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Курбатов А.М.

Точно решаемая модель ангармонического кристалла

Предложена модель кристалла, допускающая точное в термодинамическом пределе решение. В зависимости от вида потенциала она может служить для описания эффектов ангармонизма или использоваться при рассмотрении сегнетоэлектриков типа порядок-беспорядок. Исследование проводится в рамках аппроксимационной схемы на основе классического анализа теоремы Боголюбова /мл./ в теории модельных систем. Получено точное выражение для функции свободной энергии в виде функционала от решения интегрального уравнения самосогласования.

Работа выполнена в Лаборатории теоретической физики, ОИЯИ.

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Kurbatov A.M.

Exactly Soluble Model of Classical Anharmonic Crystal

The model of a crystal that may be solved exactly in the thermodynamic limit is proposed. Depending on the form of the potential it may be used for describing anharmonic effects or in considerations of the ferroelectrics of the order-disorder type. The investigation is carried out in the frame of an approximation scheme on the basis of the classical analogue of the Bogolubov, Jr. theorem in the theory of model systems. The exact expression for the free energy as a functional of the solution of a self-consistent integral equation is obtained.

The investigations has been performed at the Laboratory of Theoretical Physics, JINR.

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Let us consider a(three-dimensional)lattice the sites of which are labeled by vectors $\underline{x} \in \mathbb{N} \in \mathbb{Z}^3$, $\underline{x} = \langle x_1, x_2, x_3 \rangle$. The indices x_1 , x_2 , x_3 run over intergers from 1 to n , i.e., the whole number of the sites $N = \|\mathbb{N}\|$ is n^3

$$N = \|\mathbb{N}\| = n^3 . \tag{1}$$

What shall we do is to describe the vibrations of such a lattice proceeding from the following model. In each site there is a particle of mass m which may move in the region $\mathbb{V}$ of volume V around the center of the site

$$VN = \mathcal{V} , \tag{2}$$

$\mathcal{V}$ is the volume of the lattice. The state of the particle labeled by $\underline{x}$ is specified by the vector $\underline{z}_{\underline{x}}$ equal to the difference of its position vector and the position vector of its site and by momentum $\underline{p}_{\underline{x}}$. The Hamiltonian of the system

$$H = \sum_{\underline{x} \in N} \frac{p_{\underline{x}}^2}{2m} + U^{(N)}(\underline{z}\langle 1,1,1\rangle, \ldots, \underline{z}\langle n,n,n\rangle) \tag{3}$$

contains pair interaction between the particles. The potential $u(\underline{\xi}, \underline{\eta})$ of this interation may be of different form, i.e., it may be anharmonic. In our model

$$U^{(N)}(\underline{z}\langle 1,1,1\rangle, \ldots, \underline{z}\langle n,n,n\rangle) = \frac{1}{2}\frac{K}{N} \sum_{\underline{x}, \underline{x}' \in N} u(\underline{z}\,\underline{x}, \underline{z}\,\underline{x}'), \tag{4}$$

$$u(\underline{\xi}, \underline{\eta}) \geq 0, \quad K > 0, \tag{5}$$

and labelling the sites by integers $1 \leq i, j \leq N$, we have

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\frac{K}{N} \sum_{i,j=1}^{N} u(\underline{z}_i, \underline{z}_j). \tag{6}$$

If the function $u(\underline{\xi}, \underline{\eta})$ has one minimum, the model (6) may be used for describing thermal vibrations of solids. In the case of several minima of $u(\underline{\xi}, \underline{\eta})$ our system represents a model for ferroelectrics.

