Statistical approaches to the problem of homogeneous melting of solids in the microcanonical ensemble

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Abstract. Melting is a common phenomenon in our daily life, and although it is understood in thermodynamic (macroscopic) terms, the transition itself has eluded a description from the point of view of microscopic dynamics. While there are studies of metastable states in classical spin Hamiltonians, cellular automata, glassy systems and other models, the statistical mechanical description of the microcanonical superheated solid state is lacking.

Our work is oriented to the study of the melting process of superheated solids, which is believed to be caused by thermal vacancies in the crystal or by the occupation of interstitial sites. When the crystal reaches a critical temperature, it becomes unstable and a collective self-diffusion process is triggered. These studies are often observed in a microcanonical environment, revealing long-range correlations due to collective effects, and from theoretical models using random walks over periodic lattices. Our results suggest that the cooperative motion made possible by the presence of vacancy-interstitial pairs (Frenkel pairs) above the melting temperature can induce long-range effective interatomic forces even beyond the neighboring fourth layer. From microcanonical simulations it is also known that an ideal crystal needs a random waiting time until the solid phase collapses. Regarding this, our results also point towards a description of these waiting times using a statistical model in which there is a positive quantity $X$ that accumulates from zero in incremental steps, until it exceeds a threshold value.

1. Introduction

Melting is a common phenomenon in our daily life, and a clear example of a first-order, or discontinuous, phase transition. Although it is understood in thermodynamic (macroscopic) terms, the transition itself has eluded a complete description from the point of view of microscopic dynamics. The melting process in most cases turns out to be an heterogeneous process, since it is commonly triggered on the surface of the crystal. Melting under heterogeneous conditions occurs exactly at the melting temperature $T_m$ and is well described by the classical nucleation theory [?]. On the other hand, in homogeneous melting, without surfaces or defects, eventually as we increase the energy of the crystal, we reach a critical temperature $T_{LS}$, called the limit of superheating, such that the metastable solid structure cannot exist at a higher temperature than this without being spontaneously transformed into liquid [?, ?]. This process of collapse of the crystalline state is believed to originate from the diffusion of mobile vacancy-
interstitial pairs that occurs as the solid surpasses \( T_m \). In the superheated solid state, the atoms in the crystal can temporarily occupy interstitial sites, creating vacancies \([\ldots]\) and allowing neighboring atoms to diffuse occupying the vacant sites, resulting in a cooperative motion involving several atoms \([\ldots]\).

**Figure 1.** Isochoric (Z) curve obtained from 31 different 80 ps simulations of high-density argon. From Ref. \([\ldots]\).

Fig. 1 shows the melting temperature \( T_m \) and the superheating limit \( T_{LS} \) obtained in molecular dynamics simulations of high-density argon \([\ldots]\), while Fig. 2 shows the spontaneous melting occurring at a random time during a typical microcanonical molecular dynamics simulation. In order to reveal the existence of extreme events and interatomic correlations in the superheated phase leading to the melting process of a solid as time passes, in this work we will consider a model where vacancies are created as a consequence of the thermal vibration of the atoms, and are able to diffuse through the crystal by means of random walks on a lattice \([\ldots]\).

2. Random walks on a lattice

We define a starting point \( r_0 \) in the lattice, from which there are \( n \) possible sites to which the particle can move, hence the position of the particle after \( n \) steps is given by

\[
    r_n = r_0 + \sum_{j=1}^{n} (\Delta r)_j
\]

where \( (\Delta r)_j \) is the \( j \)-th displacement vector. This allows us to define a structure factor \( \lambda(k) \)

\[
    \lambda(k) = \sum_{j=1}^{m} P(\Delta r = R_j|I) \exp(ik \cdot R_j)
\]

that indicates the type of network topology as well as the probabilities \( P(\Delta r|I) \) for each possible jump. The probability \( P(r_n = r|I) \) of finding the particle at the position \( r \) after \( n \) steps is given by \([\ldots]\)

\[
    P(r_n = r|I) = \frac{1}{(2\pi)^d} \int_B dk \lambda^n(k) \exp(-ik \cdot (r-r_0))
\]

**Figure 2.** Instantaneous temperature \( T(t) \) for a simulation of high-density argon at an initial temperature \( T_0 = 12600 \) K. Only the first 30 ps of the simulation are shown, as after the melting process occurs at time \( t_w = 9 \) ps the system remains in the liquid phase. From Ref. \([\ldots]\).
In order to solve this integral, we can define a generating function $f(r, \xi)$ that allows us to establish a relationship between probabilities and coefficients $\xi$, according to

$$f(r, \xi) = \sum_{n=0}^{\infty} P(r_n = r| I) \xi^n.$$  \hspace{1cm} (4)

Our objective is to determine the probability of return to origin $r = 0$ after $n$ steps, which implies that our generating function is now given by

$$f(0, \xi) = \frac{1}{(2\pi)^d} \int_B dk \frac{1}{1 - \xi \lambda(k)}.$$ \hspace{1cm} (5)

