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A method for the enumeration of the floppy modes and the calculation of the associated entropy

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Abstract

We present a method that is based on the Ladd–Frenkel (LF) thermodynamic integration for the study of the rigidity of networks of particles bonded together by short-ranged square well attractive potentials. We show that, by taking the limit of the attractive range going to zero, the celebrated Baxter limit, the degrees of freedom per particle of the system reduces to the fraction of floppy modes, i.e. those modes associated with movements at constant bonding distance. This method allows us to enumerate this fraction in a straightforward way and to calculate precisely the entropy associated with the sampling of phase space due to these floppy modes. In particular, we shall discuss how this quantity changes in the case of three (3D) and two dimensions (2D).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Short range attractive systems have attracted a considerable amount of interest in the last few decades, especially for their applications in colloidal science [1, 2]. At high density, they represented an important benchmark for glass theory predictions that, for these systems, are highly non-trivial [3–6]. At low density, a gel phase emerges when the attraction between particles is strong enough, a fact that has been interpreted as an arrested phase separation both in numerical and experimental work [7–9]. Moreover, a lot of protein systems have also been modeled by short range interactions [10].

In numerical studies, among the potentials that have been used, the square well model has proven to be particularly useful. The fact that such a highly non-realistic potential can be used to describe real systems, like colloids or proteins, relies on the fact that, when the attractive range of the potential is much shorter than the diameter of the particles, the properties of the system are insensitive to the shape of the potential [11]. This fact has been successfully used to interpret experimental results for colloidal gels [8] as well as for protein systems [12, 13]. One of the main advantages of this model is represented by the fact that the bonds are unambiguously defined. More specifically, the potential energy is directly proportional to the number of bonds.

Another important advantage is that, for square wells, the study of the potential energy landscape (PEL) is particularly simple. This approach, which has been successfully applied to liquids and glasses, divides the PEL into basins around minima [14–16]. After this step, the system can be described in terms of the statistical properties of the minima and the basins. Square well systems are a special case because their PEL is not continuous. Each bonding pattern, however, is always a minimum. In particular, if no bonds are formed or broken the system is restricted to a minimum and to the sampling of its basin. The only quantity that needs to be calculated is the entropy associated with such a basin, i.e. the way the system samples the phase space once it is restrained in a specific minimum (or configuration) [17, 18]. To calculate this quantity the Ladd–Frenkel (LF) method [19] for the calculation of the free energy of solids has been used.

We begin by introducing a Hamiltonian $\mathcal{H}_0$ that does not allow the formation or breaking of bonds. In other words,

the system can evolve freely as long as all the bonds are conserved. The LF method complements this interaction with a harmonic term $\lambda \sum_i (\mathbf{r_i} - \bar{\mathbf{r}}_i)^2$ centered around a reference configuration $(\bar{\mathbf{r}}_1, \ldots, \bar{\mathbf{r}}_N)$ acting on the particles in the positions $(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.

The idea behind this method relies on the possibility of performing a thermodynamic integration over λ from a state of known free energy to the state where the harmonic part of the Hamiltonian is not present ($\lambda = 0$). When $\lambda \to \infty$, each particle moves as a harmonic oscillator around the reference state and the system behaves like an Einstein solid. The unperturbed system is identified with a specific initial bonding pattern and the result of the thermodynamic integration provides an exact measure of the basin free energy. No energy change is associated with the sampling of space within the fixed bond pattern basin since the energy surface is flat: consequently the only contribution to the basin free energy is entropic. The basin entropy per particle in units of k_B, σ_{basin}, can be formally written as [17, 20]

$$\sigma_{\text{basin}} = -\beta f_E(T, \lambda_\infty) + \int_{-\infty}^{\ln(\lambda_\infty)} \lambda \left\langle \sum_i (\mathbf{r_i} - \bar{\mathbf{r}}_i)^2 \right\rangle_\lambda \Big/ N \, \mathrm{d} \ln \lambda \tag{1}$$

where $f_E(T, \lambda)$ is the free energy of $3N$ harmonic oscillators coupled by an elastic constant λ and $\langle \cdot \rangle_\lambda$ is an ensemble average at a fixed value of λ. The value λ_∞ is chosen such that the harmonic contribution is dominant. and thus $\langle \lambda \sum_i (\mathbf{r_i} - \bar{\mathbf{r}}_i)^2 \rangle_\lambda \approx \frac{3}{2} N k_B T$. The quantity $\langle \lambda \sum_i (\mathbf{r_i} - \bar{\mathbf{r}}_i)^2 \rangle_\lambda$ is evaluated via MC simulations, rejecting all moves which modify the bond pattern.