In the notations of ref.1 the state space of our system is

$$\Omega = \Omega_{V, \underline{N}}, \tag{7}$$

and the thermodynamic potential - the free energy - is given by

$$F[N, V, \beta; H] = -\frac{1}{\beta} \ln N!\,(\rho_H, \mathbb{1})_{\Omega_{V,N}} = -\frac{1}{\beta} \ln \int_{\Omega_{V,N}} e^{-\beta\left[\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\frac{K}{N}\sum_{i,j=1}^{N} u(\underline{z}_i, \underline{z}_j)\right]} d\underline{z}_1 \ldots d\underline{p}_N =$$

$$= -\frac{1}{\beta} \ln\left[\left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N - \frac{1}{\beta} \ln \int_V e^{-\frac{\beta}{2} \cdot \frac{K}{N} \sum_{i,j=1}^{N} u(\underline{z}_i, \underline{z}_j)} d\underline{z}_1 \ldots d\underline{z}_N. \tag{8}$$

Let the function be symmetric and continuous. Then the integral equation

$$\int_V u(\underline{\xi}, \underline{\eta})\, \varphi(\underline{\eta})\, d\underline{\eta} = \lambda \varphi(\underline{\xi}) \tag{9}$$

has a countable orthonormal in $L^2[V]$ set of eigenfunctions $\{\varphi_\alpha(\underline{\xi})\}$ with corresponding eigenvalues $\{\lambda_\alpha\}$, and

$$\|u_s - u\|_\infty = \sup_{\underline{\xi}, \underline{\eta} \in V} |u_s(\underline{\xi}, \underline{\eta}) - u(\underline{\xi}, \underline{\eta})| = \varepsilon(s) \xrightarrow[s \to \infty]{} 0, \tag{10}$$

where

$$u_s(\underline{\xi}, \underline{\eta}) = \sum_{\alpha=1}^{s} \lambda_\alpha \varphi_\alpha(\underline{\xi}) \varphi_\alpha(\underline{\eta}). \tag{11}$$

We denote

$$U_s^{(N)}(\underline{z}_1, \ldots, \underline{z}_N) = \frac{1}{2}\frac{K}{N} \sum_{i,j=1}^{N} u_s(\underline{z}_i, \underline{z}_j) \tag{12}$$

and estimate the average $\langle U_s^{(N)} - U^{(N)} \rangle_{H}$ for an arbitrary Hamiltonian H

$$\langle U_s^{(N)} - U^{(N)} \rangle_{H} \leqslant \| U_s^{(N)} - U^{(N)} \|_{\infty} \leq \frac{1}{2}\frac{K}{N} N^2 \| u_s - u \|_{\infty} = \frac{1}{2} K N \varepsilon(s). \tag{13}$$

Let us consider now the Hamiltonian

$$H_s = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_s^{(N)}(\underline{z}_1, \dots, \underline{z}_N). \tag{14}$$

We rewrite it in the form

$$\begin{aligned} H_s &= N T(\underline{p}_1, \dots, \underline{p}_N) + \frac{1}{2}\frac{K}{N} \sum_{i,j=1}^{N} \sum_{\alpha=1}^{s} \lambda_\alpha \varphi_\alpha(\underline{z}_i) \varphi_\alpha(\underline{z}_j) = \\ &= N T(\underline{p}_1, \dots, \underline{p}_N) + \frac{1}{2}\frac{K}{N} \sum_{\alpha=1}^{s} \sum_{i,j=1}^{N} \lambda_\alpha \varphi_\alpha(\underline{z}_i) \varphi_\alpha(\underline{z}_j) = \\ &= N T(\underline{p}_1, \dots, \underline{p}_N) + N \sum_{\alpha=1}^{s} A_\alpha(\underline{z}_1, \dots, \underline{z}_N) A_\alpha(\underline{z}_1, \dots, \underline{z}_N), \end{aligned} \tag{15}$$

where

$$T(\underline{p}_1, \dots, \underline{p}_N) = \frac{1}{N} \sum_{i=1}^{N} \frac{p_i^2}{2m}, \tag{16}$$

$$A_\alpha(\underline{z}_1, \dots, \underline{z}_N) = \frac{1}{N} \sum_{i=1}^{N} \sqrt{\frac{1}{2} K \lambda_\alpha}\, \varphi_\alpha(\underline{z}_i) = \frac{1}{N} \sum_{i=1}^{N} \mathcal{A}_\alpha(\underline{z}_i). \tag{17}$$

According the Cauchy-Buniakovsky inequality we have

$$|\lambda_\alpha \varphi_\alpha(\underline{\xi})| = |(u(\underline{\xi}, \cdot), \varphi_\alpha(\cdot))_{L^2[V]}| \leq \| u(\underline{\xi}, \cdot) \|_2 \, \| \varphi_\alpha(\cdot) \|_2, \tag{18}$$

