Journal of Statistical Physics, Vol. 57, Nos. 5/6, 1989

Statistical Mechanics of Convex Bodies

F. Bavaud[1]

Received May 19, 1989

The difficulties inherent in the construction of two-dimensional pressure ensembles are discussed, and are tackled by defining an energy cost depending on the convex hull of the set of particles. An energy proportional to the area of the convex hull is not able to prevent evaporation of the system, whereas an energy proportional to the area of the circumcircle of the convex hull ensures a thermodynamic behavior. In the latter model, which turns out to be exactly solvable, various characterizations are given of the geometry of a typical state.

KEY WORDS: Pressure ensemble; container-free systems; two-dimensional random polytopes; isoperimetric deficit.

1. INTRODUCTION

It appears to anyone working on problems such as the equilibrium shape of a finite crystal, ground state of an assembly of atoms, evaporation mechanisms, and related questions that the prescription of enclosing the particles in a fixed container is, to say least, ill-adapted in these cases. The remedy should consist of course in allowing the container to vary while fixing the pressure: this is the so-called *pressure ensemble* which has often been referred to in the litterature.[1,2] However, to the author's knowledge, and operational definition is available for one-dimensional systems only[3]: in that case, the class of "possible boxes" constitutes a one-parameter family index by the length of the box. In two dimensions (and beyond), the following difficulties immediately arise:

(a) How can we generate the (noncountable) class of all possible containers and adjoin to it an *a priori* distribution?

(b) Having to described the shape of a container by an infinite

[1] Department of Mathematics, Heriot–Watt University, Edinburgh, Scotland.

0022-4715/89/1200-1059$06.00/0

number of parameters (for instance, the Fourier coefficients of its curvature radius[4]), we should allow for a corresponding infinite set of conjugate variables of "pressures."

Before giving my point of view on these questions, let me first observe that, when we think about the volume of a finite crystal, we clearly mean the volume occupied by the particles themselves, and not the volume of any hypothetical box containing the crystal. *I shall therefore identify in a natural way the fluctuating container with the system itself*, or, more precisely, with the smallest set containing all the particles, that is, *its convex hull.* In this approach the shape of a system of N particles in a plane becomes an observable: in particular, its area, perimeter, diameter, and so on are defined by the coordinates of all the particles and cannot be considered as independent data. The *a priori* distribution of the shape of a finite system (determined by the polygonal boundary of its convex hull) is now generated in a natural way by the *product over the uniform distributions of the configurations of each particle.* Observe that a finite number of parameters is required to describe a finite polygon, and recall that the set of polygons (endowed with a suitable metric) is dense in the set of convex bodies.[5,6] These elements together permit us to tackle problem (a).

To prevent possible evaporation, one now has to define a cost increasing with the size of the system: this role is played by the energy, which, accordingly to (b), has the form of a sum over the geometric parameters describing the shape of the convex hull, each being multiplied by the conjugate coupling constant. There is an infinite number of possible choices of energy, among which I feel unable to hazard a preference ordering: the simplest choice, which consists in taking the energy proportional to the area of the system, fails to ensure the cohesion of its constituents, as shown below.

In this introductory and self-contained paper, I have made the deliberate choice of concentrating on and solving a limited number of (two-dimensional) problems, rather than giving incomplete answers to a larger number of questions, however important they might be. In Section 2, I define the general class of systems to which this approach is intended to apply. In Section 3, I show that an energy proportional to the area of the convex hull leads to the evaporation of the system. Finally, I investigate in Section 4 the properties of the model whose energy is taken proportional to the area of the circumcircle of the convex hull: it turns out that the partition function is exactly computable; moreover, the geometry of a typical state can be characterized rather precisely.