The structure function is not unique, as a given lattice may usually be represented by more than one set of basis vectors. For the regular two-dimensional and three-dimensional lattices the first coefficients of the power series expansion of $f(0, \xi)$ are

$$f(0, \xi)_{\text{square}} = 1 + \frac{1}{4} \xi^2 + \frac{9}{64} \xi^4 + O(\xi^6),$$ \hspace{1cm} (6a)

$$f(0, \xi)_{\text{triang}} = 1 + \frac{1}{4} \xi^2 + \frac{2}{36} \xi^3 + \frac{3}{216} \xi^4 + O(\xi^5),$$ \hspace{1cm} (6b)

$$f(0, \xi)_{\text{honeycomb}} = 1 + \frac{1}{3} \xi^2 + \frac{5}{27} \xi^4 + O(\xi^6),$$ \hspace{1cm} (6c)

$$f(0, \xi)_{\text{sc}} = 1 + \frac{1}{6} \xi^2 + \frac{5}{72} \xi^4 + O(\xi^6),$$ \hspace{1cm} (6d)

$$f(0, \xi)_{\text{bcc}} = 1 + \frac{1}{8} \xi^2 + \frac{27}{512} \xi^4 + O(\xi^6).$$ \hspace{1cm} (6e)
We see that the particle returns to the origin after the second (coefficient accompanying $\xi^2$) and fourth (coefficient accompanying $\xi^4$) steps for the lattice in two and three dimensions, except for the triangular lattice, which can also return to the origin in an odd number of steps, due to the larger number of closed paths.

3. A statistical model for collapse times

In microcanonical homogeneous melting, some earlier results [?, ?] pointed towards the problem of establishing the statistical distribution of the elapsed time $t_w$ from the beginning of the simulation until melting occurs. This was reported originally as following an exponential distribution [?], which is what would be expected for a fixed probability of melting $p$ at each step. In fact, if independent melting attempts occur every $\Delta t$ with success probability $p$, we have

$$P(t_w = t | \Delta t, p) = p(1 - p)^{t/\Delta t - 1} = p \exp[(t/\Delta t - 1) \ln p]$$

which is an exponential distribution with characteristic time $\tau := -(1/\Delta t) \ln p$. However, it was later realized that the distribution more accurately resembles a gamma distribution [?], assigning zero probability to $t_w=0$. In an ongoing effort to explain these features of the waiting time distribution we will consider a statistical process where a positive quantity $X$ is accumulated from zero on incremental steps, until $X$ overcomes a threshold value $X^*$ which triggers the collapse [?]. Please note that we left the question of the meaning of the quantity $X$ for a future microscopic theory of melting. We assume that, on each trial step (of fixed duration $\Delta t$), an attempt to increase the value of $X$ is performed with success probability $p$, that is, these attempts form a Bernoulli process. On every successful trial, $X$ increases by an amount $\Delta X$ which may be fixed or random.

After $n$ accumulation events, according to the continuous-time random walk formalism [?], the total elapsed time and the total amount of $X$ should be given by

$$T_n := \sum_{i=1}^{n} (\Delta T)_i,$$  \hspace{1cm} (8a)  

$$X_n := \sum_{i=1}^{n} (\Delta X)_i,$$ \hspace{1cm} (8b)

and thus the quantity $T_n$ is the sum of $n$ exponential variables which is gamma-distributed, with shape parameter $k = n$,

$$P(T_n = t_w) = \frac{\exp(-t_w/\tau)(t_w)^{n-1}}{\tau^n \Gamma(n)}.$$  \hspace{1cm} (9)
Figure 8. Representation of the statistical process leading to the system collapse for the case where the increment \( \Delta X \) a positive constant. The dotted line corresponds to the value of the threshold \( X^* \).

Figure 9. Representation of the statistical process leading to the system collapse for the case where \( X \) accumulates on each step \( \Delta t \) by random, exponentially-distributed increments \( \Delta X \). The dotted line corresponds to the value of the threshold \( X^* \).

At this point the distribution of waiting times can be written formally as

\[
P(t_w | I, \tau) = \sum_{n=1}^{\infty} P(n_c = n | I) \cdot P(T_n = t_w | \tau)
\]  

which is a mixture of gamma distributions that can be interpreted as a superstatistical model [?].

We will now consider several cases for the quantity \( \Delta X \), namely constant and positive, drawn from a normal distribution and drawn from an exponential distribution.

3.1. \( \Delta X \) a positive constant.

We first consider the case where \( \Delta X \) is a positive constant. After every interval \( \Delta T \) the increment \( \Delta X \) has a single possible value,

\[
P(\Delta X = \xi | I) = \delta(\Delta X - \xi)
\]  

And sum of \( n \) successive increments \( X_n \) is clearly given by a Dirac delta distribution. From the definition of \( n_c \) we can make use of Bayes’ theorem [?] as

\[
P(n_c | C, I) = \frac{P(n_c | I) \times P(C | n_c, I)}{P(C | I)},
\]  

where \( P(n_c | C, I) \) is the probability of \( n \) critical events given the propositions, \( P(C | n_c, I) \) set of occurrence events given conditionality \( C \) and \( P(C | I) \) Total probability of occurrence of all events.