Since the function $u(\cdot,\cdot)$ is continuous and the set $\{\varphi_\alpha(\cdot)\}$ is orthonormal, there exists M such that for any α and $\underline{\xi}$

$$|\lambda_\alpha \varphi_\alpha(\underline{\xi})| \leq M, \tag{19}$$

whence

$$\| \mathcal{A}_\alpha \|_{\infty} \leq \sqrt{\frac{1}{2} K} \cdot \frac{M}{\sqrt{\lambda_\alpha}} = M_{\alpha N}, \tag{20}$$

$$\sum_{\alpha=1}^{s} \| A_\alpha \|_{\infty} = \sum_{\alpha=1}^{s} M_{\alpha N} = \sqrt{\frac{1}{2} K}\, M \sum_{\alpha=1}^{s} \frac{1}{\sqrt{\lambda_\alpha}} = M_s. \tag{21}$$

Thus, if we introduce the Hamiltonian

$$H_{s0}(a_1, \dots, a_s) = N T(\underline{p}_1, \dots, \underline{p}_N) + N \sum_{\alpha=1}^{s} \left(2 a_\alpha A_\alpha(\underline{z}_1, \dots, \underline{z}_N) - a_\alpha^2 \right), \tag{22}$$

by virtue of Theorem 2 of ref.2 the difference between its free energy at $a_\alpha = \bar{a}_\alpha^{(s,N)}$ determined from the absolute maximum condition

$$F[N,V,\beta; H_{s0}(\bar{a}_1^{(s,N)}, \dots, \bar{a}_s^{(s,N)})] = \max_{\langle a_1, \dots, a_s \rangle} F[N,V,\beta; H_{s0}(a_1, \dots, a_s)], \tag{23}$$

(this solution always exists, and $|\bar{a}_\alpha^{(s,N)}| \leq M_{\alpha N}$) and the free energy of the Hamiltonian H is bounded by

$$-K M^2 \left(\sum_{\alpha=1}^{s} \frac{1}{\sqrt{\lambda_\alpha}} \right)^2 \frac{1}{N} \leqslant$$

$$\le \frac{1}{N} F[N,V,\beta; H_{s0}(\bar{a}_1^{(S,N)},\dots,\bar{a}_s^{(S,N)})] - \frac{1}{N} F[N,V,\beta; H_s] \le 0. \tag{24}$$

From the other hand, making use of the Bogolubov inequality for classical systems/1/ we have

$$\langle U_s^{(N)} - U^{(N)} \rangle_{H_s} \le F[N,V,\beta;H_s] - F[N,V,\beta;H] \le \langle U_s^{(N)} - U^{(N)} \rangle_{H} \tag{25}$$

and in view of (13)

$$-\frac{1}{2} K\varepsilon(s) \le \frac{1}{N} F[N,V,\beta;H_s] - \frac{1}{N} F[N,V,\beta;H] \le \frac{1}{2} K\varepsilon(s). \tag{26}$$

Adding (24) and (25) together, for the difference of the free energy dencities

$$f_N[N,V,\beta;\mathcal{H}] = \frac{1}{N} F[N,V,\beta;\mathcal{H}] \tag{27}$$

of the Hamiltonians $\mathcal{H} = H$ and $\mathcal{H} = H_{s0}(\bar{a}_1^{(S,N)},\dots,\bar{a}_s^{(S,N)})$ we obtain the estimation

$$-\frac{1}{2} K\varepsilon(s) - KN^2 \left(\sum_{\alpha=1}^{S} \frac{1}{\sqrt{\lambda_\alpha}} \right)^2 \frac{1}{N} \le$$

$$\le f_N[N,V,\beta; H_{s0}(\bar{a}^{(S,N)},\dots,\bar{a}_s^{(S,N)})] - f_N[N,V,\beta;H] \le \frac{1}{2} K\varepsilon(s). \tag{28}$$