2. Let us denote by $x_i \in \mathbf{R}^2$ ($i = 1,\dots, N$) the coordinates of the ith particle. The smallest convex set containing all the particles, i.e., the *convex* *hull* of the set $\{\mathbf{x}_N\} := \{x_1,..., x_N\}$, will be denoted by $K(\mathbf{x}_N)$. Assuming that its diameter $D(K) := \max_{i<j} |x_i - x_j|$ is finite, K is a v-sided bounded polygonal body $(1 \leqslant v \leqslant N)$ of area $|K|$ and perimeter $|\partial K|$. The Hamiltonians $\mathscr{H}(\mathbf{x}_N)$ I shall consider are of the form

$$\mathscr{H}(\mathbf{x}_N) = H(K(\mathbf{x}_N)) + V(\mathbf{x}_N) \tag{1}$$

where H is required to depend on the convex hull $K(\mathbf{x}_N)$ only and to be translationaly invariant. $V(\mathbf{x}_N)$ is the "usual part" of the interaction, typically a two-body Lennard-Jones-like potential. (The kinetic part, which plays a trivial role, is omitted.) The canonical partition function is defined as

$$Q_N(\beta) = \int_{\mathbf{R}^{2N}} dx_1 \cdots dx_N \, \delta(\omega(\mathbf{x}_N)) \exp[-\beta H(K(\mathbf{x}_N)) - \beta V(\mathbf{x}_N)] \tag{2}$$

The term $\delta(\omega(\mathbf{x}_N))$ breaks the translational invariance of the system and therefore prevents the divergence of the integral. The class of functions $\omega(\mathbf{x}_N)$ to consider is defined in the following lemma.[2]

Lemma 1. If $V(\mathbf{x}_N)$ is translationally invariant (i.e., does not contain any external field), and $\omega(\mathbf{x}_N)$: $\mathbf{R}^{2N} \to \mathbf{R}^2$ satisfies, for all $a \in \mathbf{R}^2$,

$$\omega(x_1 + a,..., x_N + a) = \omega(x_1,..., x_N) + a \tag{3}$$

then the partition function is independent of the particular choice of $\omega(\mathbf{x}_N)$.

Proof. We shall show that the partition function (2) can be written as

$$Q_N(\beta) = \int_{\mathbf{R}^{2N}} d\mathbf{x}_N \, \delta(x_l) \exp[-\beta \mathscr{H}(\mathbf{x}_N)] \tag{4}$$

where l $(1 \leqslant l \leqslant N)$ is a fixed index. To that end, consider the transformation $x_i' = \omega(\mathbf{x}_N) + x_i - x_l$ for $i = 1,..., N$. The Jacobian is

$$\frac{\partial(\mathbf{x}_N')}{\partial(\mathbf{x}_N)} = \det\left(\sum_{i=1}^{N} \nabla_{x_i} \omega(\mathbf{x}_N)\right) = \det I = 1 \tag{5}$$

by virtue of (3). ∎

First of all, let us investigate the properties of the model which is the closest analog of the one-dimensional pressure ensemble: that is, we enclose the interacting system in a *circular* container of fixed origin. Allowing the

[2] I owe this lemma to O. Penrose.

radius of the container to fluctuate by fixing the pressure P, we get the partition function

$$Z_N(\beta, P) = \int_0^\infty dA \exp(-\beta PA) \int_{B^N(0,r)} d\mathbf{x}_N \exp[-\beta V(\mathbf{x}_N)] \tag{6}$$

where $B(0, r)$ is the disk of radius r centered at the origin, and $A = \pi r^2$ is its area. The Laplace transform in (6) reflects the Legendre transform $G = F + PV$, where G and F are, respectively, the Gibbs and the Helmoltz free energy. For a finite system, the former has to be defined here as

$$G_N(\beta, P) = -\beta^{-1} \ln[Z_N(\beta, P)/N!] \tag{7}$$

Proposition 1. The ensemble defined by (6) is thermodynamically equivalent [without the factor $\delta(\omega(\mathbf{x}_N)]$ to an ensemble of the form (2), with

$$\mathscr{H}(\mathbf{x}_N) = H_0(\mathbf{x}_N) + V(\mathbf{x}_N) := P\pi R^2(\mathbf{x}_N) + V(\mathbf{x}_N) \tag{8}$$

and

$$R(\mathbf{x}_N) := \max_{1 \leqslant i \leqslant N} |x_i| \tag{9}$$

Proof. The proof is straightforward: denoting by $\chi_M(x)$ the characteristic function of the set $M \subset \mathbf{R}^2$, (6) transformed into:

