Lettere al Nuovo Cimento VOL.28 B, N. 1, PAG. 274-286 26 Dicembre 1970

Statistical Mechanics of the Electron-Phonon System

G. GALLAVOTTI(1) J. GINIBRE(2) G. VELO(3)

(1) *Istituto di Matematica dell'Università - Roma*
(2) *Laboratoire de Physique Thèorique, Faculté des Sciences, - Orsay*
(3) *Istituto di Fisica dell'Università - Bologna Instituut voor Theoretische Fysica, Nijmegen*

(ricevuto 11 Novembre 1970; approvato)

The electron-phonon system has received considerable attention in connection with the phenomenon of superconductivity, where the condensation of electron pairs is believed to arise from the attraction produced by the phonons (1) The system is usually described by the Frölich Hamiltonian (1), where the phonons are represented by a scalar field coupled to the electron density. Although this interaction has been widely used for approximate calculations, it has never been proved that it provides a statistical mechanical description in the usual sense, in particular that it allows the infinite volume limit to be taken for the thermodynamic quantities. Here, we shall consider this problem, concentrating on the statistical mechanics of the electrons. We therefore us the method of Feynman (2), in which the statistical operator of the electrons is given by a path integral representation and the phonon field is eliminated at the expense of introducing a non instantaneous interaction between the electrons. Except for this last feature, the situation is then similar to the one encountered in the case of quantum systems with instantaneous potentials (3).

The Hamiltonian we start from is

$$(1) \qquad H = \frac{1}{2}\sum_{i=1}^{n} o_i^2 + \sum_k \omega(k) a_k^* a_k - \mu n + \frac{1}{V^2}\sum_{i=1}^{n}\sum_k \frac{v(k)}{(2\omega(k))^2}(a_k + a_{-k}^*)e^{ik\cdot x_i}.$$

where n is the number of electrons, x_i and p_i are respectively the positions and momenta of the electrons, and μ is their chemical potential. The phonon field is quantized in a periodic box of volume V_0, a_k and a_k^* are its annihilation and creation operators, $v(k)$ is a real even function, and $\omega(k) = (k^2 + m^2)^{1/2}$ is the phonon energy with $m \geq 0$.

We consider the statistical operator $e^{-\beta H}$ for this system, take the partial trace in the Hilbert space of the phonons, divide out by the partition function of the free phonons, and go to the harmless limit of infinite V_0. We then obtain the statistical operator of the electrons in the form of an integral kernel (4):

---

(1) J. Blatt: *Theory of superconductivity* (New York, 1964).
(2) R.P. Feynman, Phys. Rev., **97**,660, 1955.
(3) J. Ginibre, Lecture Notes (Leas Houches, 1970).
(4) T.D. Schultz: n *Polarons and Excitons*, edited by C. Kuper and G. Whitfield (Edinburgh, 1963).

$$W(x^n,y^n)=\int P^\beta_{x^n,y^n}(d\xi^n)e^{U(\xi^n)+\beta\mu n} \tag{2}$$

where $x^n=(x_1,\ldots,x_n)$ and $y^n=(y_1,\ldots,y_n)$ are the initial and final positions of the n electrons. The electrons are described by n Wiener trajectories $\xi^n=(\xi_1,\ldots,\xi_n)$ with time interval β, starting from x^n and ending at the points y^n, and $P^\beta_{x^n,y^n}(d\xi^n)$ denotes Wiener integration. Furthermore

$$U(\xi^n)=\frac12\sum_{i,j}U(\xi_i,\xi_j). \tag{3}$$

The interaction between the trajectories ξ_i and ξ_j is given by

$$U(\xi_i,\xi_j)=\int_0^\beta dsdt\int\frac{dk}{(2\pi)^\nu}\widehat\phi(k,s-t)e^{ik(\xi_i(s)-\xi_j(s))}, \tag{4}$$

where

$$\widehat\phi(k,u)=\frac{v(k)^2}{2\omega(k)}\frac{e^{\omega(k)(\beta-|u|)}+e^{\omega(k)|u|}}{e^{\beta\omega(k)}-1} \tag{5}$$

and ν is the dimension of the space ($\nu=3$ for physical purposes).

We first assume that v^2/ω^2 is integrable (this condition is satisfied for the actual electron–phonon system). In this case, as will be shown below, W is well define.