Thus,

$$\lim_{S\to\infty} \lim_{N\to\infty} \{ f_N[N,V,\beta; H_{s0}(\bar{a}_1^{(S,N)},\dots,\bar{a}_s^{(S,N)})] - f_N[N,V,\beta;H] \} = 0. \tag{29}$$

To calculate $f_N[N,V,\beta; H_{s0}(\bar{a}_1^{(S,N)},\dots,\bar{a}_s^{(S,N)})]$ we write the Hamiltonian $H_{s0}(a_1,\dots,a_s)$ as follows

$$H_{s0}(a_1,\dots,a_s) = NT(\underline{p}_1,\dots,\underline{p}_N) + N\left[\sum_{\alpha=1}^{S} a_\alpha^2 + \sum_{\alpha=1}^{S} 2a_\alpha \frac{1}{N} \sum_{i=1}^{N} \sqrt{\frac{1}{2K}\lambda_\alpha}\, \varphi_\alpha(\underline{q}_i) \right] =$$

$$= NT(\underline{p}_1,\dots,\underline{p}_N) + N\left[-\sum_{\alpha=1}^{S} a_\alpha^2 + \frac{K}{N} \sum_{i=1}^{N} \Psi_s(\underline{q}_i) \right], \tag{30}$$

where

$$\Psi_s(\underline{\xi}) = \sum_{\alpha=1}^{S} 2a_\alpha \sqrt{\frac{1}{2K}} \sqrt{\lambda_\alpha}\, \varphi_\alpha(\underline{\xi}). \tag{31}$$

Then $f_N[N,V,\beta; H_{s0}(a_1,\dots,a_s)]$ may be represented in the form

$$f_N[N,V,\beta; H_{s0}(a_1,\dots,a_s)] = -\frac{1}{\beta N} \ln\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} \right]^N -$$

$$-\frac{1}{\beta N} \ln \int_V e^{-\beta N\left[-\sum_{\alpha=1}^{S} a_\alpha^2 + \frac{1}{N}\sum_{i=1}^{N} \Psi_s(\underline{q}_i)\right]} d\underline{q}_1 \dots d\underline{q}_N =$$

$$= -\frac{1}{\beta} \ln\left(\frac{2\pi m}{\beta}\right)^{3/2} - \sum_{\alpha=1}^{S} a_\alpha^2 - \frac{1}{\beta} \ln \int_V e^{-\beta K \Psi_s(\underline{\xi})} d\underline{\xi}. \tag{32}$$

Since the quantities $\bar{a}_1^{(S,N)}, \dots, \bar{a}_s^{(S,N)}$ are determined from the absolute maximum condition (23), they are to satisfy the set of equations

$$\partial f_N[N,V,\beta; H_{s0}(a_1,\dots,a_s)] / \partial a_\alpha = 0. \tag{33}$$

Taking into account that

$$\frac{\partial \Psi_s(\underline{\xi})}{\partial a_\alpha} = 2\sqrt{\frac{1}{2K}}\sqrt{\lambda_\alpha}\,\varphi_\alpha(\underline{\xi}), \tag{34}$$

we have

$$-a_\alpha + \sqrt{\tfrac{1}{2}K}\;\frac{\int\limits_V \sqrt{\lambda_\alpha}\,\varphi_\alpha(\underline{\eta})\,e^{-\beta K \Psi_s(\underline{\eta})}\,d\underline{\eta}}{\int\limits_V e^{-\beta K \Psi_s(\underline{\eta})}\,d\underline{\eta}} = 0. \tag{35}$$

Multiplying these equations by $2\sqrt{\frac{1}{2K}}\sqrt{\lambda_\alpha}\,\varphi_\alpha(\underline{\xi})$ and adding them together we obtain the integral equation

$$\Psi_s(\underline{\xi}) = \frac{\int\limits_V U_s(\underline{\xi},\underline{\eta})\,e^{-\beta K \Psi_s(\underline{\eta})}\,d\underline{\eta}}{\int\limits_V e^{-\beta K \Psi_s(\underline{\eta})}\,d\underline{\eta}}, \tag{36}$$

the function $\Psi_s(\underline{\xi})$ satisfies to.