In this paper we shall show how this approach can be used to evaluate the fraction of floppy modes in networks of bonded particles, a quantity that is related to the rigidity of such networks. In general, floppy modes are defined as those movements that do not change the potential energy of the system. For particles with permanent square well bonds, all the movements obey this definition. However, we shall see that, when the range of the square well goes to zero, i.e. in the Baxter limit [21], the number of degrees of freedom is reduced to the rolling of particles on each other at constant distance, which we interpret as the floppy modes for square well systems. In order to characterize the rigidity, geometric algorithms are often used to calculate the amount of floppy modes [22]. In this work, however, we will present a method that is based on the LF scheme. This method presents the great advantage of unifying a direct counting of the fraction of floppy modes with a thermodynamic integration that allows direct calculation of the entropy associated with the sampling of phase space due to these modes.

We shall begin our discussion by introducing a toy model that can be exactly solved and that will give an indication of the essence of the method. This simple model will then be generalized to real particle networks in three (3D) and two dimensions (2D).

2. A toy model: the dimer

Before performing the Ladd–Frenkel integration, we begin our discussion on the enumeration of the floppy modes by introducing a toy model that will help in clarifying the whole approach. We examine the behavior of two particles bonded by a square well in three dimensions. Particle 1 is fixed at the origin so that the degrees of freedom associated with the center of mass are excluded. A second particle 2 is bonded to the first by a square well permanent bond. This means that the position of particle 2, $\mathbf{r}_2$, is always within a corona, i.e. $\sigma < |\mathbf{r}_1 - \mathbf{r}_2| < \sigma + \Delta$, where σ is the diameter of the particles and Δ is the width of the corona. An Einstein reference site acts at an arbitrary position $\bar{\mathbf{r}}_2 = (x, 0, 0)$ with $\sigma < x < \sigma + \Delta$. The model is represented pictorially in the cartoon in figure 1.

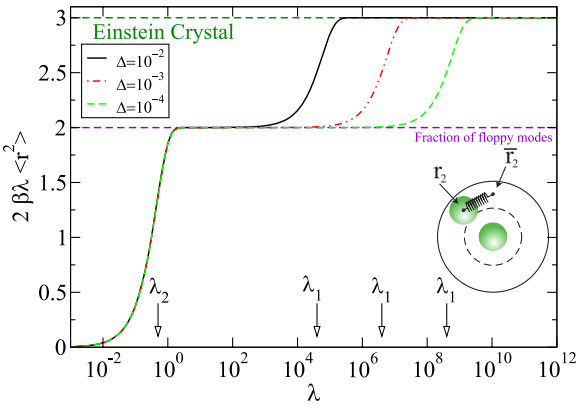

Figure 1. Exact result for the quantity $2\beta\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_2)^2\rangle_\lambda$ ($2\beta\lambda\langle\mathbf{r}^2\rangle$ in brief in the graph) for a single particle elastically bound to a reference point with an elastic constant λ and restricted in a square well of width Δ (see text for details). The horizontal lines represent the large λ limit, i.e. the Einstein crystal, and the intermediate λ limit representing the fraction of floppy modes. This case is in three dimensions (3D). The cartoon is a pictorial representation of the toy model.

