PICO-CANONICAL ENSEMBLES: A THEORETICAL DESCRIPTION OF METASTABLE STATES

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Abstract

We define restricted ensembles, called pico-canonical ensembles, for a statistical-mechanical description of the metastable and glassy phases. In this approach, time-evolution is Markovian, with temperature dependent rates. Below a particular glass-temperature, the system is strongly non-ergodic, and the phase space breaks up into a large number of mutually disconnected sectors. Averages are calculated over states within one such sector, and then averaged over sectors. As a soluble example, we calculate these explicitly for a one dimensional lattice gas with nearest neighbor couplings.
1 Introduction

It is perhaps not an exaggeration to say that the general principles of determining equilibrium properties of systems are quite well understood by now. Given a system of $N$ molecules, interacting with each other with a given pair potential, one calculates the partition function. Various thermodynamic quantities such as pressure, specific heat can be obtained by differentiating the free energy with respect to appropriate variables. When the exact calculation of partition function is not possible, different approximation schemes such as high- or low-temperature expansions, mean-field or other variational approximations can be used to get the qualitative and quantitative behavior.

This procedure, however, fails completely for metastable phases, such as diamonds or ordinary glass. This is because, the partition function, if correctly calculated, would only give properties of crystalline states of graphite, or quartz. In the standard Boltzmann-Gibbs prescription, if the system could easily explore all parts of the phase space available to it, the probability that the system will be found in a configuration corresponding to the diamond- or the glassy structure, is negligible. The reason for the failure of the Boltzmann-Gibbs prescription is non-ergodicity. The system in the glassy state is said to be trapped in a local minimum of the free energy [1]. Transitions away from a local neighborhood of these states occur at very slow rate (the time scale in case of window-glass is centuries). Once the system gets out of these trapping states, it is very unlikely to return to them, and these states do not have a significant weight in the equilibrium state, which may be defined as the very-long-time steady state. However, these states determine the averages of macroscopic quantities measured at the laboratory time scales, quite different from the “truly long-time averages”, calculated correctly by equilibrium statistical mechanics.

Usually, one treats glasses as systems relaxing to equilibrium very slowly, and there is a lot of interest in the study of such slow relaxations. On the other hand, the properties of a piece of diamond, or glass do not change appreciably over a period of days, or years. An experimentalist can put them in a calorimeter, and measure the specific heat, or apply pressure to determine the bulk modulus. But for a theorist, these are non-equilibrium states of matter, and notions like free energy are not ‘well-defined’. In this paper, we show how the conventional framework of equilibrium statistical mechanics can be extended
to include a description of such systems, and look upon glasses and diamonds, not as *evolving to equilibrium*, but as *in equilibrium*.

The macroscopic description of the glassy state should involve only a small number of variables, and certainly not the precise specification of all positions and momenta of all the atoms. Hence we necessarily deal with only a probabilistic description giving the probability of occurrence of different microstates. However, the ensemble of available microscopic states must be restricted to those which are ‘nearby’, and are accessible to the system within times comparable to the experimental time-scales. Such an ensemble in these systems is much smaller than the corresponding microcanonical ensemble. The ratio of number of states in one such ensemble to that of the standard micro-canonical ensemble decreases exponentially with the size of the system. We shall call such ensembles *pico-canonical ensembles*.

While the general idea outlined above is well-known, and accepted, it has not been possible so far to define precisely this concept of restricted ensembles in a way which allows calculation of such partition functions, and thus determine the averages in any nontrivial case, *with short-ranged interactions*. This is what we shall try to do here for the simple toy model of Ising spins on a line, with nearest neighbor interactions, and a non-ergodic dynamics \[2, 3\]. In this paper, we will argue that this analytically tractable model provides a useful paradigm for the statistical description of the glassy phase. We shall not attempt to review here the very large body of work which already exists dealing with the phenomena of ageing, i.e. long-time relaxation in glasses and spin-glasses \[4\].

The key observation here is to note that the processes operating in a glass may be divided into two classes: fast and slow. Fast processes are those whose time scales are much shorter than that of observation, e.g. the vibratory motion of atoms about their mean positions. Slow processes are those involving rearrangement of atomic configurations, particle- or vacancy diffusion, creep etc. To define a quasi-equilibrium state of glassy systems, we have to imagine that “all the fast things have happened”, and the slow things have not even started \[5\]. To be precise, we postulate that the system dynamics is such that if the slow processes *do not occur at all*, the dynamics becomes *nonergodic* and the phase space breaks up into a large number of *disconnected* pieces, called sectors. The number of such sectors increases exponentially with the size of the system. We shall call such system many-sector decomposable (MSD), and in pico-canonical ensembles we sum over
only one of these disconnected sectors.