A necessary condition on the interactions, for a statistical mechanical description to be possible at all, is stability ([5]), namely the binding energy per particle must be bounded from below. Here however, U can be written as

$$U=\frac1{2\beta}\int\frac{dk}{(2\pi)^\nu}\sum_{m=-\infty}^{\infty}\frac{v(k)^2}{\omega(k)^2+(2\pi m/\beta)^2}\Big|\sum_{j=1}^n\int_0^\beta dte^{2\pi im\,t\beta^{-1}+ik\xi_j(t)}\Big|^2.$$

Th is interaction is attractive and therefore unstable ([5]).

A natural method to obtain a stable interaction is to introduce an instantaneous potential between the electrons. Physically, such an interaction is provided by the (possibly screened) Coulomb repulsion between the electrons. We now show that this modification suffices to ensue stability. In fact, from

$$\Big|\sum_{i,j}e^{ik(\xi_i(s)-\xi_j(s))}\Big|\le\frac12\Big\{\Big|\sum_i e^{ik\xi_i(s)}\Big|^2+\Big|\sum_j e^{ik\xi_j(s)}\Big|^2\Big\}$$

it follows that

([5]) D. Ruelle: *Statistical Mechanics* (New York, 1969).

$$U(\xi^n) \leq \frac{1}{2} n\beta\varphi(0) + \sum_{i<j} \int_0^\beta dt\, \varphi(\xi_i(t) - \xi_j(t)|. \tag{6}$$

where

$$\varphi(x) = \int_0^\beta \phi(x,t) \tag{7}$$

and

$$\phi((x,t) = \int \frac{dk}{(2\pi)^\nu} \widehat{\phi}(k,t)\, e^{ikx}, \tag{8}$$

so that

$$\varphi(x) = \int \frac{dk}{(2\pi)^\nu} \frac{v(k)^2}{\omega(k)^2}\, e^{ikx}. \tag{9}$$

By our assumption $\varphi(0)$ is finite and $\varphi(x)$ is a continuous positive definite function. Equation (6) shows that W is well defined, as mentioned before. If we add an instantaneous two body interaction $\varphi'(x)$ between the electrons, then the exponent in (2) is replaced by $U - U' + n\beta\mu$ where

$$U' = \sum_{i<j} \int_0^\beta dt\, \varphi'(\xi_i(t) - \xi_j(t)) \tag{10}$$

and $\varphi' - \varphi$ is stable (respectively superstable, see ref. ([5]), p.40, it follows immediately from (6) that the total interaction is stable (respectively superstable). We now turn to the problem of the existence of he infinite volume limit for the Gibbs potential of the electrons:

$$\pi(\beta,\mu) = \lim_{V\to\infty} \frac{1}{V} \log Z \tag{11}$$

where Z is the grand partition function of the electron system enclosed in a box Λ of volume V. Z is obtained from equation (2) by restricting he integration over ξ^n to those trajectories which stay in Λ, identifying the end points after proper symmetrization, integration over them over the box Λ and summing over n. The situation is now identical to the one encountered in the case of instantaneous interactions and the proof goes through the standard methods for the Boltzmann or Bose statistics ([3,5]), provided the interaction satisfies a weak tempering condition of the following form.

There exist $C > 0, \varepsilon > 0, L_0 \geq 0$ such that

$$-U(\xi_i, \xi_j) + U(\xi_i, \xi_j) \leq CL^{-(\nu+\varepsilon)} \tag{12}$$

for all ξ_i, ξ_j such that $\inf_{s,t} |\xi_i(s) - \xi_j(t)| \geq L \geq L_0$.

This condition follows from a) and b) below:

a) $\varphi' - \varphi$ is weakly tempered,

b) there exists $C' \geq 0$ such that for $L \geq L_0$

$$\int dtds \sup_{|x|\geq L} |\phi(x,t)| \leq C' L^{-(\nu+\varepsilon)}. \tag{13}$$

Condition b) is satisfied if $v(k)$ is sufficiently regular, for instance if $v(k)$ belongs to the Schwartz space $\mathcal{S}(\mathbb{R}^\nu)$.

Unfortunately, the proof using functional integral representation does not work for fermions.