The Hamiltonian of the two-particle system is

$$\mathcal{H} = \mathcal{H}_0 + \lambda \cdot (\mathbf{r_2} - \bar{\mathbf{r}}_2)^2 \tag{2}$$

where λ is the elastic constant and $\mathcal{H}_0$ is the unperturbed Hamiltonian that, in practice, enforces the bonding between the two particles. For the 3D case the average displacement $\langle(\mathbf{r_2} - \bar{\mathbf{r}}_2)^2\rangle_\lambda$ can be calculated by

$$\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_2)^2\rangle_\lambda = -\frac{\partial}{\partial\beta} \log \mathcal{Z}_\lambda(\beta), \tag{3}$$

where the generating (or partition) function $\mathcal{Z}_\lambda(\beta)$ is

$$\mathcal{Z}_\lambda(\beta) = 2\pi \int_d^{d+\Delta} \frac{\mathrm{e}^{-\beta\lambda(r+x)^2}(\mathrm{e}^{-4\beta\lambda rx} - 1)}{2\beta\lambda} r \, \mathrm{d}r. \tag{4}$$

The resulting λ dependence of $2\beta\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_2)^2\rangle_\lambda$ is shown in figure 1 for three different values of Δ. In the harmonic limit, i.e. $\lambda \to \infty$, the quantity $2\beta\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_2)^2\rangle_\lambda$ goes to 3, the total number of degrees of freedom, since in the harmonic limit $\lambda\langle\sum_i (\mathbf{r_i} - \bar{\mathbf{r}}_i)^2\rangle_\lambda = \frac{3}{2} k_B T$.

Upon decreasing λ, the function decays in two steps to zero. At intermediate values of λ a plateau develops with a height of a value of two. The crossovers from 3 to 2 take

place at $\lambda_1 \approx (2/\Delta)^2$ while the one from 2 to 0 at a value of $\lambda_2 \approx (2/\sigma)^2$. To interpret this behavior we recall that for very large λ ($\lambda > \lambda_1$) confinement is provided by the harmonic potential. For $\lambda_2 < \lambda < \lambda_1$, confinement of the harmonic potential has become larger than Δ and the bond distance becomes the relevant quantity controlling the mean square displacement. For $\lambda < \lambda_2$, the confinement is originated by the finite bond volume of the corona of width Δ and inner surface $4\pi\sigma^2$. This two-step crossover allows us to count the number of modes which are connected to the sampling of the bond width and the number of those which come from the sampling of space at fixed interparticle distance. In particular, the first crossover is Δ-dependent while the second one is Δ-independent. The LF method can estimate not only the total change in entropy but it is able to count and separate the number of modes which are related to the sampling of the bond distance (vibrational modes) from those which are related to the sampling of the volume with rigid bonds (floppy modes).

In particular, approaching the Baxter limit, i.e. $\Delta \to 0$, $2\beta\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_\mathbf{2})^2\rangle_\lambda$ reaches a limiting form that goes to the number of floppy modes. As we shall see later, in this limit the thermodynamic integration expressed by equation (1) is restricted only to those modes that are related to fixed bond distance movements—the floppy modes—and this is the core of the method we are discussing here.

We want now to test if the splitting of the mean square displacement in the small Δ limit depends on dimensionality. For this reason we extend the previous model to the 2D case. As before, one disc is at the origin and cannot move while the second one is forced to move in the attractive well of the first one and cannot escape. An elastic term acts between the centers of particle 2 and a reference point $\bar{\mathbf{r}}_\mathbf{2}$. The Hamiltonian of the two-particle system is the same as described by equation (2). Again, the mean square displacement $\lambda\langle(\mathbf{r_2} - \bar{\mathbf{r}}_\mathbf{2})^2\rangle_\lambda$ can be calculated by the generating function $\mathcal{Z}_\lambda(\beta)$ defined in equation (3). In three dimensions, however, the angular part of the generating function could be explicitly integrated, a task that cannot be performed in 2D. This complicates the calculation of the integral expressed by

$$\mathcal{Z}_\lambda(\beta) = \int_d^{d+\Delta} \mathrm{e}^{-\beta\lambda(\mathbf{r}_2 - \bar{\mathbf{r}}_2)^2}\, \mathrm{d}^2 r \tag{5}$$

which has been performed numerically by Monte Carlo integration.

