Statistical mechanics of nonlinear elasticity

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Running title: statistical mechanics of nonlinear elasticity *or* nonlinear elasticity

Abstract

A method is suggested for defining a deformation-dependent free energy in microscopic terms for a deformed elastic solid and applied to a simple microscopic model of such a solid. Some of the convexity and continuity properties of this free energy function are derived.

Keywords: nonlinear elasticity, restricted ensembles in statistical mechanics.

AMS and Mathematical Reviews classification numbers: 82B05 classical equilibrium statistical mechanics (general), 74B20 nonlinear elasticity

1 Introduction

The standard way of defining the (bulk) thermodynamic free energy density in statistical mechanics is the one developed by Ruelle[3] and Fisher[5] and expounded in Ruelle's book [4]. One of the main consequences of this definition is the theorem that the free energy density f for a classical system with interactions of a suitable type depends only on the temperature T and the particle number density ρ (or, in the case of a mixture of particle types, the number densities of all the particle types). The free energy density does not depend on the shape of the container. According to thermodynamic limit theory, therefore, the system behaves like a fluid, offering virtually no resistance to changes of shape, and there is no such thing as elasticity in the

thermodynamic equilibrium theory: a body under a finite elastic strain is regarded as being at best in metastable equilibrium.

Possibly as a result of this fact, very little work has been done on the statistical mechanics of elasticity. That which has been done[1, 2, 6] concentrates on ideas which enable us to define the elastic moduli of linear elasticity theory in terms of equilibrium properties of the system. However not all elastic effects are linear, and non-linear elasticity presents some phase transition phenomena which should be very interesting to practioners of statistical mechanics, particularly the austenite-martensite transition and the possibility of designing shape-memory materials which take advantage of this transition[8].

In non-linear elasticity theory the material is regarded as a continuous medium which has reached its present state by deformation from an undeformed reference state; if we denote the position of a material point in the reference state by a vector $\mathbf{x}$ and its position in the deformed state by $\mathbf{y}$, then the local elastic strain is determined by the *deformation gradient* $\nabla_{\mathbf{x}}\mathbf{y}(\mathbf{x})$. The fundamental assumption of the theory is that the total free energy of the system is obtained by summing the contributions from the separate elementary parts of the material, and that the free energy of each elementary part depends only on the local elastic state of that part. Thus, the total free energy can be written as an integral over the region Ω_0 occupied by the undeformed system

$$F = \int_{\Omega_0} f_{el}(\nabla_{\mathbf{x}}\mathbf{y}(\mathbf{x}))\, d\mathbf{x} \tag{1}$$

where the 'stored-energy function' f_{el}, a function of the deformation gradient, is the free energy of the deformed material per unit pre-deformation volume. The equilibrium state $\mathbf{y}(\cdot)$ of the deformed specimen can be found by minimizing F with respect to the function $\mathbf{y}(\cdot)$ subject to boundary conditions describing the tractions or other constraints applied at the surface of the specimen. The minimization is not trivial, because the deformation gradients at different points in the specimen cannot be varied independently, and if in addition the function f_{el} is non-convex a rich variety of phenomena become possible, such as the austenite-martensite transition mentioned above.

To apply statistical mechanics to nonlinear elasticity, it is clearly necessary to do something different from the standard thermodynamic limit theory based on the Gibbs canonical ensemble. The approach used in the present paper is to use a modified ensemble, based on constraints which model the fact that a real solid would take an absurdly long time to reach

the equilibrium state predicted by the canonical ensemble. The philosophy is similar to that used in the statistical mechanics of metastable states[12, 9], where constraints can be used to model the fact that the nucleation of the new phase may be extremely slow.

The main purpose of the present paper is to suggest a way of defining the free energy f_{el} appearing in eqn (1) in terms of a restricted partition function, and to derive some of the simplest properties of this function, particularly some convexity properties. It is to be hoped that, eventually, a formula such as (1) will come out of the theory, but no such derivation will be attempted here.

2 A microscopic model for a deformable solid

To see how statistical mechanics might be applied to deformed states of a solid, consider for simplicity a two-dimensional monatomic system for which the equilibrium state at sufficiently low temperatures and high densites is a crystal in which the mean positions of the atoms lie on a square lattice. The principles should be equally applicable in three dimensions and to other lattices, but everything would be more complicated.

