Quasi-One-Dimensional Thermal Breakage

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Breakage is generally understood in mechanical terms, yet nano-structures can rupture not only under external loads but also via thermal activation. Here we treat in a general framework the thermally induced breakage at the nano-scale for one-dimensional systems. We test it on a simple approximation and find that the probability of breakage controls distinct regimes, characterized by sharp crossovers and narrow peaks in the thermal fluctuations and specific heat. Our work provides predictions on clustering of new phases, of relevance in nano-fabrication.

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Mesoscopic quasi-one-dimensional structures (Q1DS), such as nano-wires \textsuperscript{1}, polymers \textsuperscript{2} and biological molecules \textsuperscript{3} are of great current interest in science and technology. Such systems can now be manipulated at a molecular level and engineered to a desired specification using patterned substrates as templates \textsuperscript{1,4,5}. As a result, there is a growing theoretical appreciation for subtle phenomena activated or suppressed by thermal fluctuations in \textit{individual} systems: e.g. bubble opening and DNA denaturation under external load, nano-island to nano-wire transitions in Stranski-Krastanov growth, local narrowing in nano-wires, local collapse in nano-tubes, selection of growth direction in vapor deposition, or nanodot to nano-ring transition in droplet epitaxy \textsuperscript{6,7}.

However, no general framework exists to treat \textit{thermally induced full breakage} in Q1DS, despite its emergence in supramolecular chemistry of non-covalent polymers \textsuperscript{14,15} or of vapor deposition of nano-wires \textsuperscript{1,4,5,6,7}. Theoretically, this problem is quite distinct from the study of bistabilities, instabilities or local failures \textsuperscript{9,10} where narrowing, collapsing or kinking, but not breakage, produces a local change in functionality.

Here, we study complete breakage by treating distinct, broken fragments. To set the scene, let us consider a sub-critical planar Ising ferromagnet. The magnetized domains are typically rectangles with rounded corners, one dimension of which will typically be reduced by imposing strip boundary conditions. Entropic repulsion \textsuperscript{20} from the lattice edges will compress domains laterally, tending to elongate domains, not necessarily to form wires. Yet, entropic repulsion between the sides of the domain on average parallel to the strip extrema will promote widening of the putative nano-wire segment. We suspect strongly that these entropic interactions will not suffice to produce the desired narrow, wire-like structures with a width asymptotically independent of the channel width. There are a number of possible ways of achieving this. For instance, introducing 4-body interactions in a model of Baxter type can induce a binding-unbinding transition; in the bound state, the nano-wire segment has a width essentially independent of the strip width provided this is wide enough—yet not too wide, otherwise a Privman-Fisher argument \textsuperscript{21} indicates that nano-segments will multiply laterally. Other factors with potential to control the width are differential chemical potential and elastic strain. A further crucial problem in discussing nano-wires is that of analyzing configurations in the channel for connectedness at the nano-level. A development of the Fisher approach to surface phase transitions through the theory of recurrent events on the line \textsuperscript{20} is ideally suited to this task, as we shall show.

As a special case of this formalism, we establish a connection with the 1-d Ising model on a line with special boundary conditions which is useful for discussing our results. We emphasize that our model is a great deal more general and that the Ising model of itself does not contain our results. The only additional technique needed is the quantum mechanics of a particle on a finite line with a localized potential. We establish and discuss conditions for the formation of nano-wires. A key point is that given the channel width the temperature should be necessarily low in a controlled way for nano-wires to form. Further, we show that when breakages coalesce in Q1DS they give rise to narrow crossovers: steep changes of relevant observables and narrow peaks in thermal fluctuations. These crossovers might have escaped the attention of experimentalists as pathological to desired result, e.g. the realization of long nano-wires in vapor deposition. Yet they are indicative of new phases of clustering which could be explored for nano-manufacturing.