We can explicitly compute the partition functions corresponding to such pico-canonical ensembles in our simple model. These can, and do, vary from sector to sector. Which one corresponds to the experimental system? A precise specification of the sector is not possible in a macroscopic description. As the number of sectors grows exponentially with system size, one would need order \( N \) binary bits just to characterize the sector, where \( N \) is the number of atoms in the system. In an experiment, one can, at best, hope to give some specification of how the system is prepared. In a theoretical calculation, this implies that in addition to calculating the free energies in different sectors, given the cooling schedule etc., one has to also determine the probability distribution that one ends up in one of the many sectors. Thus, the free energy must then be further averaged over sectors with a suitable weight for each sector, which will depend on the history of the system etc.

This averaging is similar to that over quenched disorder in the usual approach to glasses, but this disorder is a self-generated. Also, as we shall see in our model, the “frozen degrees of freedom” need not be frozen in real space. The relative weight of different sectors is not an additional input to calculation, but is determined by the model.

2 The Model

The model we shall choose to address these issues is a very simple one. We consider \( N \) hard-core point particles on a linear chain of \( L \) sites. There is an attractive interaction amongst the nearest neighbor particles of strength \( J \). The Hamiltonian of the model is given to be

\[
H = -J \sum_{i=1}^{L} n_i n_{i+1}
\]  

where \( n_i \) is 1 or 0 depending on whether the site \( i \) is occupied or unoccupied. Clearly \( \sum_i n_i = N \). We assume that the system evolves in continuous time by a local Markovian dynamics. We shall choose the transition rates to satisfy the detailed balance condition. Then, in the steady state all accessible configurations occur with their Boltzmann weights.
Now for a more detailed specification of the allowed transitions: We assume that the particles can diffuse to nearby sites either by simple or by assisted diffusion. In simple diffusion, a particle at site $i$ can jump to an empty neighbor with a rate $\Gamma_1 \exp(-\frac{\Delta E}{kT})$, where $\Delta E$ is the change in the energy of the configuration, and $T$ is the temperature of the system. This may be represented by the equation

$$01 \rightarrow 10$$

(2)

In the case of assisted diffusion, two adjacent occupied particles (a dimer) can jump together one step left or right with a rate $\Gamma_2 \exp(-\frac{\Delta E}{2kT})$. Then this process can be represented by a ‘chemical’ equation

$$110 \leftrightarrow 011$$

(3)

However, these pairings are not transient, and the dimers can ‘re-constitute’. Thus, for example, in the sequence of transitions

$$..11010..\rightarrow..01110..\rightarrow..01011..$$

(4)

the middle particle is first paired with particle on the left, and then in the second transition with the particle on the right.

**Fig. 1:** An example of breakup of phase space into sectors when monomer diffusion is not allowed. There are only six configurations in this sector of the phase space for $L = 11, N = 6$. All configurations have the same irreducible string 101001010. The rates of transitions amongst them are shown. In the steady state, their weights in the partition sum are $u^2 : u^2 : u : u^2 : u^2 : u$. 
Our reaction rates have been chosen to satisfy the detailed balance condition, and so the steady-state properties of the system do not depend on the precise values of $\Gamma_1$ and $\Gamma_2$. The probability of different configurations in the long-time state starting with a given initial configuration is immediately written down. It is proportional to $\exp(-\beta H)$ for all configurations within the sector in which the initial configuration lies, and 0 for others. We assume that $\Gamma_1$ has a strong dependence on temperature, so that it is effectively zero for all temperatures $T < T_G$, but is non-zero for temperatures greater that $T_G$. $\Gamma_2$ may be assumed temperature-independent. Thus, at low temperatures, this model reduces to a system of Diffusing Reconstituting Dimers (DRD) \[2\]

The assumption that monomers have a much lower diffusivity than dimers at low temperatures makes the model mathematically tractable, but it is not unrealistic: for example, platinum dimers on some surfaces have higher mobility than monomers.