A microscopic model that appears to have this property is a system of rotatable hard disks in which four special points or 'poles' are fixed to each disk at equally spaced positions around the circumference, and there is a two-body attractive interaction between any pair of disks with 'poles' that are close together (see Fig. 1).

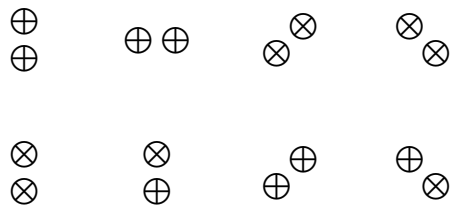

Fig. 1 A model whose molecules are interacting rotatable disks. The four 'poles' of each disk are at the places where the cross meets the circumference. For each pair of molecules in the top line the crosses are aligned with the line of centres and so the molecules attract (i.e. their interaction energy is negative); but none of the pairs in the bottom line are properly aligned and so none of them interact.

To illustrate the method, we shall consider a specific model in which the disks have mass μ, moment of inertia I and diameter D, so that the Hamiltonian is

$$H = \sum_i \left(\frac{\mathbf{p}_i^2}{2\mu} + \frac{J_i^2}{2I} \right) + U \tag{2}$$

where $\mathbf{p}_i \in R^2$ is the linear momentum of the ith particle, $J_i \in R$ is its angular momentum, and the potential energy U is a sum of one-body terms representing the interaction of the disks with the walls of the container together with a sum of two-body terms representing their interaction with each other:

$$U = \sum_i u_{wall}(\mathbf{q}_i) + \sum_{i<j} [u_{hc}(r_{ij}) + u_{ang}(\mathbf{q}_i, \phi_i; \mathbf{q}_j, \phi_j)]. \tag{3}$$

In this last formula, the term $u_{wall}(\mathbf{q}_i)$ is defined to be zero if the disk centred at $\mathbf{q}_i$ lies entirely within the container and to be $+\infty$ otherwise. The term $u_{hc}(r_{ij})$, depending only on the distance r_{ij} between the centres $\mathbf{q}_i, \mathbf{q}_j$ of the ith and jth disks, is the hard-core repulsion

$$u_{hc}(r) = \left\{ \begin{array}{rl} 0 & \text{if } r \geq D \\ +\infty & \text{if } r < D \end{array} \right\}, \tag{4}$$

while u_{ang} is an angle-dependent attractive potential, which we assume for definiteness to be

$$u_{ang}(\mathbf{q}_i, \phi_i; \mathbf{q}_j, \phi_j) = -\frac{C}{r_{ij}^{2+\epsilon}} \cos^2[2(\phi_i - \theta_{ij})] \cos^2[2(\phi_j - \theta_{ij})] \tag{5}$$

where C, ϵ are positive constants (If $C/r_{ij}^{2+\epsilon}$ in (5) were replaced by a Kac potential, some quantititive properties of the model might be rigorously obtainable, but that is not the purpose of the present paper.) In the angle-dependent factor, $\phi_i \in [0, 2\pi)$ is the orientation of one of the polar axes of the ith disk with respect to some fixed direction (say the x-axis), and θ_{ij} is the orientation of the relative displacement vector $\mathbf{q}_i - \mathbf{q}_j$ with respect to this same fixed direction. The variables $\mathbf{q}_i$ and ϕ_i are canonically conjugate to $\mathbf{p}_i$ and J_i respectively.

