

ONE-DIMENSIONAL MECHANICAL NETWORKS AND CRYSTALS

V. MALYSHEV

ABSTRACT. We propose a rigorous model of one dimensional crystal or of a biological mechanical network. We prove the thermal expansion and Hooke's law for this model.

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1. INTRODUCTION

Thermal expansion and Hooke's law are among the fundamental properties of macroscopic matter. In many cases it has satisfactory microscopic explanation in the framework of equilibrium statistical mechanics. This is a standard fact for the thermal expansion of gases and liquids. Derivation of linear theory of elasticity modules in general translation-invariant case see in [2], [1].

However, for crystals, where there is no translation invariance, the corresponding rigorous theory does not still exist. The nonstandard character of this problem is related, as we explain below, to the coordination between local and global coordinate systems. The goal of this paper is to consider the simplest natural one-dimensional model in the global coordinate system. This model can be considered as one-dimensional crystal or one-dimensional network (macromolecules, microtubules etc.) in the biological cell, see [3].

Standard courses of physics, for example [5], [6], [7], or even more specialized books, for example [12], [3] try to explain thermal and elastic expansions of crystals via the oscillation of atoms about their equilibrium positions in the crystal lattice. In particular, the so called harmonic approximation and its nonlinear analogs are normally used. Any atom is considered to be in the vicinity of the equilibrium point. This is quite natural in the (microscopically) local coordinate system. However if we assume this for ANY atom in global coordinate system, then we cannot get any macroscopic expansion.

The main idea is that the system is swelling uniformly at each point, and in any global coordinate system almost atoms become macroscopically far from their equilibrium positions. Note that similar situation was described in the so called

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random grammars, see [8]. Technically, this is achieved with another idea: to give atoms a possibility to be far away from their equilibrium position one should impose some restrictions on their motion. The simplest restriction would be to disallow particles jump through each other, that is the order of particles should be fixed. This idea of restricting the configuration space is close to one discussed by O. Penrose [9] in more complicated two and three dimensional cases. He argued that restrictions on the configuration space are necessary to get dependence of the free energy not only on the volume but also on its form. In our one-dimensional model this idea finds its rigorous justification together with very precise calculations.

It is important to note that due to our restrictions one can give sense to the partition function of finite number of particles in the infinite volume.

We consider the system of $N + 1$ particles (molecules, atoms) on the real line

$$0 = x_0(t) < \dots < x_k(t) < \dots < x_N(t)$$

where $t \geq 0$. The dynamics of this system is defined via smooth symmetric two-particle potential $V(x_i - x_j)$. We make the following assumptions concerning this potential:

(1) For $u > 0$ the potential $V(u)$ has a unique minimum at some point $a > 0$. Moreover, this minimum is quadratic.

(2) We assume that

$$V(0) = \infty$$

and make some comments on this assumption. In more realistic situation, when the real line is, for example, the x -axis in R^d , the particles can deviate from this axis in perpendicular directions, and can in principle pass through each other in the x -direction. However time scale for such transitions is slower than their movement without changing the order. Thus our assumption is a stable approximation to the realistic metastable situation.

(3) The strongest technical assumption is that is we consider only nearest neighbor interaction, that is the total energy is

$$\sum_{k=1}^N V(x_k - x_{k-1})$$

This is quite natural for the one-dimensional networks but less natural for crystal models. From this assumption it follows, in particular, that there exists a unique state with minimal energy (ground state)

$$x_k = ka$$

Without this assumption the situation with periodic ground states is more complicated, see [10], [11], but we will not need this.

(4) Our last assumption is that

$$V(u) \rightarrow \infty$$

sufficiently fast (it is sufficient like $\frac{1}{u^n}$, $n > 1$) as $u \rightarrow \infty$. This assumption is necessary to make the partition function, for finite number of particles on the real line, finite. This is also a stable approximation to the metastable situation -- to make impossible breaking the chain of particles into separate parts.