We can obtain the probability distribution \( P(C | n_c, I) \) for the number of critical events \( n_c \) as

\[
P(C | n_c, I) = \int d\Delta X \ P(r_{n-1} = r | X^*, \Delta X) \ P(\Delta X | I) \Theta(1 - r) \Theta \left( \left[r + \frac{\Delta X}{X^*}\right] - 1 \right).
\]  

Since the increment of \( \Delta X \) is constant, we have that \( P(C | n, I) \rightarrow \delta(n, n_c) \). We obtain that the waiting times until the collapse of the system follow a gamma distribution for constant
increments $\Delta X$ as

$$P(t_w|n_c, \tau) = \frac{e^{-t_w/\tau}(t_w)^{n_c-1}}{\tau^{n_c} (n_c-1)!}$$  (14)

In this case the waiting time distribution is an Erlang distribution.

### 3.2. $\Delta X$ a normal distribution.

A case of interest is when $\Delta X$ has a normal distribution, we have two cases, when $\Delta X$ has a normal distribution,

$$P(\Delta X|\mu, \sigma^2) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2\sigma^2}(\Delta X - \mu)^2\right).$$  (15)

If the quantity $\Delta X_n$ is the sum of $n$ normally distributed variables, and we have

$$P(X_n = X|\mu, \sigma^2) = \frac{1}{\sqrt{2\pi n}\sigma} \exp\left(-\frac{1}{2n\sigma^2}(X_n - \mu)^2\right).$$  (16)

Using Bayes’ theorem we obtain,

$$P(C|n_c, I) = \frac{1}{2} \left[ \text{erf}\left(\frac{n - \alpha}{\alpha s\sqrt{2(n-1)}}\right) - \text{erf}\left(\frac{-\alpha + n - 1}{\alpha s\sqrt{2(n-1)}}\right) \right]$$  (17)

where $\alpha = X^*/\langle\Delta X\rangle$. We assume a prior $P(n_c|I) = p_0$ and we obtain the distribution for waiting times,

$$P(t_w|\alpha, \tau) = \sum_{n=1}^{\infty} \exp\left(-\frac{t_w}{\tau}\frac{(t_w)^{n-1}}{\Gamma(n)} \frac{1}{\tau^n} \frac{1}{\tau}\right) \frac{\text{erf}\left(\frac{n - \alpha}{\alpha s\sqrt{2(n-1)}}\right) - \text{erf}\left(\frac{-\alpha + n - 1}{\alpha s\sqrt{2(n-1)}}\right)}{\frac{\alpha^2}{\alpha s\sqrt{2(n-1)}}}.$$  (18)

### 3.3. $\Delta X$ from an exponential distribution.

In this case, we consider $\Delta X$ as an exponentially distributed variable,

$$P(\Delta X|\lambda) = \lambda e^{-\lambda \Delta X}$$  (19)

However, now the quantity $X_n$ is, just as $T_n$, a sum of $n$ i.i.d exponential variables, hence it is also gamma-distributed with shape parameter $k = n$ and the critical number of accumulated events is $n_c$

$$P(X_n = X|\lambda) = \frac{\lambda^n e^{-\lambda X_n}(X_n)^{n-1}}{\Gamma(n)}$$  (20)

We can make use of Bayes’ theorem

$$P(C|n_c, I) = \int dr d\Delta X P(\langle r_n - 1 \rangle = r) \times \Theta(1-r)\Theta(r_n - 1) (21)$$

Now assuming a constant prior probability $P(n_c|I) = p_0$, we obtain a distribution for the waiting times,

$$P(t_w|\alpha, \tau) = \sum_{n=1}^{\infty} \frac{e^{-\alpha - t_w/\tau}}{\tau^n} \frac{I_0\left(\frac{\alpha t_w}{\tau}\right)}{\Gamma(n)}$$  (22)

where $\alpha$ takes the role of a shape parameter. We obtained a distribution of the waiting times in terms of the modified Bessel function $I_0$.

It is important to note that, in the limit of $\alpha \to 0$ we have $\lim_{\alpha \to 0} P(n_c|\alpha) = \delta(n_c, 1)$, corresponding to vanishing threshold $X^* \to 0$ which induces an immediate crossing on the first attempt.
Figure 10. Distribution of normalized waiting times $t_w/\tau$ for different values of the shape parameter $\alpha$. From Ref. [?].

Figure 11. Histogram of waiting times obtained by direct numerical sampling, together with the analytical model of Eq. (22) for $\alpha = 2.4$, $\tau = 6$ (black line) and a gamma model (red line). From Ref. [?].

4. Concluding remarks
We have reviewed some recent results on the problem of homogeneous melting of superheated ideal crystals, in which thermal vacancies produce self-diffusion loops that are correlated with the triggering of the collapse of the crystalline structure. We propose a framework based on the study of random walks on a lattice, and explore the statistics of waiting times before melting.

The connection of these results interpreted as lifetimes of metastable states with that of
metastable states in other systems such as classical spin Hamiltonians [? , ?, ?, ?] is an interesting point to be explored.

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5. References