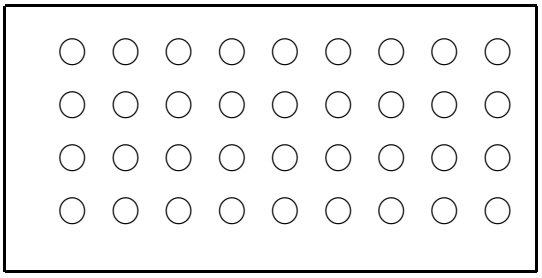

Fig 2a: undeformed state

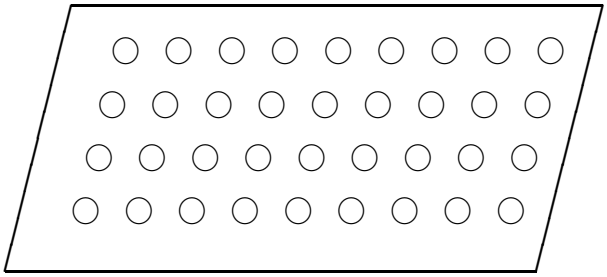

Fig 2b: deformed state

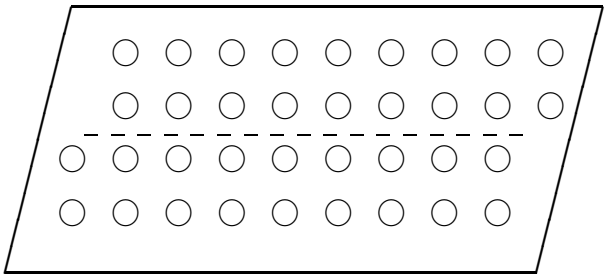

Fig 2c: new equilibrium state

Fig. 2. Undeformed and deformed states of an elasic solid.

Suppose now that a system with the Hamiltonian (2) is put into a rectangular box. At sufficiently low temperatures and high densites we would

expect its equilibrium state to be a crystal in which the mean positions of the atoms form a square lattice. Such a state is illustrated in Fig. 2a, where the circles indicate the ever-fluctuating positions of the atoms. If now the shape of the box is changed, say to a parallelogram as in Fig. 2b, one would expect the immediate response of the system to be an elastic deformation, shifting the mean positions of the atoms as illustrated in Fig. 2b. Equilibrium statistical mechanics, however, would be likely to predict (for a sufficiently large system) a final equilibrium state such as is illustrated in Fig. 2c: this state has more surface energy, but less bulk energy because the local arrangement near each of the internal particles is closer to the original equilibrium state shown in Fig. 2a. The most likely way for the system to get from the state in Fig. 2b to the one in Fig. 2c. would no doubt be for a dislocation to travel along the dotted line in Fig. 2c; but the activation energy for the nucleation of dislocations can be large, especially in three dimensions where the formation of a new dislocation involves the organized motion of many atoms. Therefore one may expect, particularly in three dimensions, that a deformed state such as the one illustrated in Fig. 2b may have a long lifetime despite not being a 'true' equilibrium, and that the methods of equilibrium statistical mechanics may have something useful to tell us about such states.

3 The unrestricted ensemble

To define the statistical mechanics more precisely, let us consider a system consisting of MN disks, where M, N are positive integers, and define a reference configuration which is similar to the one illustrated in Fig. 2a but is tightly packed: it consists of a rectangular $M \times N$ lattice with spacing D. This lattice will be denoted by Λ. When the molecules are in this configuration they can be enclosed in a rectangular box Ω_0 whose vertices have position vectors $0, MD\mathbf{i}, ND\mathbf{j}, MD\mathbf{i}+ND\mathbf{j}$ where $\mathbf{i}$ and $\mathbf{j}$ are unit vectors parallel to the x and y axes respectively. The sites of this lattice can be labelled by ordered pairs of integers (m, n), with $1 \le m \le M, 1 \le n \le N$, in such a way that the position of the (m, n) lattice site is

$$\mathbf{x}_{mn} = (m - \frac{1}{2})D\mathbf{i} + (n - \frac{1}{2})D\mathbf{j} \quad \in \Lambda \tag{6}$$

We associate each molecule of the system with one of these sites, which may be thought of as its 'home', and instead of using single subscripts i etc. as

in eqn (2) to label the particles we now label them with double subscripts to show which site of Λ is the particle's home.

Given any two vectors $\mathbf{A}, \mathbf{B}$ let us define $\Omega_{\mathbf{A},\mathbf{B}}$ to mean a parallelogram with sides $\mathbf{A}, \mathbf{B}$ and vertices at the points $0, \mathbf{A}, \mathbf{B}, \mathbf{A}+\mathbf{B}$. Suppose the system just described to be placed in a box $\Omega_{M\mathbf{a},N\mathbf{b}}$, where $\mathbf{a}, \mathbf{b}$ are two vectors with lengths somewhat greater than D and relative orientation such that $\mathbf{a} \times \mathbf{b}$ is parallel to $\mathbf{i} \times \mathbf{j}$ rather than anti-parallel. In Fig. 2b the vector $\mathbf{a}$ is a positive multiple of $\mathbf{i}$, while $\mathbf{b}$ is a positive linear combination of $\mathbf{i}$ and $\mathbf{j}$. The standard (unrestricted) canonical partition function for this system is