### 3 Calculation of the Number and Sizes of Sectors

For a linear chain of $L$ sites, the phase space consists of $2^L$ distinct configurations. The conservation of particle number implies that the total phase space can be broken into $(L + 1)$ disconnected parts, each corresponding to a different value of the total particle number. For $T > T_0$, it is easy to see that all configurations having the same number of particles can be reached from any one of them.

However, for $T < T_0$, the number of disconnected sectors becomes much bigger. The number of sectors increases as $\exp(L)$. This is easy to see. All configurations having only isolated 1’s in a background of 0’s, with no dimers cannot evolve at all. For example, \ldots 0010100010001\ldots cannot evolve, and constitutes a sector, with only one configuration in the sector. The number of such configurations increases as $\exp(L)$, and provides a lower bound on the total number of sectors.

The decomposition of phase space into disjoint sectors is described most simply in terms of a construct called the \textit{irreducible string} \[3\] \[4\]. With each of the $2^L$ possible configurations of the DRD model, we attach a binary string, called the IS corresponding to that configuration, constructed as follows: We read the $L$-bit binary string of $n_i$
specifying the configuration from left to right until the first pair of adjacent 1’s is encountered. This pair is deleted, reducing the length of the string by 2. This process is repeated until no further deletions are possible. The resulting string is the IS for the configuration. For example, for the binary string 01001110110, the irreducible string is 0100100.

By construction, for each configuration, there is a unique IS. If a dimer diffuses, the IS is not changed. Thus the IS is a constant of motion. It is easy to show that two different configurations belong to the same sector, if and only if they both have the same IS. The IS thus provides a unique label for each sector.

The DRD dynamics can be viewed as the exclusion process of a system of 3 species $A$, $B$ and $C$ of particles on a line. In this process each site of linear chain is occupied by a single particle, which may be of type $A$, $B$, or $C$. We set up a one-to-one correspondence between the configurations of the DRD model, and of the exclusion process as follows: Read the binary string of the DRD from left to right, and use the substitution rules $11 \rightarrow A, 10 \rightarrow B, 0 \rightarrow C$. The stochastic evolution rule in terms of the exclusion process configurations is simply that a particle of type $A$ can exchange position with a particle of type $B$ or $C$ at an adjacent site. Type $B$ and $C$ cannot exchange positions with each other. This model thus is a special case of the k-species exclusion process [9, 10, 11].

The conservation of IS in this language corresponds to the simple statement that as $B$ and $C$ type particles cannot exchange places, their relative order is unchanged in time. Starting with an initial configuration specified by a string composed of three characters $A$, $B$ and $C$, deleting all the occurrences of $A$’s in the string, we are left only with a string composed of $B$’s and $C$’s which is conserved by the dynamics.

In terms of the exclusion process, it is quite straightforward to write down the formulas for the number of distinct sectors for the DRD model, and also the number of configurations in each sector. In a sector having $N_A$ particles of type $A$, the length of the IS is $L - 2N_A$. The number of unpaired 1’s is $N_B = N - 2N_A$, and the number of type C particles is $N_C = L - 2N + 2N_A$.

The number of configuration within a sector with a specified IS, say $I = BCCBABBBCBC \ldots$, is the number of ways we can place $N_A$ $A$’s between $(N_B + N_C)$ $B$’s and $C$’s. So this number is
\[ \Omega(N_A | \mathcal{I}) = (N_A + N_B + N_C)!/[N_A!(N_B + N_C)!] \]
\[ = (L - N + N_A)!/[N_A!(L - N)!] \]  
(5)

The number of different sectors having a given value of \( N_A \) is the number of distinct ways of writing the IS consisting of \( N_B \) B’s and \( N_C \) C’s. This number is \((N_B + N_C)!/(N_B!N_C!)\). The numbers \( N_B \) and \( N_C \) are known once \( N_A \) is known. To calculate the total number of sectors, we have to sum the number of sectors for \( 0 \leq N_A \leq N/2 \).