$$\begin{aligned} Z_N(\beta, P) &= \int_{\mathbf{R}^{2N}} d\mathbf{x}_N \exp[-\beta V(\mathbf{x}_N)] \int_0^\infty dA \exp(-\beta PA) \prod_{i=1}^N \chi_{B(0,r)}(x_i) \\ &= 2\pi \int_{\mathbf{R}^{2N}} d\mathbf{x}_N \exp[-\beta V(\mathbf{x}_N)] \int_{\max_{1 \leqslant i \leqslant N} |x_i|}^\infty dr\, r \exp(-\beta P\pi r^2) \\ &= \frac{1}{\beta P} \int_{\mathbf{R}^{2N}} d\mathbf{x}_N \exp\{-\beta[V(\mathbf{x}_N) + P\pi R^2(\mathbf{x}_N)]\} \quad \blacksquare \end{aligned} \tag{10}$$

Proposition 1 clearly shows what happens if one considers the area of the system as an independent variable, as in (6): the corresponding Hamiltonian $H_0(\mathbf{x}_N)$ is not translationally invariant, and therefore unsuitable to model a "mechanical resorvoir" in the absence of an external field. On the other hand, one infers from the transformations made in (10) that a "pressure" ensemble is nothing but a canonical one in which some interaction of geometric origin is explicitly taken into account via the term $H(K(\mathbf{x}_N))$. Consequently, the free energy of models defined by (1) and (2) has to be interpreted as a *generalized Gibbs free energy*,

$$G_N(\beta) := -kT \ln[Q_N(\beta)/N!] \tag{11}$$

where the role of the pressure is now played by the coupling constant(s) appearing in $H(K(\mathbf{x}_N))$.

In the following, we shall set $V(\mathbf{x}_N)=0$. The next lemma sums up the trivial results.

Lemma 2. If $H(K(\mathbf{x}_N))$ is positive homogeneous of degree p ($p>0$) in the coordinates [i.e., $H(K(\lambda \mathbf{x}_N))=|\lambda|^p H(K(\mathbf{x}_N))\geqslant 0$ for all $\mathbf{x}_N \in \mathbf{R}^{2N}$, $\lambda\in\mathbf{R}$], then

$$\langle H^q(K)\rangle_{N,\beta}=(kT)^q \frac{\Gamma(q+(2N-2)/p)}{\Gamma((2N-2)/p)} \tag{12}$$

where $q\in\mathbf{R}$, and $\langle\cdots\rangle_{N,\beta}$ denotes the canonical average with respect to the ensemble (2).

Proof. It is implicitly assumed that the left-hand side of (12) makes sense (a counterexample is given in Section 3). The homogeneity implies that the ground-state energy is zero, realized when all the particles coincide. The measure of all configurations of energy E, i.e., the microcanonical partition function

$$\mu_N(E):=\int_{\mathbf{R}^{2N}} d\mathbf{x}_N\, \delta(\omega(\mathbf{x}_N))\, \delta(E-H(K(\mathbf{x}_N))) \tag{13}$$

is easily verified to be homogeneous of degree $r=(2N-2-p)/p$ in E:

$$\mu_N(E)=\sigma(N)E^r \tag{14}$$

where $\sigma(N)$ depends on N only and consitutes the nontrivial part of the problem. The result follows from the definition:

$$\langle H^q(K)\rangle_{N,\beta}=\frac{\int_0^\infty dE\, E^{q+r}\sigma(N)\exp(-\beta E)}{\int_0^\infty dE\, E^r\sigma(N)\exp(-\beta E)} \tag{15}$$

The above denominator is identical to the partition function (2). This leads to the following expression for the free energy per particle in the thermodynamic limit (if it exists):

$$\begin{aligned}\beta g(\beta)&=\beta \lim_{N\to\infty} (1/N)\, G_N(\beta)\\ &=(2/p-1)+(2/p)\ln(\beta p/2)-\lim_{N\to\infty} \ln[\sigma(N)^{1/N} N^{(2/p-1)}]\end{aligned} \tag{16}$$