$$Z(\Omega_{M\mathbf{a},N\mathbf{b}}, M, N) = \frac{\lambda^{MN}}{(MN)!} \prod_{m=1}^{M} \prod_{n=1}^{N} \left[\int_{\Omega_{M\mathbf{a},N\mathbf{b}}} d\,\mathbf{q}_{mn} \int_0^{2\pi} d\,\phi_{mn} \right] \mathrm{e}^{-U/kT}; \tag{7}$$

here the momentum integrations are taken care of by the factor λ^{MN}, where

$$\lambda = \frac{(2\pi kT)^{3/2} \mu I^{1/2}}{h^3} \tag{8}$$

and Planck's constant h is included only to ensure correspondence with the analogous quantum system.

Following the methods developed by Ruelle and Fisher [4, 5], the thermodynamic specific free energy (free energy per lattice point) can be defined by

$$f = -kT \lim_{M,N\to\infty} \frac{\ln Z(\Omega_{M\mathbf{a},N\mathbf{b}}, M, N)}{MN} \tag{9}$$

where the limit is taken at fixed $\mathbf{a}, \mathbf{b}$. The specific free energy depends only on the temperature T and on the specific area (area per lattice point), which is $2\mathbf{a} \times \mathbf{b}$. It is a convex and continuous function of the specific area; it does not depend on the shape of the container and is therefore the same as for a rectangular container with the same specific area. The physical reason for this independence is that, in the unrestricted ensemble, a configuration such as the one illustrated in Fig. 2c has (because of its lower energy) a much higher probability than the one illustrated in Fig. 2b, and so the free energy per unit volume is always close to that of the square lattice, regardless of the shape of the container.

4 The restricted ensemble

To get a free energy that depends on the shape of the container, we use a restricted ensemble. Adapting the notation used in (5), denote the direction of the line joining the centres of the disks labelled mn and $m'n'$ by $\theta_{mn;m'n'}$. In the reference configuration any particle not on the edge has four nearest neighbours, with labels $(m\pm1,n)$ and $(m,n\pm1)$, and the directions to these neighbours are $\theta_{mn;m\pm1,n}$, etc. Let us denote the four angles subtended by adjacent pairs of these neighbours by $\psi^{(\swarrow)}_{mn}$, etc, defined as in Fig. 3, or by the formulas in eqn (10).

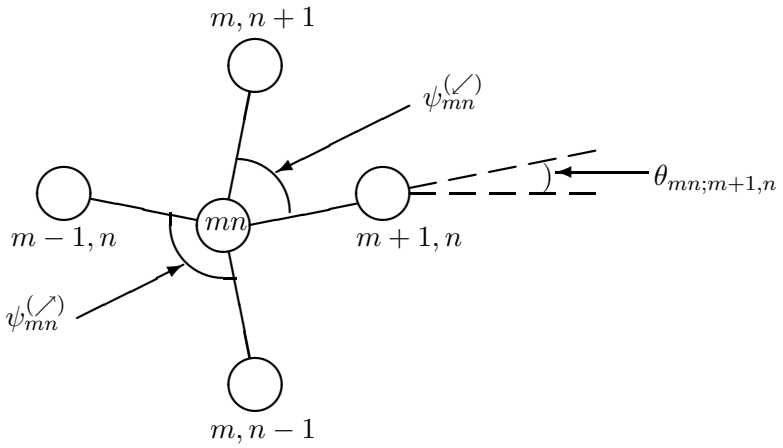

Fig.3 Some of the angles used in defining the restricted ensemble.