4 Calculating Partition Functions

Let \( \mathcal{Z}(N, L | \mathcal{I}) \) be the partition function for a linear chain with \( L \) sites with \( N \) atoms, in a sector corresponding to IS \( \mathcal{I} \). Then \( \mathcal{Z}(N, L | \mathcal{I}) \) is a polynomial in \( u = \exp(\beta J) \). We define the generating function

\[ \tilde{\mathcal{Z}}(x, z, u | \mathcal{I}) = \sum_{L=1}^{\infty} \sum_{N=0}^{L} x^L z^N \mathcal{Z}(L, N | \mathcal{I}) \]  
(6)

It is easy to see that the generating function for the IS \( \mathcal{I}' = X\mathcal{I} \), where \( X = B \) or \( C \) factorizes simply as

\[ \tilde{\mathcal{Z}}(x, z, u | X\mathcal{I}) = w_X \tilde{\mathcal{Z}}(x, z, u | \mathcal{I}) \]  
(7)

where \( w_B \) sums over substrings reducible to \( B \), i.e. \( 10 + 1110 + 1111110 \ldots \), giving

\[ w_B = x^2 z u / (1 - x^2 z^2 u^2) \]  
(8)

Similarly, we have

\[ w_C = x + x^3 z^2 u / (1 - x^2 z^2 u^2) \]  
(9)

If the number of B’s and C’s in \( \mathcal{I} \) is \( N_B \) and \( N_C \) respectively, we have

\[ \tilde{\mathcal{Z}}(x, z, u | \mathcal{I}) = w_B^{N_B} w_C^{N_C + 1} / x \]  
(10)

As a simple check, we see that the generating function for the null string is \( w_C / x \).

For temperatures above \( T_G \), we have to sum over all possible IS. This is easy. We note that a formal series over all possible string of B’s and C’s can be formally summed as
Repalcing $B$ by $w_B$, and $C$ by $w_C$, this immediately gives the partition functions for $T > T_G$ as

$$\tilde{Z}(x, z, u | .) = w_C/[x(1 - w_B - w_C)] \quad (12)$$

where the unspecified IS represented by the dot indicates a sum over all possible IS. To get $Z(L, N)$, we have to evaluate the coefficient of $x^L z^N$ in the above expression. For large $L$ this varies as $\lambda^L$, where $1/\lambda = x_c$, the singularity nearest to origin of (12). This gives us $\lambda(z, u)$ as the solution of the quadratic equation

$$\lambda^2 - \lambda(1 + z u) + z(u - 1) = 0; \quad (13)$$

a result which is also obtainable directly by the transfer-matrix method. The activity $z$ is determined using the condition $z \partial \log \lambda / \partial z = N/L$. For simplicity, we discuss below the special case $N = L/2$. This corresponds to the activity being given by the equation

$$z = 1/u, \quad \text{for } N/L = 1/2. \quad (14)$$

In the language of spin models, this case corresponds to a simple Ising chain with no external field. It is straightforward to determine different averages, and correlation functions. Differentiating $\lambda$ with respect to $u$, we get the average energy $E$ as a function of $u$

$$E = -\frac{J \sqrt{u}}{2(\sqrt{u} + 1)}, \quad \text{for } T > T_G. \quad (15)$$

Similarly, we calculate the average number of substrings of the type $01^n0$ per site. For $n = 0$, this number is $1/(2\lambda)$. For $n > 0$, it is $1/(2u\lambda^{n+1})$. Summing over the odd values of $n$, we get that the fractional number of $n_B = N_B/L$ in a typical configuration is given by

$$n_B = \frac{1}{2(1 + 2\sqrt{u})}, \quad \text{for } u < u_0. \quad (16)$$

Above $T_G$, the system can explore all configurations with different IS, and the average value of $N_B$ decreases with decreasing temperature. As we cool the system just below $T_G$, transitions that change
IS are no longer possible. Hence the system will remain in one sector, and the average value of $n_B$ remains constant

$$n_B = \frac{1}{2(1 + 2\sqrt{u_0})}, \text{ for } u > u_0 \quad (17)$$

where $u_0 = \exp(J/kT_G)$. There are $(L - N)!/(L - N - N_B)!N_B!$ equivalent sectors. The available phase space to the system shrinks by this factor as the temperature falls below $T_G$. The logarithm of this quantity gives us the component of entropy that gets frozen at the glass transition. In our special case $N = L/2$, this expression simplifies, and the frozen entropy per site is

$$\Delta S_{fr} = \frac{1}{2}H(2n_B) \quad (18)$$

where $H(x) = -x\log x - (1 - x)\log(1 - x)$.