In \textsuperscript{9}, we considered malfunction of a Q1DS (a nano-wire, a nano-tube or a bio-polymer) that comes about because two edges of the wire approach too closely as a result of thermal fluctuations. This model was treated using the Fisher recurrence idea: the partition function \(Z_n\) which satisfies (5) from \textsuperscript{9}:

\[
Z_n = \Omega_n + \sum_{m=1}^{n-1} \Omega_m Z_{n-m}.
\]  

Here \(\Omega_n\) is the partition function for the system of length \(n\) with no points of malfunction. Equation (1) can be converted into an algebraic one between generating functions...
by noting that the generating function of the convolution on the right hand is a product of the generating functions from $\Omega_n$ and $Z_n$. In this work, we consider complete breaking of nano-wires into separate parts. Unlike the macro domain, where we would be discussing mechanical rupture, we have to consider once again the effects of thermal fluctuations. To construct a sensible model, we have to place the putative nano-wire forming material in a channel of finite width.

Our approach is general, but for definiteness, we employ the language of epitaxial growth. Consider a straight channel of lateral size $D$ and length $Na$ ($a$ is a suitable discretization length and $N$ a positive integer; we take $a = 1$) in which a nano-wire is grown in equilibrium with gas as in Fig. 1. A piece of the system of length $na$ might contain a mix of gas and (possibly) broken nano-wires—and then we call $Z_n$ its partition function; or gas and a single unbroken nano-wire—$O_n$; or only gas—$G_n$. Both $O_n$ and $G_n$ are known while $Z_n$ is to be found.

The system can: (I) contain a single unbroken nano-wire, contributing $O_N$ to $Z_N$; (II) contain a shorter nano-wire of length $j$ followed by gas, contributing $O_j \times G_{N-j}$ to $Z_N$; (III) or can start with a nano-wire of length $j$, be followed by a portion of gas of length $i$, and then whatever else is allowed on the remaining $N-i-j$, contributing $O_i \times G_j \times Z_{N-i-j}$ to $Z_N$.

By summing over all these configurations, one obtains the following double convolution equation

$$Z_N = O_N + O_{N-1}G_1 + O_{N-2}G_2 + \cdots + O_1G_{N-1} + O_{N-2}(G_1Z_1) + O_{N-3}(G_1Z_2 + G_2Z_1) + \cdots + O_1(G_{N-2}Z_1 + G_{N-3}Z_2 + \cdots + G_1Z_{N-2}).$$

$(N \geq 1$ and $O_n, G_n$ are taken to be zero if $n \leq 0$.)

The linear density of free energy for the entire system is then $F = -\beta^{-1}\ln(Z_N)/N$ in the limit of large $N$, and as usual $\beta^{-1} = k_BT$. Since the gas phase approaches the thermodynamic limit faster than the solid phase, we take $G_n$ to be exponential in $n$. Then [2] maintains the same form in the relative (to the gas phase) quantities $Z_n = Z_n/G_n$, $\Omega_n = O_n/G_n$, $V_n = G_n/G_n = 1$. The relative free energy is thus $\phi = -\beta^{-1}\ln(Z_N)/N$.

We solve (2) by noting its convolution structure

$$Z_N = \Omega_N + (\Omega * V)_N + (\Omega * V * Z)_N$$

and introducing the generating functions $\tilde{Z}(u) = \sum_{n=1}^{\infty} Z_n u^n$, $\tilde{\Omega}(u) = \sum_{n=1}^{\infty} \Omega_n u^n$, $V(u) = \sum_{n=1}^{\infty} V_n u^n = u/(1-u)$.

Since the convolution product is associative, the generating function of the third term on the right of (3) is an algebraic product of generating functions. Since $\Omega_n$, and therefore its generating function $\tilde{\Omega}$ is assumed known, $\tilde{Z}$ can be obtained as:

$$\tilde{Z}(u) = \tilde{\Omega}(u)/\left[1 - (\tilde{\Omega}(u) + 1)u\right].$$

Then the partition function $Z_n$ is obtained from [4] by contour integration and the residue theorem. For this to be useful, we need the analytic structure of $\tilde{\Omega}(u)$.

The following simple example of the procedure is instructive: assume that

$$\Omega_n = p^2 \omega^n,$$

and thus $\tilde{\Omega}(u) = p^2 \omega u/(1 - \omega u)$. (5)

Here $\omega$ is the fugacity per unit length of the nano-wire and $p$ is the Boltzmann factor for a break; [5] is clearly an approximation which will be discussed critically later: we will show that it represents the first order approximation of the more general case.