In the undeformed configuration, these angles are all right angles. In the configuration shown in Fig. 2c, however, some of the angles involving molecules adjacent to the dotted line are close to 45 degrees or 135 degrees (for example, $\psi^{(\swarrow)}_{12} = \theta_{13,12} - \theta_{22,12}$ is about 45 degrees). Thus, we can exclude the configuration shown in Fig 2c from our restricted configuration space by requiring all of the angles $\psi^{(\swarrow)}_{mn}$ etc., to lie between (say) 60 and 120 degrees. In symbols, the inequalities describing these requirements are

$$\begin{aligned}
\psi^{(\swarrow)}_{mn} &\equiv \theta_{m,n+1;mn} - \theta_{m+1,n;mn} \in [\pi/3, 2\pi/3](1\le m\le M-1, 1\le n\le N-1)\\
\psi^{(\searrow)}_{mn} &\equiv \theta_{m-1,n;mn} - \theta_{m,n+1;mn} \in [\pi/3, 2\pi/3](2\le m\le M, 1\le n\le N-1)\\
\psi^{(\nearrow)}_{mn} &\equiv \theta_{m,n-1;mn} - \theta_{m-1,n;mn} \in [\pi/3, 2\pi/3](2\le m\le M, 2\le n\le N)\\
\psi^{(\nwarrow)}_{mn} &\equiv \theta_{m+1,n;mn} - \theta_{m,n-1;mn} \in [\pi/3, 2\pi/3](1\le m\le M-1, 2\le n\le N)
\end{aligned} \tag{10}$$

where the symbol $\equiv$ means that the expressions it connects differ by an integer multiple of 2π chosen so that all the angles ψ are in $[0, 2\pi)$.

Besides these inequalities to prevent dislocations, which affect all the molecules, we shall also impose some conditions which affect only the molecules on the edge of the system, anchoring them to particular positions relative to the nearby wall. Suppose, as before, that the system is contained within the parallelogram $\Omega_{M\mathbf{a},N\mathbf{b}}$ whose vertices are $0, M\mathbf{a}, N\mathbf{b}, M\mathbf{a} + N\mathbf{b}$. This parallelogram can be obtained from the rectangle $\Omega_0 = \Omega_{MD\mathbf{i},ND\mathbf{j}}$, which just fits around the disks when they are in the close-packed configuration Λ, by the affine mapping $\mathbf{x} \to \mathbf{G} \cdot \mathbf{x}$, where $\mathbf{G}$, a tensor of rank 2, is defined in terms of dyadics as

$$\mathbf{G} = (\mathbf{a}\mathbf{i} + \mathbf{b}\mathbf{j})/D \tag{11}$$

Alternatively, $\mathbf{G}$ can be thought of as $1/D$ times a 2×2 matrix $[\mathbf{a}|\mathbf{b}]$, whose first and second columns consist respectively of the components of the vector $\mathbf{a}$ and those of $\mathbf{b}$. By applying the same mapping to the close-packed lattice Λ, the formula for whose points $\mathbf{x}_{mn}$ is given in (6), we obtain a new lattice $\mathbf{G}\Lambda$ whose points are

$$\mathbf{y}_{mn} = (m - \frac{1}{2})\mathbf{a} + (n - \frac{1}{2})\mathbf{b} \tag{12}$$

It is to be expected that the average positions of the particles in the restricted ensemble will be these lattice points, and our condition will ensure that the particles on the edge of the lattice (but not the other particles) are indeed very close to the appropriate lattice points $\mathbf{y}_{mn}$. The condition has to be chosen carefully, because the proof of our main theorem will require that when two parallelograms are joined together and the wall between them removed, the new larger system has a demonstrably larger free energy than the two smaller ones taken together. The condition is

$$|\mathbf{q}_{mn} - \mathbf{y}_{mn}| < \delta \quad \text{if } m = 1 \text{ or } m = M \text{ or } n = 1 \text{ or } n = N \tag{13}$$

where δ is a positive length parameter which can be arbitrarily small but must not exceed a certain value, which depends on the vectors $\mathbf{a}, \mathbf{b}$ in a way to be specified later (see eqn(19)).

For the proof of our main theorem it will be necessary to ensure that none of the particles can stray far from its average position; it may be that the restriction (10) is already enough to ensure this, but to avoid having to prove such things we shall impose one further restriction

$$|\mathbf{q}_{mn} - \mathbf{y}_{mn}| < R \tag{14}$$

where R is another length constant, which may be arbitrarily large. Since this constraint affects all the particles, the value of R will affect the bulk elastic free energy we are going to define, but it is to be hoped that for large enough R the effect on the elastic free energy will be small, and can be eliminated altogether by taking the limit $R \to \infty$ after the thermodynamic limit.