The mean square displacement for three representative values of Δ is presented in figure 2. The results confirm that, as for the 3D case, a limiting function is achieved when $\Delta \to 0$. Having changed the dimensionality of the system, the number of degrees of freedom is now reduced to 2, one vibrational (the movements along the line joining the centers of the particles) and one floppy mode (the particles rotating around each other at a fixed distance). As before, this division of the degrees of freedom is reflected in the mean square displacement. When the range goes to zero, only movements along the only floppy modes are allowed. It is interesting to note that, different from the 3D case, in two dimensions the limiting function presents a peak roughly located at $\lambda_2 \approx (2/d)^2$, a fact that enforces the idea of a Δ-independent function with a specific form which is,

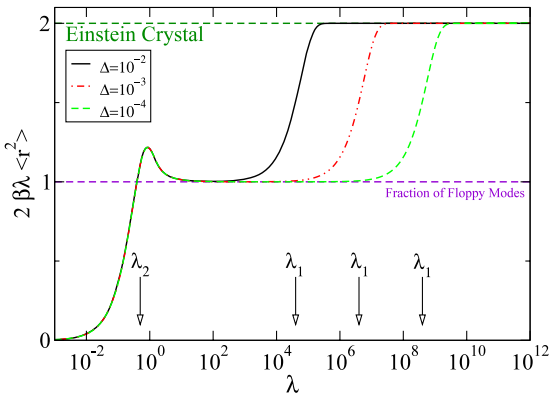

Figure 2. The same as figure 1 but in two dimensions (2D).

as we shall see, directly related to the entropy of the constant distant movements, i.e. the floppy modes.

Summarizing, in both cases, there is just one bond in the system, i.e. $N_\mathrm{b} = 1$, and one particle, $N = 1$, since particle 1 is not moving. Since the number of floppy modes is 2 for the 3D case and 1 for the 2D case, we can say that the fraction of floppy modes can be inferred from the number of bonds per particle that are present in the system by the formula

$$f_\mathrm{f} = d - \frac{N_\mathrm{b}}{N} \tag{6}$$

where f_f is the fraction of floppy modes and d is the dimensionality of the system. The expression in equation (6) coincides exactly with the plateau of the mean square displacement. In the next section we shall consider the case of several particles and we shall discuss if we can extend the conclusions drawn here for a simple toy model to the real case.

3. The real case: network of particles

We begin by taking a system of N particles connected together in a network characterized by a total number of bonds N_b. This has been done by taking an equilibrated configuration of particles interacting by a square well potential, above the critical temperature. In particular, these configurations were taken at a density ranging between $\rho = 0.38$ and $\rho = 0.95$, a reduced virial coefficient between $B_2^* = -0.40$ and $B_2^* = -0.69$ and a range $\Delta = 10^{-3}$. The use of the square well model is particular appropriate because the total number of bonds in the system is directly related to the potential energy by the relation $N_\mathrm{b} = -U$. A percolating cluster has been extracted and used as the initial configuration for the LD integration. The number of particles in these initial configurations ranges between $N = 159$ and 200. The simulations were performed with a fixed center of mass and this means that the three trivial infinite frequency floppy modes associated with the translations have been eliminated. The fact that the initial configuration is made of a single percolating cluster guarantees that no contribution to the counting comes from rigid rotations or translations of isolated clusters.

As discussed before, the simulations are performed by a Monte Carlo scheme that refuses any step that involves

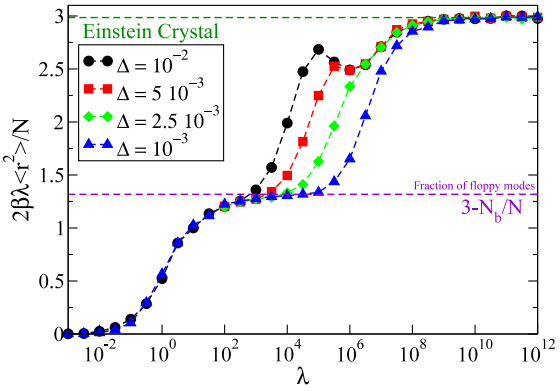

Figure 3. The mean square displacement $(2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N)$ from the reference points for a specific bonding pattern of hard-sphere particles as a function of the elastic constant λ for various values of the bond length Δ. At large λ the Einstein values is reached. For intermediate values, a plateau develops with a height equal to the fraction of floppy modes, $3-N_b/N$. This case is characterized by $N_b/N = 1.68$ and $N = 200$.