2. THERMAL EXPANSION

Assume that the left coordinate is fixed $x_0 = 0$ and put

$$u_i = x_i - x_{i-1} > 0, \quad i = 1, \dots, N.$$

One can write the Gibbs density of the vector (u_1, \dots, u_N) for temperature $T = \beta^{-1}$ as the following expression, which allows factorization,

$$Z_N^{-1} \exp\left(-\beta \sum_{i=1}^N V(u_i)\right) dx_1 \dots dx_N = Z_N^{-1} \prod_{i=1}^N \exp(-\beta V(u_i)) du_i.$$

It follows that the random variables u_i are independent, identically distributed, and do not depend on N . This makes the thermodynamic limit as $N \rightarrow \infty$ trivial. In particular the means $\langle u_i \rangle$ do not depend on N, i and can be written as

$$\langle u_i \rangle = m(T) = \frac{\int_0^\infty u \exp(-\beta V(u)) du}{\int_0^\infty \exp(-\beta V(u)) du}. \quad (2.1)$$

Then the total length of the chain is

$$\langle x_N \rangle = Nm(T).$$

We will consider here two cases: low temperatures, that is small deviations from the ground state and small perturbations around the state with fixed temperature. We will find conditions on the potential when macroscopic thermal expansion holds.

2.1. Low temperatures. Assume that the potential has the following Taylor expansion at the point $x = a$

$$V(a + y) = V(a) + c_2 y^2 + c_3 y^3 + c_4 y^4 + o(y^4), \quad c_2 > 0.$$

Theorem 2.1. For low temperatures $T = \beta^{-1}$

$$m(T) = a + m_1 T + o(T)$$

where we will call m_1 the coefficient of thermal expansion. If $c_3 \neq 0$, then

$$m_1 = -\frac{3c_3}{4c_2^2}.$$

This coefficient is positive if and only if $c_3 < 0$. If on the contrary $c_3 = 0, c_4 \neq 0$, then

$$m_1 = 0.$$

Remark. If in the vicinity of a the potential is purely quadratic, that is it equals $(x - a)^2$, then also $m_1 = 0$.

The physical example of the case $c_3 < 0$ can be the Lennard-Jones potential (except of the sufficiently large values of the argument)

$$V_{LJ} = \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

where (for $\sigma = 1$) at the minimum $a = \sqrt[6]{2}$ we have

$$c_3 = -\frac{63}{\sqrt{2}}.$$

Proof. Consider the asymptotic expansion (for large β) of the numerator and the denominator in (2.1). The standard Laplace method can be used. Then

$$\int_0^\infty \exp(-\beta V(u)) du = \sqrt{\frac{\pi}{\beta}} \exp(-\beta V(a))(b_0 + b_2(2\beta)^{-1} + O(\beta^{-2})),$$

$$\int_0^\infty u \exp(-\beta V(u)) du = \sqrt{\frac{\pi}{\beta}} \exp(-\beta V(a))(d_0 + d_2(2\beta)^{-1} + O(\beta^{-2})).$$

The coefficients can be found from the equations

$$\chi'(z) = \sum_{k=0}^\infty b_k z^k \tag{2.2}$$

or correspondingly

$$(a + \chi(z))\chi'(z) = \sum_{k=0}^\infty d_k z^k \tag{2.3}$$

where the function χ , in the vicinity of the point $z = 0$, is defined by the conditions

$$V(a + \chi(z)) = V(a) + z^2, \quad \chi(0) = 0, \quad \chi'(0) > 0, \tag{2.4}$$

see Theorem 1.2.4 in [4]. Put

$$\chi(z) = f_1 z + f_2 z^2 + \dots$$

Then by (2.4)

$$f_1 = c_2^{-\frac{1}{2}}, \quad f_2 = -\frac{c_3}{2c_2^2}, \quad f_3 = -\frac{c_2 f_2^2 + 3c_3 f_1^2 f_2 + c_4 f_1^4}{2f_1}.$$

Then from (2.2), (2.3) we get

$$b_0 = f_1, \quad b_2 = 3f_3, \quad d_0 = a f_1, \quad d_2 = 3(f_1 f_2 + a f_3).$$