On the other hand, at low electron density, the system can be studied for all statistics by the same method as systems with instantaneous interactions. One can write integral equations of the Kirkwood-Salzburg type for the reduced density matrices of the electrons, and show that they, as well as the Gibbs potential, are analytic functions of the fugacity $z = e^{\beta\mu}$ for $|z| < R$, where

$$\begin{aligned} R = &\max_{0<\alpha<e^{-\beta\varphi(0)}} \\ &\left\{\alpha e^{-\beta(\varphi(0)+2B)-\beta\lambda^{-\nu} g_{\nu/2}(\alpha)\int \varphi'(x)dx - B\lambda^{-\nu} g_{\nu/2}(\alpha e^{\beta\varphi(0)})\int_0^\beta dt \int dx |\phi(x,t)|}\right\} \end{aligned} \tag{14}$$

Here $\lambda = (2\pi\beta)^{1/2}$ is the thermal wavelength, B is the stability constant for $\varphi' - \varphi$, and

$$g_{\nu/2}(w) = \sum_{j=1}^{\infty} w^j j^{-\nu/2}.$$

The compensating potential has been assumed positive and integrable for simplicity. The last term in the exponent of (14) is finite if v is sufficiently smooth, for instance if $v \in \mathcal{S}(\mathbb{R}^\nu)$. Equation (14) corresponds to Bose or Fermi statistics. A simple expression for R can be obtained for the Boltzmann statistics.

Up to now, we have assumed v^2/ω^2 to be integrable. If this condition does not hold it is not clear whether W exists. We are going to show that if $\nu = 2$ and $v(k) = 1$, in which case $\varphi(0)$ is logarithmically divergent, W is well defined. In order to prove this result, we introduce a cut-off σ in the k integrations of the interaction U. The cut-off interaction U_σ can be shown to satisfy the following two estimates:

$$|U| \leq C \log \sigma, \qquad \int P^\beta_{x^n,y^n}(d\xi^n)\, |U_\sigma - U_\rho|^2 \leq D\rho^{-2} \text{ for } \rho \leq \sigma.$$

It then follows from an argument of Nelson ([6]) ([7]) that e^U is Wiener integrable and therefore W exists.

([6]) E. Nelson: in *Mathematical Theory of Elementary Particles*, edited by R. Goodman and I. Segal, (Cambridge, 1966).

([7]) S.R.S. Varadhan: *Proc. S.I.F.*, Course XLV (New York, 1970), p.219.

In this case it is possible to achieve stability by adding an instantaneous potential with a hard core of arbitrarily small diameter a. In fact, let $a > 0$, let

$$\varphi_a(x) = \sup_{0\le s\le\beta} \int_0^\beta dt \sup_{|y|\le a} |\phi(x+y, s-t)|. \tag{15}$$

For each trajectory ξ, define $\varepsilon(\xi) = \inf\{|t-s| : |\xi(t) - \xi(s)| > a\}$. Then

$$\begin{aligned} U(\xi^n) \le & \frac{1}{2}\sum_{i=1}^n \Big\{ \int_{|s-t|\le\varepsilon(\xi_i)} ds\, dt\, \phi(\xi_i(s) - \xi_i(t), s-t) + \int_{|s-t|\ge\varepsilon(\xi_i)} ds\, dt\, \phi(0, s-t)\Big\} \\ & + \frac{1}{2}\sum_{i<j} \int_0^\beta ds\, \varphi_a(\xi_i(s) - \xi_i(s)). \end{aligned} \tag{16}$$

The first term in the r.h.s. of (16) is taken care by the previous argument. The second diverges logarithmically at small ε. From the standard estimate

$$P^\beta_{xy}\{\xi : |\xi(t) - \xi(s)| > a \text{ for some } s,t \text{ with } |s-t| \le \varepsilon\} \le \frac{C_1}{\varepsilon} e^{-c_2 a^2 \varepsilon^{-1}}$$

it follows that the exponential is integrable. The third term is an interaction between different trajectories via the instantaneous hard core potential φ_a. The system can then be made stable by adding a compensating instantaneous potential φ' such that $\varphi' - \varphi_a$ is stable. Obviously φ' must have a hard core of diameter at least a. The proof of the existence of the Gibbs potential in the infinite volume limit extends also to this more singular case, provided φ' satisfies suitable temperedness conditions.