The zeros in the denominator of (4), which give simple poles of the integrand, are given by the solutions of $\tilde{\Omega}(u) = u^{-1} - 1$, which in the case of (5) is simply a quadratic equation. This model is a somewhat disguised version of a 1-d Ising chain with fixed spins on the extremities. Each segment of the nano-wire is represented by an up spin, whereas the gas has down spins.

The energy of any configuration in the channel, with the same edge conditions as before, is:

$$\beta E = -2K \sum_{n=1}^{N-1}(1 - \sigma_n \sigma_{n+1})/2 + 2h \sum_{n=1}^{N}(1 + \sigma_n)/2$$

with: $p = \exp(-2K)$ and $\omega = \exp(2h)$. At the left hand end we always have an element of nano-wire, so that extreme spin is up, but the spin at the other end is down. Thus identical answers can be obtained in either way:

$$Z_n = [\omega p^2/(\omega_+ - \omega_-)] \left(\omega_+^n - \omega_-^n\right),$$

where the $\omega_{\pm}$, which are closely related to the $d = 1$ Ising transfer matrix eigenvalues, are given by:

$$2\omega_\pm = 1 + \omega \pm \left[(\omega - 1)^2 + 4\omega p^2\right]^{1/2}.$$
with $\omega_+ > \omega > 0$. The limiting free energy $\phi$ per unit channel length is given by: $\phi = -\beta \ln \omega_+$. To study the ordering in this model, we can write $Z_N$ as a polynomial in $p$, the power being $n_b$, the number of breakages, and the coefficient multiplying such a term independent of $p$. It is then easy to show the fraction of breakages and its variance are given by:

$$n_b = -\beta p \partial_p \phi, \quad \sigma^2(n_b) = p \partial_p n_b.$$  \hfill (9)

An analogous argument applies to the fraction $s$ of up spins or nano-wire, giving:

$$s = -\beta \omega \partial_\omega \phi, \quad \sigma^2(s) = \omega \partial_\omega s.$$  \hfill (10)

This gives directly:

$$s = (\omega_+ - 1)/(2\omega_+ - \omega - 1), \quad n_b = 2(\omega_+ - \omega)s/\omega_+.$$  \hfill (11)

The average channel length lacking a nano-wire is given by $g = 1 - s$, so the average length of a nano-wire is $l_s = 2s/n_b$ and that of a gap is $l_g = 2g/n_b$. Thus:

$$l_s = \omega_+/\omega_+ - \omega, \quad l_g = \omega_+/(\omega_+ - 1).$$  \hfill (12)

We can check these equations for the obvious symmetry $\omega \to 1/\omega$: then $\omega_+ \to \omega_+ / \omega$, $n_b \to n_b$, $l_s \to l_g$. The condition for producing large $l_s$ is then $\omega_+ - \omega \to 0+$, which is the case if $p \to 0$ and $\omega - 1 \to 0+$. In 1-d Ising language, this is completely obvious, as this is the critical point from one side.

Also, there is the scaling: note that if $x$ is defined by sinh $x = (\omega - 1)/(2p \sqrt{\omega})$, then $s = \exp x/(2 \cosh x)$. Similarly, for the gas fraction, one has $g(x) = s(-x)$. Now if we take the scaling limit (denoted slim) $\omega \to 1 \pm$, $p \to 0$, such that sinh $x$ has a definite limit, then: slim $l_s = \text{sech} x$ and slim $l_g = \exp(-x)$. Thus, to have long nano-wires, take $p$ small, then adjust the relative weights of wire and gas using $x$ as a control parameter. The behavior in this case is ferromagnetic. There is another scaling limit which has $|\ln \omega| \to \infty$, $p \to \infty$ such that sinh $x = \text{slim}[\pm \omega^{\pm 1/2}/(2p)]$ (plus when $\omega \to \infty$ and minus when $\omega \to 0+$). This is anti-ferromagnetic in character.