Using now the fact that in view of (35)

$$-\sum_{\alpha=1}^{s}\left[\bar{a}_\alpha^{(s,N)}\right]^2 = -\sum_{\alpha=1}^{s} K\,\frac{\int\limits_V \sqrt{\frac{1}{2K}}\sqrt{\lambda_\alpha}\,\varphi_\alpha(\underline{\xi})\,e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}}{\int\limits_V e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}} =$$

$$= -K\,\frac{\int\limits_V \bar{\Psi}_s(\underline{\xi})\,e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}}{\int\limits_V e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}}; \tag{37}$$

we find the expression for the free energy $f_N\left[N,V,\beta;H_{s0}\left(\bar{a}_1^{(s,N)},\ldots,\bar{a}_s^{(s,N)}\right)\right]$, in terms of the function $\bar{\Psi}_s(\underline{\xi})$ only which satisfies the equation (36)

$$f_N\left[N,V,\beta;H_{s0}\left(\bar{a}_1^{(s,N)},\ldots,\bar{a}_s^{(s,N)}\right)\right] =$$

$$= -\frac{1}{\beta N}\ln\frac{1}{N!}\left[\left(\frac{2\pi m}{\beta}\right)^{3/2} V\right]^N -$$

$$-K\,\frac{\int\limits_V \bar{\Psi}_s(\underline{\xi})\,e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}}{\int\limits_V e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}} -$$

$$-\frac{1}{\beta}\ln\int\limits_V e^{-\beta K \bar{\Psi}_s(\underline{\xi})}\,d\underline{\xi}\;. \tag{38}$$

It is not difficult to show that, since $U_s(\underline{\xi},\underline{\eta}) \xrightarrow[s\to\infty]{} U(\underline{\xi},\underline{\eta})$,

$$\bar{\Psi}_s(\underline{\xi}) \xrightarrow[s\to\infty]{} \bar{\Psi}(\underline{\xi}), \tag{39}$$

where $\bar{\Psi}(\underline{\xi})$ satisfies the equation

$$\Psi(\underline{\xi}) = \frac{\int\limits_V U(\underline{\xi},\underline{\eta})\,e^{-\beta K \Psi(\underline{\eta})}\,d\underline{\eta}}{\int\limits_V e^{-\beta K \Psi(\underline{\eta})}\,d\underline{\eta}}, \tag{40}$$

and hence

$$\lim_{s\to\infty}\lim_{N\to\infty} f_N\left[N,V,\beta;H_{s0}\left(\bar{a}_1^{(s,N)},\ldots,\bar{a}_s^{(s,N)}\right)\right] = -\frac{1}{\beta}\ln\left(\frac{2\pi m}{\beta}\right)^{3/2} -$$

$$-\kappa \frac{\int\limits_V \bar{\Psi}(\underline{\xi})\, e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}}{\int\limits_V e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}} - \frac{1}{\beta}\ln\int\limits_V e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}. \tag{41}$$

Therefore by virtue of (29) the limit, as $N \to \infty$, of the free energy dencity $f_N[N,V,\beta;H]$ exists and is equal to

$$\lim_{N\to\infty} f_N[N,V,\beta;H] = -\frac{1}{\beta}\ln\left(\frac{2\pi m}{\beta}\right)^{3/2} -$$

$$-\kappa \frac{\int\limits_V \bar{\Psi}(\underline{\xi})\, e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}}{\int\limits_V e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}} - \frac{1}{\beta}\ln\int\limits_V e^{-\beta\kappa\bar{\Psi}(\underline{\xi})}\, d\underline{\xi}, \tag{42}$$

where $\bar{\Psi}(\underline{\xi})$ is the solution of the equation (40).

Thus, we have obtained the exact in the thermodynamic limit $N \to \infty$, $\mathcal{V} \to \infty$, $\mathcal{V}/N = V = \mathrm{const}$, expression for the free energy dencity of the system (4) with arbitrary potential of interaction between the lattice sites.

R e f e r e n c e s

1. A.M.Kurbatov. JINR E5-12431, Dubna, 1979.

2. A.M.Kurbatov. JINR E5-12432, Dubna, 1979.

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