3. As announced above, I shall show in this section that a Hamiltonian proportional to the area of the convex hull

$$H_1(K(\mathbf{x}_N)):=\lambda\,|K|, \qquad \lambda>0 \tag{17}$$

is not sufficiently confining to prevent the evaporation of the system:

Proposition 2. The canonical partition function (2) diverges for $\mathscr{H}=H_1$:

$$Q_N(\beta)=\infty \qquad \text{for all} \quad \beta, N \tag{18}$$

Proof. Consider $\tilde{K}$, the smallest rectangle of given orientation containing K, and call the lengths of its sides L_x, L_y. Obviously, $H_1 \leqslant \lambda L_x L_y$. Taking into consideration that 4 out of the $2N$ coordinates determine $\tilde{K}$, we get

$$\begin{aligned} Q_N(\beta) &\geqslant N^2(N-1)^2 \int_0^\infty dL_x \int_0^\infty dL_y\, (L_x L_y)^{N-2} \exp(-\lambda L_x L_y) \\ &= N!\, N(N-1)\lambda^{-N+1} \int_0^\infty \frac{dL_x}{L_x} = \infty \quad \blacksquare \end{aligned} \tag{19}$$

The above divergence is prooduced by "stretched" configurations possessing a direction along which a particle can be sent to infinity while increasing the area $|K|$ by an arbitrary small factor, provided the width of the system in the perpendicular direction is sufficiently small. On the other hand, it seems plausible that the logarithmic divergence could be removed by dealing with a hard-core system or by adding to $H_1(K)$ a term of the form $\mu|\partial K|^\alpha$, for some judiciously chosen α.

4. Let $B(C_e, r_e)$ be the circumcircle (of center C_e and radius r_e) of the set $(x_1,\ldots,x_N)$, that is the smallest circle containing $K(\mathbf{x}_N)$. Let us call *obtuse* (*acute*) a polygon having two (three) intersections with the boundary of its circumcircle: this generalizes to arbitrary polygons the usual nomenclature for triangles (note that the circumcircle of a triangle is often defined in the litterature as the circle passing through the three vertices). The set of configurations involving more than three intersections is of measure zero and therefore discarded. In an equivalent way, K is obtuse iff its diameter $D(K)$ satisfies $D(K)=2r_e(K)$, and acute iff $D(K)<2r_e(K)$. In this section, we investigate the properties of the following Hamiltonian:

$$H_2(K)=\lambda\pi r_e^2(K), \qquad \lambda>0 \tag{20}$$

Let us compute the microcanonical partition function (13) by choosing $\omega(\mathbf{x}_N)$ as $C_e(\mathbf{x}_N)$. In the obtuse case, let x_1 and x_2 be the particles which define the diameter of K. Then

$$\begin{aligned} \mu_{\text{obtuse},N} &= \binom{N}{2} \int_{\mathbf{R}^4} dx_1\, dx_2\, (\pi x_1^2)^{N-2} \delta\left(\frac{x_1+x_2}{2}\right) \delta(E-\lambda\pi x_1^2) \\ &= \frac{2}{\lambda} N(N-1) \left(\frac{E}{\lambda}\right)^{N-2} \end{aligned} \tag{21}$$

In the acute case, let x_1, x_2, and x_3 be the particles defining the circumcircle. We shall use a coordinate system with C_e at the origin:

$$x_i = \tilde{x}_i + C_e, \qquad i = 1, 2, 3 \tag{22}$$

where

$$\tilde{x}_i = \begin{pmatrix} r_e \cos \alpha_i \\ r_e \sin \alpha_i \end{pmatrix}, \qquad i = 1, 2, 3 \tag{23}$$

The Jacobian of the transformation is[7]

$$dx_1\, dx_2\, dx_3 = dC_e\, r_e^3\, dr_e\, |S(\alpha_1, \alpha_2, \alpha_3)|\, d\alpha_1\, d\alpha_2\, d\alpha_3 \tag{24}$$

where

$$S(\alpha_1, \alpha_2, \alpha_3) := \sin(\alpha_2 - \alpha_1) + \sin(\alpha_3 - \alpha_2) + \sin(\alpha_1 - \alpha_3) \tag{25}$$