That is why

$$d_0 b_0^{-1} = a$$

and

$$m_1 = \frac{d_2}{2b_0} - \frac{d_0 b_2}{2b_0^2} = \frac{d_2}{2b_0} - \frac{a b_2}{2b_0} = \frac{3}{2} f_2.$$

The theorem follows. □

2.2. Small perturbations. One can write

$$m\left(\frac{1}{\beta - \epsilon}\right) = m(T = \beta^{-1}) + m_1 \epsilon + o(\epsilon)$$

and the differentiation gives

$$m_1 = \langle uV \rangle_\beta - \langle u \rangle_\beta \langle V \rangle_\beta.$$

It follows that the criterion of the positive expansion is the positivity of the correlation between random variables u and V . Again, if $c_3 \neq 0$, then for large β the latter correlation is positive iff $c_3 < 0$.

3. HOOKE'S LAW

Hooke's law for the change Δl of the length of cylindrical bar under the action of the force F is the following

$$\frac{F}{S} = \kappa \frac{\Delta l}{l}$$

where S —the area of the cylinder cross-section, l —is the length of the bar.

Under the previous conditions assume also that there is an external potential $V_{\text{ext}}(x) = -Fx$, acting on the rightmost particle x_N . Remind that $x_0 = 0$ is assumed to be fixed. Then

$$\exp\left(-\beta \sum_{i=1}^N V(u_i) - \beta V_{\text{ext}}(x_N)\right) = \exp\left(-\beta \sum_{i=1}^N (V(u_i) - Fu_i)\right)$$

as $x_N = u_1 + \dots + u_N$. Define

$$m(T, F) = \frac{\int_0^\infty u \exp(-\beta(V(u) - Fu)) du}{\int_0^\infty \exp(-\beta(V(u) - Fu)) du}.$$

Then the elastic expansion is

$$m(T, F) - m(T, 0).$$

Theorem 3.1. For fixed temperature T , sufficiently small F and any potential V , satisfying the conditions in the introduction, the elastic expansion is positive for positive F and negative for negative F . Moreover,

$$m(T, F) - m(T, 0) = RF + o(F)$$

where the elastic modulus

$$R = \left. \frac{\partial m(T, F)}{\partial F} \right|_{F=0} = \beta(\langle u^2 \rangle - \langle u \rangle^2). \quad (3.1)$$

Proof. The formula (3.1) is proved by simple differentiation. It is sufficient to observe now that the right hand side of (3.1) is the variance of nonzero random variable. \square

4. REMARK ABOUT THE ABSENCE OF EXPANSION FOR OSCILLATIONS AROUND GROUND STATE EQUILIBRIUM

In the standard courses of physics normally the so called harmonic approximation is used with the hamiltonian (see for example [6, Section 2.14]),

$$\sum_{k,m=1}^N C_{km} \xi_k \xi_m + \sum_{k=1}^N \frac{1}{2} \left(\frac{d\xi_k}{dt} \right)^2$$

with symmetric matrix C_{km} , where $\xi_i = x_i - ia$ are the deviations from ground state coordinates. There is however an evident statement concerning joint distribution of the random variables ξ_i .

Proposition 4.1. *Let the distributions of $\xi_i(t)$ are such that for any t, i and any sufficiently large x*

$$P(|\xi_i(t)| > x) = o(x^{-1}).$$

Then for $N \rightarrow \infty$ and any t we have

$$X(t) = \max_i x_i(t) - \min_i x_i(t) \sim Na.$$

In fact, for any $\epsilon > 0$ the union of the events

$$A_i = \{|\xi_i(t)| > \epsilon N\}$$

has the probability which tends to zero as $N \rightarrow \infty$.

Thus, one cannot get any macroscopic expansion in this way.

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FACULTY OF MECHANICS AND MATHEMATICS, MOSCOW STATE UNIVERSITY, 1, VOROBYEVY GORY, 119992, MOSCOW, RUSSIA

E-mail address: malyshev2@yahoo.com