Now we can define the restricted partition function. It is defined by

$$Z_{el}(\mathbf{a}, \mathbf{b}; M, N) = \lambda^{MN} \prod_{m=1}^{M} \prod_{n=1}^{N} \left[\int_{\Omega_{M\mathbf{a}, N\mathbf{b}}} d\,\mathbf{q}_{mn} \int_0^{2\pi} d\,\phi_{mn} \right] \chi(\mathbf{q}_{11} \ldots \mathbf{q}_{MN}) \mathrm{e}^{-U/kT}; \tag{15}$$

where χ is defined to be 1 if the position vectors satisfy all the inequalities (10), (13) and (14), but to be 0 otherwise. There is no $(MN)!$ in the formula this time; such a factor would be inappropriate because the definition of χ is not symmetrical under permutations of the particles. For some values of its arguments Z_{el} may be zero; in particular if the angle between $\mathbf{a}$ and $\mathbf{b}$ is less than 60 degrees or greater than 120 then the angular constraints (10) cannot all be satisfied.

Later on we shall need an upper bound on Z_{el}. A simple modification of the corresponding proof for central forces[11, 5] shows that the potential defined in (3) is stable, i.e. there exists a positive constant B such that the potential U for a system of MN particles satisfies $U > -MNB$, and it follows from (15) and (14) that

$$Z_{el} \leq (\lambda(\pi R^2) 2\pi)^{MN} \tag{16}$$

5 Properties of the restricted free energy

The following theorem and its proof are modelled on the results of Ruelle[3, 4] and Fisher[5] for the unrestricted free energy.

Theorem 1 *(i) The elastic free energy per particle, defined for parallelogram-shaped regions by*

$$f_{el}(\mathbf{a}, \mathbf{b}) = -kT \lim_{k \to \infty} \frac{\log Z_{el}(\mathbf{a}, \mathbf{b}; 2^k, 2^k)}{4^k} \tag{17}$$

and taking values in $R \cup \{+\infty\}$, exists for all non-zero vectors $\mathbf{a}, \mathbf{b}$ such that the angle $\angle(\mathbf{a}, \mathbf{b})$ between these vectors satisfies $\pi/3 < \angle(\mathbf{a}, \mathbf{b}) < 2\pi/3$ (this

angle being reckoned positive when the vector product $\mathbf{a}\times\mathbf{b}$ *is parallel to* $\mathbf{i}\times\mathbf{j}$ *rather than anti-parallel).*

(ii) For given $\mathbf{a},\mathbf{b}$*,* $f(\alpha\mathbf{a},\beta\mathbf{b})$ *is a convex function of the positive real numbers* α,β*, wherever it is bounded above.*

The proof depends on the following lemma:

Lemma 1 *Let* $\mathbf{a}',\mathbf{a}'',\mathbf{b}',\mathbf{b}''$ *be vectors such that* $\mathbf{a}''$ *is a positive scalar multiple of* $\mathbf{a}'$*, and* $\mathbf{b}''$ *is such a multiple of* $\mathbf{b}'$*, and let* M',M'',N',N'' *be positive integers. Define* $M=M'+M'', N=N'+N'', \mathbf{a}=(M'\mathbf{a}'+M''\mathbf{a}'')/M, \mathbf{b}=(N'\mathbf{b}'+N''\mathbf{b}'')/N$*. Then we have*

$$\begin{aligned} Z_{el}(\mathbf{a},\mathbf{b};M,N) \;\geq\; & Z_{el}(\mathbf{a}',\mathbf{b}';M',N')Z_{el}(\mathbf{a}',\mathbf{b}'';M',N'')\times \\ & \times Z_{el}(\mathbf{a}'',\mathbf{b}';M'',N')Z_{el}(\mathbf{a}'',\mathbf{b}'';M'',N'') \end{aligned} \tag{18}$$

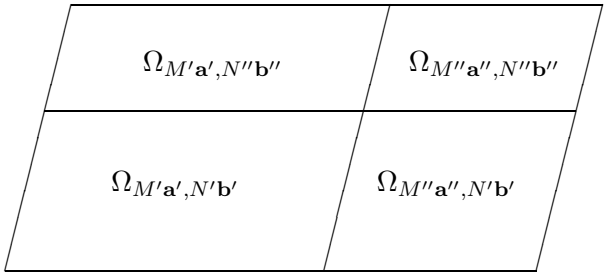

Fig. 4: Four parallelograms fitted together to make the parallelogram $\Omega_{M\mathbf{a},N\mathbf{b}}$.