The admissible phase space for $(\alpha_1, \alpha_2, \alpha_3)$ is not the totality of $[0, 2\pi]^3$: $B(C_e, r_e)$ being by hypothesis the smallest circle containing $K(\mathbf{x}_N)$, configurations such that there exists a half-circle containing the three particles in its interior are forbidden. Taking into account some obvious symmetries, we obtain finally

$$\begin{aligned} \mu_{\text{acute}, N}(E) &= 4\pi \int_0^\infty dr_e\, r_e^3 (\pi r_e^2)^{N-3} \int_{\mathbf{R}^2} dC_e\, \delta(C_e)\, \delta(E - \lambda \pi r_e^2) \\ &\quad \times \int_0^\pi d\alpha_2 \int_\pi^{\pi + \alpha_2} d\alpha_3\, |S(0, \alpha_2, \alpha_3)| \\ &= \frac{1}{\lambda} N(N-1)(N-2) \left(\frac{E}{\lambda}\right)^{N-2} \end{aligned} \tag{26}$$

It is instructive, at this stage, to compare the total microcanonical partition function for $H_2 = \lambda \pi r_e^2$,

$$\mu_N(E) = \mu_{\text{obtuse}, N}(E) + \mu_{\text{acute}, N}(E) = \frac{1}{\lambda} N^2 (N-1) \left(\frac{E}{\lambda}\right)^{N-2} \tag{27}$$

to the corresponding expression for H_0 [as given by (8)] for $N-1$ particles (recall that one out the N particles of H_2 is frozen). One immediately gets

$$\tilde{\mu}_{N-1}(E) = \frac{1}{\lambda} (N-1) \left(\frac{E}{\lambda}\right)^{N-2} \tag{28}$$

The factor N^2, by which the two models differ, does not grow sufficiently rapidly to ensure different free energies in the thermodynamic limit: (14) and (16) yield

$$g(\beta, [H_2]) = g(\beta, [H_0]) = kT \ln(\beta\lambda) \tag{29}$$

An interesting open problem consists in determining whether models like

$$H_3(K) = \frac{\lambda\pi}{4} D^2(K), \qquad H_4(K) = \frac{\lambda}{4\pi} |\partial K|^2 \tag{30}$$

possess the free energy (29) or not.[3]

The next proposition is a direct consequence of (21) and (26).

Proposition 3. The probability for the convex hull of N points to be obtuse (acute) is

$$p_{\text{obtuse}}(N) = \frac{2}{N}, \qquad p_{\text{acute}}(N) = 1 - \frac{2}{N} \tag{31}$$

(Recall that the probability in question is the conditional probability generated by throwing uniformly N particles in $\mathbf{R}^2$, their circumradius being fixed.)

One can actually go further into the characterization of a typical configuration generated by the Hamiltonian H_2 by using some results of Rényi and Sulanke.[8,9] These authors give asymptotic expressions for the average area $|K|$, perimeter $|\partial K|$, and number of vertices v of the convex hull $K(\mathbf{x}_N)$ of N particles *uniformly distributed in a bounded convex set M*. Specialized to $M = B(0, r)$, their expressions become

$$\langle\!\langle |K| \rangle\!\rangle_{N,r} = \pi r^2 [1 - aN^{-2/3} + O(N^{-1})] \tag{32}$$

$$\langle\!\langle |\partial K| \rangle\!\rangle_{N,r} = 2\pi r [1 - bN^{-2/3} + O(N^{-1})] \tag{33}$$

$$\langle\!\langle v \rangle\!\rangle_{N,r} = cN^{1/3} + O(1) \tag{34}$$

where $a = (2/9)(12\pi)^{2/3}\, \Gamma(2/3)$, $b = (\pi^2/12)^{1/3}\, \Gamma(2/3)$, and $c = 2\pi(16/81\pi)^{1/2}$ $\Gamma(2/3)$.

The distribution of particles we are concerned with is different: either two or three particles are required to belong to the *boundary* of the circumcircle: the corresponding averages are therefore greater than the above ones. On the other hand, if we remove these boundary particles from the definition of K, we obtain lower bounds to (32)–(34). The difference between these two bounds affects N only and therefore does not appear in

[3] Note added in proof: this problem is now solved and the answer is affirmative for both models (F. Bavaud, to be published).

the leading terms of the asymptotic expansion. Passing to the canonical ensemble and using Lemma 2, we get the following result.