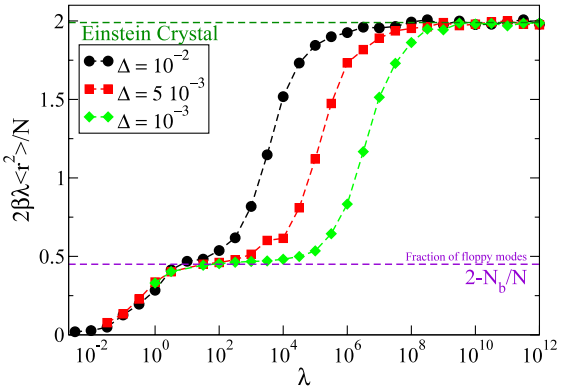

Figure 4. The same as figure 3 but in two dimensions (2D). In this case the fraction of floppy modes is $2-N_b/N$. This case is characterized by $N_b/N = 1.51$ and $N = 207$.

the formation or breaking of bonds, i.e. the bonding pattern conservation is enforced. The typical LF harmonic term connects each particle at a position $\mathbf{r_i}$ to its initial position, $\bar{\mathbf{r}}_i$, by an elastic term as was done for the toy model (equation (2)). The temperature is fixed to unity ($\beta = 1$) and does not influence the results since no thermal fluctuations can actually break a bond and a change of temperature would simply renormalize the elastic constant λ. After a first equilibration run, the quantity $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$, which enters in the calculation of the entropy by equation (1), is calculated as a function of the elastic constant λ.

In figure 3, the mean square displacement $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ is plotted for various values of Δ for a 3D case. The bonding pattern is the same for each run.

As for the toy model introduced in the previous section, the shape of the curve shows two parts, one Δ-independent and one Δ-dependent. Following equation (1), the area under the $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ versus $\ln\lambda$ curve is a measure of σ_{basin}, the entropy associated with the sampling of space at a fixed bonding pattern. The Δ-independent and Δ-dependent parts of $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ give rise to two different contributions to σ_{basin}, which we can identify as the floppy [23] Δ-independent and the vibrational Δ-dependent part. As for the exactly solvable model, discussed before, the Δ-independent part of the curve presents a plateau. As clearly indicated in figure 3, the height of this plateau can be interpreted as the fraction of floppy modes in the system, as was defined by equation (6), i.e. $f_f^{(3D)} = 3 - N_b/N$ (see figure 1), a value consistent with the existence of N_b independent vibrational degrees of freedom. In fact, this follows exactly the behavior that was found for the toy model. This is particularly important since $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ enters the expression for the free energy in LF thermodynamic integration, equation (1).

Having tested that the observations for the toy model extend to the real case in 3D, we can now test the 2D case. Similar to what has been discussed above, we took a configuration of discs interacting by permanent square well bonds. The quantity $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ has been calculated for the same bonding pattern at different values of the interaction range Δ and the results are presented in figure 4. As expected, we obtain the same behavior as in the 3D case. For large values of λ the number of degrees of freedom per particle is recovered, i.e. $d = 2$, while the usual plateau emerges at intermediate values. The height of the plateau is again the fraction of floppy modes per particle as directly calculated from the numbers of bonds, i.e. $f_f^{(2D)} = 2 - N_b/N$ (equation (6)). We can then confirm that this approach is valid also in the two-dimensional case.

Next we want to test how our method works when the number of bonds is increased, i.e. when the network becomes more rigid. To this aim we study several configurations with increasing numbers of bonds per particle. As before, these were the largest percolating clusters of equilibrated configurations of square well particles above the critical temperature. As a matter of fact the essence of the method, and one of the aims of this paper, is that the fraction of floppy modes depends solely on the number of bonds in the system. Configurations with different bonding patterns but the same number of bonds per particle N_b are expected to behave similarly. We expect that approaching a number of bonds per particle equal to dimensionality, the fraction of floppy modes vanishes. The results for the 3D case are presented in figure 5. As expected, the height of the plateau decreases when the network gets more structured. For each case, regardless of the particles' spatial distribution, the fraction of floppy modes, represented by the plateau, continues to follow the relation $f_f^{(3D)} = 3 - N_b/N$. The area below the Δ-independent part of $2\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ is expected to vanish for $N_b/N \simeq 3$ and we will show how this correlates to the entropy associated with the floppy modes.