Proof of lemma. Translates of the four parallelograms $\Omega_{M'\mathbf{a}',N'\mathbf{b}'}$ etc. can be fitted together as shown in Fig. 4 to make the parallelogram $\Omega_{M\mathbf{a},N\mathbf{b}}$. Use the definition (15) to write the right side of (18) as the product of four multiple integrals. In the integral representing $Z_{el}(\mathbf{a}',\mathbf{b}'';M',N'')$, transform to new position variables defined by $\mathbf{q}_{m,n+N'}=\mathbf{q}_{mn}+N'\mathbf{b}', \phi_{m,n+N'}=\phi_{mn}$; the region of integration for the new position vectors $\mathbf{q}_{m,n+N'}$ is the upper left-hand parallelogram in Fig. 4. Likewise in $Z_{el}(\mathbf{a}'',\mathbf{b}';M'',N')$ use the new variables $\mathbf{q}_{m+M',n}=\mathbf{q}_{mn}+M'\mathbf{a}'$, integrated over the lower right-hand parallelogram, and in $Z_{el}(\mathbf{a}'',\mathbf{b}'';M'',N'')$ use $\mathbf{q}_{m+M',n+N'}=\mathbf{q}_{mn}+M'\mathbf{a}'+N'\mathbf{b}'$. Then the resulting product of four multiple integrals can be thought of a single multiple integral over the position coordinates of all the MN particles. This multiple integral differs from the one representing the one on the left side of (18) in the following respects:

1. the region of integration is smaller, since each particle is restricted to one of the four smaller parallelograms in Fig. 4 instead of being allowed to go into the other ones as well (as far as the constraint (14) permits);

2. the condition (13) restricts the space available to the particles adjacent to the boundary between any two of the smaller parallelograms;

3. the one-body contribution to the Boltzmann factor $\mathrm{e}^{-U/kT}$ is smaller, since the particle centres must keep their distance from the inner boundaries separating the smaller parallelogams;

4. the two-body contribution to the $\mathrm{e}^{-U/kT}$ is smaller, since the attractive interaction between particles in different sub-parallelograms is not included.

All four of these differences make the integral representing the right side of (18) smaller than the one for the left side. The only difference that could spoil the inequality is that the constraint (10) is potentially less restrictive on the right side of (18) than on the left, since on the right side it does not include inequalities affecting particles that are adjacent to the boundaries between different sub-parallelograms. However, by choosing the positive number δ small enough, we can ensure that these particles do in fact satisfy the additional inequalites, so that including these inequalities in the list does not decrease the value of the integral. A suitable condition on δ to achieve this is

$$\arcsin[\delta/\min(|\mathbf{a}'|,|\mathbf{a}''|,|\mathbf{b}'|,|\mathbf{b}''|)] < \frac{1}{2}\min(\angle(\mathbf{a},\mathbf{b})-\pi/3, 2\pi/3-\angle(\mathbf{a},\mathbf{b})) \tag{19}$$

The right side of (19) is positive, by virtue of the condition on $\mathbf{a}$ and $\mathbf{b}$ in the statement of the theorem. The condition (19) ensures (for example) that neither of the arms of the angle $\psi^{(\swarrow)}_{mN'}$, which involve particles on both sides of the horizontal inner boundary in Fig. 4, can deviate from the directions of $\mathbf{a}$ and $\mathbf{b}$ respectively by a large enough amount to permit $\psi^{(\swarrow)}_{mN}$ to go outside the interval allowed to it by the constraint (10) as it affects the integral for the left side of (18). □

Proof of part (i) of the theorem. In (18), set $M''=M', N''=N', \mathbf{a}''=\mathbf{a}'=\mathbf{a}, \mathbf{b}''=\mathbf{b}'=\mathbf{b}$, then take logarithms and divide on both sides by $4M'N'$. The result is

$$\frac{\log Z_{el}(\mathbf{a},\mathbf{b};2M',2N')}{(2M')(2N')} \geq \frac{\log Z_{el}(\mathbf{a},\mathbf{b};M',N')}{M'N'} \tag{20}$$