Proposition 4. The canonical averages (2) of the area, perimeter, and number of vertices of a system of N particles with Hamiltonian $H_1(K) = \lambda\pi r_e^2$ are given asymptotically by

$$\frac{1}{N}\langle |K|\rangle_{N,\beta} = \frac{kT}{\lambda}[1 - aN^{-2/3} + O(N^{-1})] \tag{35}$$

$$\frac{1}{N^{1/2}}\langle |\partial K|\rangle_{N,\beta} = 2\pi\left(\frac{kT}{\lambda\pi}\right)^{1/2}[1 - bN^{-2/3} + O(N^{-1})] \tag{36}$$

$$\frac{1}{N^{1/3}}\langle v\rangle_{N,\beta} = c + O(N^{-1/3}) \tag{37}$$

It is important to realize that the *density* of the system under consideration [and, more generally, of any system of the form (1)] is a (fluctuating) *observable.* It appears natural to define is as

$$\rho(\mathbf{x}_N) := \frac{N}{|K(\mathbf{x}_N)|} \tag{38}$$

One deduces from (35) the following limit:

$$\lim_{N\to\infty} \langle \rho \rangle_{N,\beta} = \lambda/kT \tag{39}$$

which constitutes the familiar ideal gas equation of state, λ playing the role of the pressure. Note that, in contrast to the usual fixed-container ideal gas, the equation of state (39) holds strictly in our model in the thermodynamic limit only.

I conclude the geometric description of the average configurations of the model H_2 by the observation that, for growing N, the typical convex hulls are increasingly circular:

Proposition 5. The average *isoperimetric deficit* satisfies

$$0 \leqslant \frac{1}{N}\left\langle \frac{|\partial K|^2}{4\pi} - |K| \right\rangle_{N,\beta} \leqslant \frac{kT}{\lambda}[AN^{-2/3} + O(N^{-1})] \tag{40}$$

with $A = a - \pi/3c^2 \approx 14.95$.

Proof. The isoperimetric deficit attains its lower bound zero in the case of circles only. On the other hand, the perimeter of a v-sided polygon satisfies[10]

$$|\partial K| \leqslant 2r_e v \sin(\pi/v) \tag{41}$$

Therefore

$$E_N\left(\frac{|\partial K|^2}{4\pi}\right) \leqslant \pi r^2 E_N\left(\left(\frac{v}{\pi}\sin\frac{\pi}{v}\right)^2\right)$$
$$\leqslant \pi r^2 E_N\left(\left(1-\frac{\pi}{3v^2}\right)^2\right) \leqslant \pi r^2\left(1-\frac{\pi}{3E_N^2(v)}\right)^2 \tag{42}$$

(I have used successively an integrated form of Jordan's inequality and Jensen's inequality). Using (35) and (37) and passing to the canonical ensemble achieves the proof.

ACKNOWLEDGMENTS

I am most grateful to Prof. O. Penrose and Dr. M. Van den Berg for useful suggestions and comments.

REFERENCES

1. T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).
2. K. W. Kratky, *Phys. Rev. A* **31**:945–950 (1985).
3. E. H. Lieb and D. C. Mattis, *Mathematical Physics in One Dimension* (Academic Press, New York, 1966).
4. M. A. Hurwitz, *Ann. Ecole Normale Sup.* **19**:357–408 (1902).
5. T. Bonnensen and W. Fenchel, *Theorie der konvexen Körper* (Springer, Berlin, 1934).
6. H. G. Eggleston, *Convexity* (Cambridge University Press, Cambridge, 1958).
7. L. A. Santaló, *Integral Geometry and Geometric Probability* (Addison-Wesley, London, 1976).
8. A. Rényi and R. Sulanke, *Z. Wahrsch.* **2**:75–84 (1963).
9. A. Rényi and R. Sulanke, *Z. Wahrsch.* **3**:138–147 (1964).
10. L. F. Tóth, *Regular Figures* (Pergamon Press, Oxford, 1964).