The same reasoning can be followed for the 2D case. In figure 6 we show three systems of discs with increasing bonding. As for the 3D case we can see that the plateau height is again the fraction of floppy modes, i.e. $f_f^{(2D)} = 2 - N_b/N$. At this point, it must be stressed that the range for which we can vary the number of bonds per particle is narrower than in the 3D case since it can vary between $N_b/N = 1$ and

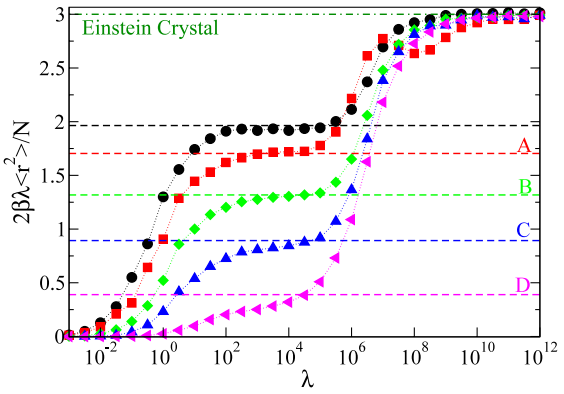

Figure 5. The mean square displacement $(2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N)$ for $\Delta = 10^{-3}$ for various bonding patterns. The dashed lines represent the fractions of floppy modes $f_f = 3 - N_b/N$. The curves correspond to: $N_b/N = 1.03$ (circles), $N_b/N = 1.30$ (circles), $N_b/N = 1.68$ (square), $N_b/N = 2.12$ (triangle up) and $N_b/N = 2.61$ (triangle left).

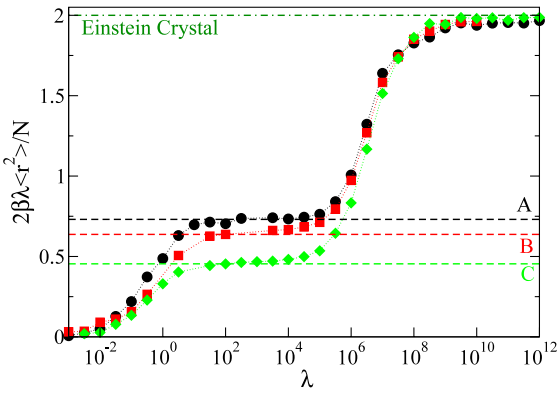

Figure 6. The same as figure 5 for the 2D case. The dashed lines represent the fractions of floppy modes $f_f = 2 - N_b/N$. The curves correspond to: $N_b/N = 1.27$ (circles), $N_b/N = 1.38$ (circles) and $N_b/N = 1.51$ (square).

$N_b/N = 2$. Below the lower bound the system is disconnected while above the upper one it is overconstrained. Differently from the three-dimensional case, the square well system in 2D has a strong tendency to crystallize. The configurations that are obtained in this way are always overconstrained, i.e. $N_b/N > 2$. Consequently we took these configurations and we started deleting particles until the desired number of bonds was obtained in the largest percolating cluster. This was used as the initial configuration in the simulations. The surface density (N/L^2) ranges between 0.09 and 0.34, with the number of particles between 52 and 207. Also for the 2D case the scenario is confirmed; the area below $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda/N$ that gives rise to the floppy entropy tends to disappear as the number of bonds per particle is equal to the dimensionality, i.e. $N_b/N \simeq 2$.

So far we have shown that an outcome of the LF method is the possibility of counting floppy modes: now that we have found a convincing way of separating the vibrational modes (those that are along the direction joining the centers of two bonded particles) from the floppy modes (those that come from fixed distance rotations) we can see how this separation can be used in the calculation of their relative entropies, focusing, in particular, on the one coming from the former.