It follows by iteration that the sequence

$$\frac{\log Z_{el}(\mathbf{a},\mathbf{b};2^k,2^k)}{4^k} \quad (k=1,2,\ldots) \tag{21}$$

increases. However, by (16), the sequence is bounded above by $\log(2\pi^2R^2\lambda)$, and it therefore has a limit.□

Proof of part (ii) of the theorem. In (18), set $M''=M'=N''=N'=2^k$. Then, proceeding as in the derivation of (20), we obtain

$$\frac{\log Z_{el}(\mathbf{a},\mathbf{b};2^{k+1},2^{k+1})}{4^{k+1}} \geq \frac{\log Z_{el}(\mathbf{a}',\mathbf{b}';2^k,2^k)}{4^k}\,\frac{\log Z_{el}(\mathbf{a}'',\mathbf{b}'';2^k,2^k)}{4^k} \tag{22}$$

where $\mathbf{a}=(\mathbf{a}'+\mathbf{a}'')/2, \mathbf{b}=(\mathbf{b}'+\mathbf{b}'')/2$. Taking the limit $k\to\infty$ and using (17), we obtain the convexity relation

$$f_{el}(\frac{1}{2}[\mathbf{a}'+\mathbf{a}''],\frac{1}{2}[\mathbf{b}'+\mathbf{b}'']) \leq \frac{1}{2}[f_{el}(\mathbf{a}',\mathbf{b}')+f_{el}(\mathbf{a}'',\mathbf{b}'')] \tag{23}$$

in which $\mathbf{a}'$ must be parallel to $\mathbf{a}''$ and $\mathbf{b}'$ parallel to $\mathbf{b}''$. This result shows that the function $f_{el}(\alpha\mathbf{a},\beta\mathbf{b})$ in part (ii) of Theorem 1 is convex in α and β. As we saw in the proof or part 1, this function is bounded below; therefore, by the theorem[13] that a bounded convex function is continuous, $f(\alpha\mathbf{a},\beta\mathbf{b})$ is continuous both with respect to α and to β in any region of the α,β plane where f is bounded above. (For a proof that the definition (23) of convexity implies the more usual one where the weights in the average on the right need not be equal, see ref.[7]). □

6 Concluding remarks

The restricted free energy defined above is not a useful concept for fluids and gases. At very low densities, for example, our system would behave like an ideal gas, but f_{el} as defined would be different from the thermodynamic free energy of an ideal gas, if only because of the constraint (14). In the case of a solid phase, however, it is plausible that the f_{el} does give a good approximation to the actual free energy. If it does not, the most likely reason is a failure of our assumption that the unconstrained equilibrium probability of a violation of the angular constraints (10) due to the nucleation of a dislocation is extremely small.

The theorem given above is only a part of what can be done with the restricted free energy function defined in Theorem 1. It should be possible

also to prove a theorem analogous to that of Fisher[5] that the specific free energy is independent of the shape of the container. It should also be possible to prove further convexity properties, in particular rank-1 convexity. Rank-1 convexity is defined by the same formula (23) as was used in Theorem 1, but the requirement that $\mathbf{a}'$ must be parallel to $\mathbf{a}''$ and $\mathbf{b}'$ parallel to $\mathbf{b}''$ is replaced by the weaker requirement that the matrices $[\mathbf{a}'|\mathbf{b}']$ and $[\mathbf{a}''|\mathbf{b}'']$ must differ by a matrix of rank 1. The physical significance of this condition is that if the crystal can form a pair of twins the deformation gradient matrices for the two twins must differ by a matrix of rank 1. Looking further ahead, it may also be possible to prove the integral formula (1) for general deformations and derive the corresponding convexity property of f_{el}, which is known as quasi-convexity and which implies rank-1 convexity[10].

When martensitic crystals are discussed in non-linear elasticity theory, much use is made of stored-energy functions which are not rank-1 convex; on the contrary, they can have a separate minimum for each of two twin variants whose deformation gradient matrices are rank-1 connected. To bring such stored-energy functions within the scope of the statistical mechanics theory, it would probably be necessary to use a separate restricted ensemble for each of the variants. The inequalities analogous to (10) would be replaced by similar but more restrictive inequalities, the inequalities for the different variants being incompatible with one another, so that $\mathbf{a}, \mathbf{b}$ space would split up into several parts with different free energy functions, one for each variant, together with an intervening part in which the definition of elastic free energy proposed here would be inapplicable.

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