. H. E. Gross and E. V. Votyakov, Eur. Phys. J. B **15**, 115 (2000).

[8] M. D'Agostino, F. Gulminelli, P. Chomaz, M. Bruno, F. Cannata, R. Bougault, F. Gramegna, I. Iori, N. Le Neindre, G. V. Margagliotti, et al., Phys. Lett. B **473**, 219 (2000).

[9] D. Lynden-Bell, Physica A **263**, 293 (1999).

[10] H.-L. Davis, J. Jellinek, and R.-S. Berry, J. Chem. Phys. **86**, 6456 (1987).

[11] D. J. Wales and J. P. K. Doye, in *Large clusters of atoms and molecules*, edited by T. P. Martin (Kluwer, Dordrecht, 1996), pp. 241–279.

[12] M. Schmidt, R. Kusche, W. Kronmuller, B. von Issendorff, and H. Haberland, Phys. Rev. Lett. **79**, 99 (1997).

[13] M. Schmidt, R. Kusche, B. von Issendorff, and H. Haberland, Nature **393**, 238 (1998).

[14] F. Gobet, B. Farizon, M. Farizon, M. J. Gaillard, J. P. Buchet, M. Carre, P. Scheier, and

T. D. Mark, Phys. Rev. Lett. **89**, 183403 (2002).

[15] G. A. Breaux, R. C. Benirschke, T. Sugai, B. S. Kinnear, and M. F. Jarrold, Phys. Rev. Lett. **91**, 215508 (2003).

[16] G. A. Breaux, B. Cao, and M. F. Jarrold, J. Phys. Chem. B **109**, 16575 (2005).

[17] F. Chirot, P. Feiden, S. Zamith, P. Labastie, and J.-M. L'Hermite, J. Chem. Phys. **129**, 164514 (2008).

[18] D. Ruelle, *Satistical Mechanics: Rigorous Results* (Addison-Wesley, Redwood City, CA, 1988).

[19] R.-G. Littlejohn and M. Reinsch, Rev. Mod. Phys. **69**, 213 (1997).