We can relate \cite{2} to thermodynamics via $\omega = \exp(\beta \mu)$, $p = M \exp(-\beta \tau)$: $\mu = \mu_g - \mu_s$ is the difference in chemical potential between gas and solid per unit length, $M$ accounts for the lateral degeneracy of a broken piece, and $\tau$ is the energy cost of a rupture. Then $x$ generalizes the quantity $\beta \mu/2$ when $p \neq 1$. Indeed $p \sinh x = \sinh(\beta \mu/2)$, and $x = \beta \mu/2$ when $p = 1$. This corresponds to $K = 0$ in the Ising model, or noninteracting spins in a field, and could describe the case of a noncovalent polymer \cite{17} \cite{18} inside a long nano-tube \cite{22}.

We now offer predictions in the context of nano-wires deposition, and in terms of the experimentally controllable parameters $\mu$ and $p$. Particularly interesting is the “ferromagnetic” scaling limit $p \to 0^+$, $\omega \to 1 \pm$, which corresponds, as we will see, to a crossover through nano-clustering. Plots of the fraction of solid $s$ (Fig. 2 bottom) and its fluctuations (Fig. 2 middle and top) vs. the difference in chemical potential $\mu$ show a sharp crossover around $\mu = 0$ in the limit of small $p$. As $p \to 0^+$, the crossover becomes sharper, as the plot for $s$ tends to a step, and a narrow peak in thermal fluctuations grows around $\mu = 0$: the system tends asymptotically to the bulk transition described above ($p = 0$). For small $x$, one can approximate $x \sim \beta \mu/p$ and thus the width of the crossover in terms of the chemical potential difference is $\beta \Delta \mu \simeq 2p$.

This crossover represents formations of spaced nano-clusters. Equation \cite{9} shows that for $\mu = 0$ one has $n_b = p/(1 + p)$ and therefore $l_s = l_g = (1 + p)/p \simeq 1/p$.
for small $p$. Since at $\mu = 0$ one has $s = g = 1/2$, the crossover exists in a narrow (in $\mu$) region composed of nano-structures of finite length $a/p$ separated by intervals of equal length.

At crossover the scaling limit mentioned above implies, experimentally, a data collapse in the scaling parameter $y \equiv (\omega - 1)/2p$. The expression for $\omega_\ast$ in (5) returns $\sinh 2y_\ast = y + \sqrt{y^2 + 1}$, where $y_\ast \equiv (\omega - 1)/2p$, and as above the scaling limit corresponds to $p$ and $(\omega - 1) \to 0+$ with $y$ finite. It is then simple to prove that $\sinh x = y$ and therefore $s$ is a function solely of the scaling parameter $y$. To find $n_b$: since $\omega_\ast = 1 + p \exp x$, the linear density of free energy for the system $F = -k_B T \log (\omega_\ast) + \mu_g$ at first order in $p$ is $F \simeq \mu_g - p k_B T \exp x$; from (11) we obtain $n_b = \text{psec} x$ where $\sinh x = y$. Then the expansion of $F$ at $x = 0$ returns $F \simeq -k_B T p + (\mu_g + \mu_s)/2 + (\mu_g - \mu_s)^2/(8 k_B T p)$; the first term is the expression for the free energy of breakages between degenerate phases and can be obtained via heuristic treatments; the second term reaffirms the equal mixture of solid and gas at transition ($s = g = 1/2$); the third shows that the lowest order contribution in the difference between chemical potentials is quadratic: this ensures a peak in the specific heat, which diverges as $p \to 0$.

A nano-clustering crossover could be accessible when the surface energy cost of a breakage (which is proportional to the size of the pore) is much larger than temperature. For Stranski-Krastanov deposition in a channel [29], Tersoff and Tromp have predicted on purely energetic grounds [11] the growth of wires of defined lateral size as the result of a shape-anisotropy transition whose thermal stability we have investigated elsewhere [10] to explain further experimental results [14, 15]. Our current analysis completes our previous treatment and shows that even at a temperature at which the shape anisotropy transition is stable, long nano-wire fabrication can be compromised by thermally activated breakage.

The antiferromagnetic limit corresponds to large $p$, which models growth in a broad yet not too broad channel (see above): a larger channel implies larger entropy gained by the broken pieces as they can move laterally. It corresponds to a phase of interspersed atomic clustering.