For $T < T_G$, we have to calculate the pico-canonical partition function in one of these sectors. This is easily evaluated using Eq.(10). Since it only depends on $N_B$ and $N_C$, and these have only $O(\sqrt{L})$ fluctuations between different sectors, we see that the pico-canonical free energy in each of these sector is the same. Averaging over different sectors is then trivial, and has no effect. The average energy is a continuous function of temperature at $T_G$.

Within a given sector, the relative weights of different configurations are functions of temperature, and the average energy and entropy decrease with temperature. The temperature dependence of average energy can be determined from Eq.(10), or directly as follows: There are exactly $(L - N)$ zeroes in a configuration. Let the number of type $A$ particles that are followed by a type-$C$ particle be $K$. [We shall include in this count a type $A$ particle at the end of chain.] In the configuration, the energy of the configuration is $(-N + N_B + K)J$. There are $(N_C + 1)!/K!(N_C - K + 1)!$ ways of putting the $K$ particles just left of these $N_C + 1$ symbols (treating the end mark as a 0). Then, for any such choice, we have to distribute $(N_A - K)$ additional dimers left of these $N_B + K$ symbols. This is the standard problem of distributing $m$ identical balls in $n$ boxes, with more than one ball in a box allowed. The answer is $(m + n - 1)!/[m!(n - 1)!]$. In our problem, the dimers can be distributed in $(N_A + N_B - 1)!/(N_A - K)!(N_B + K - 1)$ ways. This gives us
\[ Z(L, N | I) = \sum_{K=0}^{N_A} \frac{(N_A + N_B - 1)!(N_C + 1)!}{(N_A - K)!(N_B + K - 1)!K!(N_C - K + 1)!} u^{N - N_B - K} \]  

As a simple check, we can verify that this correctly gives the partition function of the sector shown in Fig.1.

In the limit of large \( L \), we can use steepest descent to evaluate this sum. The maximum contribution comes from \( K = kL \), where \( k \) satisfies the equation

\[ k(n_B + k) = (1/2u)(1 - n_B - 2k)(1/2 - n_B - k) \]  

where \( n_B \) is given Eq. (17). For temperature tending to zero, \( u \) tends to infinity, and \( k \) tends to zero. As \( k \) is equal to the excess energy at temperature \( T \) above the zero-temperature value, this gives us the energy density at any temperature in the low-temperature phase.

The minimum energy corresponds to \( k = 0 \). We see that even at \( T = 0 \), we have a residual energy \( N_B J \) above the ground state energy. Also, in addition to the frozen entropy, there is also a contribution to the zero temperature entropy coming from the macroscopic degeneracy of the ground state within the sector.

## 5 Concluding Remarks

In this paper, we described a simple model where the phase space shows many-sector decomposition in the low temperature phase. We showed that this sector decomposition can be characterized fully in terms of a constant of motion called the irreducible string. The exact partition function can be calculated easily in each of these sectors. The relative weights of different sectors in calculation of other observable averages can also be calculated similarly within the model. In our model, it depends only on the temperature at which ergodicity breaking occurs. More generally, it would depend on the history of the sample.

In calculating thermodynamical quantities like the average energy, we found that different sectors are not so different. In particular, the free energy depended only on \( N_B \) and \( N_C \), and not on the arrangement of characters of the irreducible string. And so, the average over sectors
was same as value in one sector. This property of self-averaging is expected to work for other quantities as well, e.g. correlation functions.

Of course, the breaking of ergodicity is put into the model ‘by hand’. However, it allows us to see explicitly, in a simple setting, concepts like frozen entropy, and disallowing slow processes completely makes possible discussion of glassy states as equilibrium states of matter. This is admittedly an idealization, but useful, and perhaps no different from other idealizations like the thermodynamic limit, ideal heat-baths (which exchange energy with the system, but otherwise do not perturb it) etc. well-known in equilibrium statistical mechanics. The main advantage is that the arbitrariness in defining the notion of ‘nearby’ states is avoided. The naive implementation of the latter makes the ensemble depend on the initial state, and on the maximum distance allowed.

Some generalizations of the model are straightforward, e.g. inclusion of next-nearest neighbor interactions. One can also allow some other relaxation processes, like 0010 → 0100. These reduce the number of disjoint sectors, but the number still grows exponentially with the volume of the system. Work on more realistic models, or higher dimensional cases seems like a promising area for further study.

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