The possibility of separating in a precise way the volume of phase space associated with vibrational modes and the one associated with floppy modes allows us to also evaluate the (Δ-independent) volume in configuration space sampled by a specific bonding pattern when all bond distances are fixed. This volume corresponds to the free rolling motions of the particles with no bond breaking or forming and it is essentially the basin volume accessible to the Baxter model. It is interesting to investigate the dependence of this quantity on the number of bonds, since one expects that, on increasing the connectivity, the entropy of the floppy modes should decrease. Before proceeding, however, we want to divide effectively the basin entropy, equation (1) into two parts. For this reason, it is natural to break the integrand of equation (1), for small enough Δ, into two parts:

$$2\beta\lambda\left\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\right\rangle_\lambda\Big/N = f_f\alpha_f(\lambda) + f_v\alpha_v(\lambda) \tag{7}$$

where $\alpha(\lambda)$ are two generic functions, to be evaluated numerically, sharing the property

$$\alpha_{f;v}(\lambda) = \begin{cases} 1 & \lambda \to \infty \\ 0 & \lambda \to 0 \end{cases} \tag{8}$$

and keeping in mind that $f_f + f_v = d$. The sum expressed by equation (7) is represented schematically in figure 7. The curve $2\beta\lambda\langle\sum_i(\mathbf{r_i}-\bar{\mathbf{r}}_i)^2\rangle_\lambda$ is split into two parts: the first one $f_f\alpha_f(\lambda)$ is the Δ-independent part while the second one $(f\alpha_v(\lambda))$ is the Δ-dependent one. In the Baxter limit, $\Delta \to 0$, only the former will remain since all the entropy comes from the floppy modes. By equation (7), we can now divide the entropy of the basin into two contributions:

$$\sigma = \sigma_{\text{floppy}} + \sigma_{\text{vib}} \tag{9}$$

where the two terms are given by

$$\begin{aligned}\sigma_{\text{floppy}} &= \frac{1}{2}f_f\left(-\frac{2\beta}{d}f_E(T,\lambda_\infty) + \int_{-\infty}^{\ln(\lambda_\infty)}\alpha_f(\lambda)\,\mathrm{d}\ln\lambda\right)\\ \sigma_{\text{vib}} &= \frac{1}{2}f_v\left(-\frac{2\beta}{d}f_E(T,\lambda_\infty) + \int_{o}^{\lambda_\infty}\alpha_v(\lambda)\,\mathrm{d}\ln\lambda\right)\end{aligned} \tag{10}$$

where $f_E(T,\lambda_\infty)$ is the free energy of the Einstein reference system[1].

We can now calculate the entropy associated with the floppy modes by equation (10) for the different cases discussed before. Clearly we expect that, when $N_b/N \to d$, the entropy vanishes. The results both for the 2D as well as for the 3D cases are presented in figure 7. For the 3D case, the floppy entropy goes to zero as a power law $\sigma_{\text{floppy}} \propto f_f^3$. The value of

[1] The free energy of the reference system is indeed different for a simple Einstein crystal since the center of mass is fixed. We used the correction due to such a constraint both for the 3D and for the 2D cases.