Figure 2, right inset, shows a plateau for the ratio of gas and solid phase at large $p$. The top panel shows that for large $p$, $n_b \simeq 1$ and therefore, since $s = g = 1/2$ on the plateau, then $l_s = l_g = 1$. For large $p$, the system can access an antiferromagnetic phase of adsorbed solid and gas alternating at the unit cell length scale. Using the scale limit argument one can show that data collapse depends now in the scaling parameter for the left and right crossover $y_{cL}^{\pm} \equiv \omega^{\pm 1/2}/(2p)$, for which $\sinh x = y^{\pm 1}$ depending on the side of the crossover. Since $y_{cL}^{+} = \exp\{[\pm \beta \mu - 2 \ln(2p)]/2\}$, the crossovers occur at $\mu / k_B T = \pm 2 \ln(2p)$. These crossovers are characterized by peaks in the fluctuation of both the solid fraction and of the density of breakages (Fig. 2).

Thus far, we have extended the renewal ideas of Fisher [20] to tackle the problem of connectedness of nano-wire configurations. We have illustrated this with a simple assumed form for $\Omega$, that surely does not exhaust the complexity of real possibilities. We need now to analyze $\Omega$ in a critical way. A putative nano-wire inserted into a strip of “gas” is a strip of solid inserted between two boundaries running roughly parallel to the strip axis. Each boundary has an independent incremental free energy, but there may be additional interactions due to differential fugacity, elastic mis-match and 4-body terms, to name but three. These can produce bound states between the opposite sides of the wire, with nano-wire width determined by these parameters, considerably less than, and only weakly dependent on, the channel width $D$. The key idea is that one side of the nano-wire can partially wet the other side. Thus we are in familiar wetting, or equivalently pinning-depinning territory [21, 22].

Under these conditions, it makes sense to treat the relative and center of mass coordinates independently. To a good approximation, the center of mass mode has an energy per unit length given by $E = ak^2$ and takes discrete values given by the solution of an equation of the form $\exp(i D k) = f(k)$, where $a$ is the interfacial stiffness [29], and $f$ is an analytic function [28]. For instance, the transfer matrix solution of the planar Ising strip affords us just such an example, the energy expression being well-approximated by the free particle form above and the momenta being given to good approximation by $k_j = \pi j / D$, $j = 1, ..., D$.

In this approximation we can show that:

$$\Omega(u) = p^2 \sum_{j=1}^{D} q_j u w / \{ \exp \left[ a (\pi j / D)^2 \right] - \omega u \}, \quad (13)$$

with $q_j = 2 D^{-1} \cot^2(\pi j / 2D)$. This has the interesting large $D$ behavior $q_j = 2D/\pi$, a manifestation of transverse entropy.

To complete the job, we have to solve for the zeros of the denominator in $Z(u)$, either by sketching a graph.
(Fig. 3) or otherwise. The key point is that there is a unique minimal such value, denoted $u_0$, which is the only one to report in the incremental free energy $\phi$. This justifies the interpretation of the solid as a nano-wire and also the ultimate application to this system of the 1-d Ising analysis in (4); the other, non-minimal $u$ values are indeed there, but they do not report in the limiting free energy $\phi$, as we have demonstrated.

Comparing (13) with (5), we see that for the channel problem we now have $D$ terms. Provided $a(\pi/D)^2 \gg 1$, in looking for the minimal solution of $\Omega(u) = u^{-1} - 1$, we can treat terms with $j > 1$ as a perturbation of the $j = 1$ solution which we have already found; all that is needed is to replace $\omega$ and $p$ by $\omega' = \omega \exp \left[-a(\pi/D)^2\right]$ and $p' = q_1^{1/2} p$. Then to first order we can take over the calculation based on (5).

The condition for this is, as stated above, that $D$ is small enough, or, given $D$, that the stiffness is large enough. This implies that the nano-wire will be relatively free of kinks, clearly a desideratum. Provided we can also satisfy $2D \gg \pi$, then $q_1 \sim 8D/\pi^2$. The linearity in width when the nano-wire is reasonably stiff makes good sense as a manifestation of transverse translational degeneracy.

In summary, we have introduced an extension of Fisher’s renewal theory of surface phase transitions [20] and analyzed the connectedness of nano-wires assembled in a channel when complete rupture can occur. We have given theoretical conditions for facilitating nano-wire growth. Our method has potential for application in a much wider setting; all that is needed is to calculate $\Omega_n$.

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