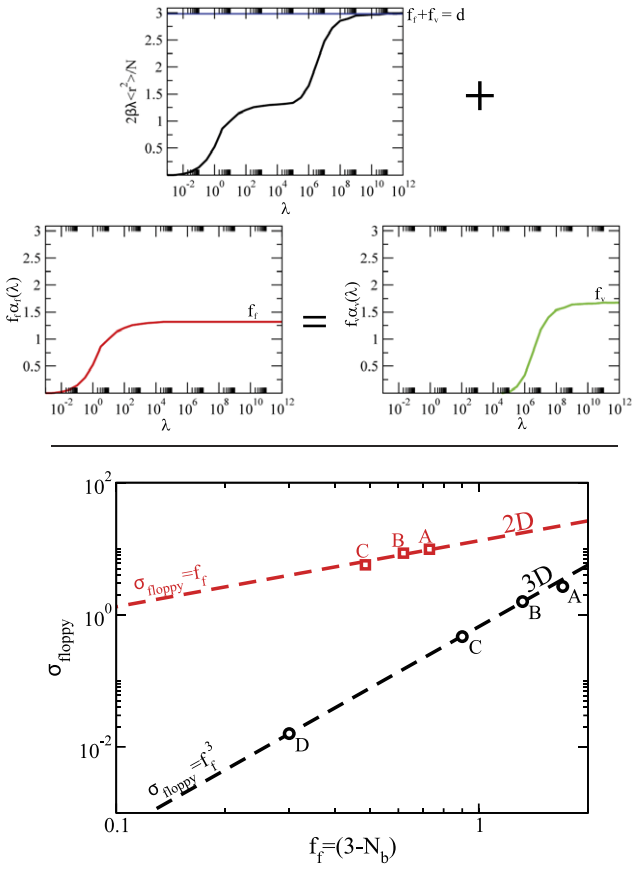

Figure 7. (Top) A graphical representation of equation (7) (see the text for details). (Bottom) The floppy entropy per particle σ_{floppy} as a function of the fraction of floppy modes $f_{\text{f}} = d - N_{\text{b}}/N$ for the 2D and 3D cases. The letters refer to figures 5 and 6.

the exponent suggests that not only the number of modes but also the floppy entropy per mode vanishes with a power law close to $f_{\text{f}} = 0$. It is interesting to observe that. at the state point where $N_{\text{b}} \approx 3N$, the full entropy of the system would be given only by the logarithm of the number of topologically different bonding patterns, since the vibrational modes are not present in the limit of $\Delta \to 0$. For the 2D case a different trend emerges. In this case, the floppy entropy goes to zero as a power law of unitary exponent $\sigma_{\text{floppy}} \propto f_{\text{f}}$. This implies that, while the fraction of floppy modes is counted in a similar way in the two cases, i.e. $f_{\text{f}} = d - N_{\text{b}}/N$, the way the floppy entropy varies going to the overconstrained limit does depend on the dimensionality in a non-trivial way. The reason is still not completely clear and one interesting direction would be to test higher dimensions.

4. Conclusions

In this paper we have discussed a method to enumerate the number of floppy modes in networks of particles with no directional bonds. This method derives directly from the Ladd–Frenkel scheme introduced to evaluate the free energy of solids [19]. This approach has been already proven to be useful for the calculation of the statistical properties of the potential energy landscape for systems interacting with square well interactions [17, 18]. The new results comes from the fact that, when taking the limit of the range of the square well going to zero, i.e. the Baxter limit, a system of spheres (or discs) loses those degrees of freedom associated with the vibrations along the directions joining the centers of the particles and it is left only with those associated with the particles rolling on each other at fixed distance σ. These modes are the floppy modes of the system. This intuitive picture is then reflected in the mean square displacement with respect to the reference points that is the integrand in the LF thermodynamic integration. A clear splitting of this function allows us to divide it into Δ-independent and Δ-dependent parts. The former is associated with the floppy modes and shows a plateau whose height is exactly related to the number of bonds of the system and that counts the fraction of floppy modes. We have been able to establish the entropy associated with the floppy modes, a task that is not possible with the technique that involves direct counting by geometric algorithms [22, 23]. We have found that, when the number of bonds per particle goes to the dimensionality of the system, the floppy entropy goes to zero—as expected for a system that is overconstrained. The method works both for 3D and 2D. More specifically, the fraction of floppy modes has the same functional dependence while the floppy entropy σ_{floppy} goes to zero with a power law with an exponent that depends on dimensionality.

In conclusion, we have presented a method to evaluate the fraction of floppy modes and their entropy for any specific bonded configuration, a method which can be used in studies of the rigidity of hard particle systems [22]. It would be of great interest to test if this method can be extended to systems with directional interactions. Rigidity in this kind of system is particularly important and has given interesting results with the geometric approach for manganites [24] as well as for the internal structure of proteins [25]. Indeed, the LF method can be extended to molecular systems with non-isotropic potential [19] and we are investigating if the present approach for the enumeration of floppy modes can be extended as well.

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