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Wigner-like expansion for the quantum-statistical mechanics of solids: Application to the sine-Gordon chain

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A semiclassical expansion for the quantum partition function of solids is presented. With respect to the usual Wigner method, the temperature range where the expansion is significant is broadened owing to the correct quantum-statistical treatment of the harmonic modes, while a Wigner-like expansion is retained only for the anharmonic part. As an application, the lowest quantum correction to the specific heat of a one-dimensional sine-Gordon model is calculated analytically.

Most of the problems of statistical mechanics are studied in the classical limit because, in this case, calculations of thermodynamic quantities are reduced to the simpler problem of evaluating phase-space integrals. In this approximation Monte Carlo and molecular-dynamics methods have revealed themselves as powerful tools. Moreover, for one-dimensional systems thermodynamic properties can be calculated exactly by means of the transfer-matrix technique. However, because of the intimately quantum-mechanical nature of real systems, theories which take into account the contribution of the quantum fluctuations may be important. Of course some problems require an *ab initio* quantum treatment, while in the so-called "almost-classical" systems it is possible to expand physical quantities in terms of $\hbar$. For this kind of system, many years ago, Wigner[1] introduced into quantum mechanics a phase-space distribution function which is an analog to the distribution function of classical statistical mechanics. This distribution function is particularly useful in order to obtain quantum corrections for the classical partition function because it gives a systematic method of expanding physical quantities in terms of $\hbar$. The Wigner theory has been recently reviewed and extended by Kubo,[2] Imre, Ozizmir, Rosenbaum, and Zweifel,[3] and Nienhuis,[4] while Fujiwara, Osborne, and Wilke[5] have shown that the same results can be derived by using the Feynman path-integral description of the partition function.

In particular, the Wigner expansion of this quantity as a power series in $\hbar^2$ is

$$Z_q^w = Z_{\rm cl}(1+\hbar^2 C_1+\hbar^4 C_2+\cdots) \ , \tag{1}$$

where $Z_{\rm cl}$ is the classical partition function of the system, while the coefficients C_i's are expressed in terms of classical thermodynamic averages. For example, if it is assumed that[4]

$$\mathscr{H}_{\rm cl} = (2m)^{-1}\mathbf{p}^2+\Phi(\mathbf{r}) \ , \tag{2}$$

then one finds for the first coefficient ($\beta = 1/k_B T$)

$$C_1 = -(\beta^2/24m)\langle \partial^2\Phi/\partial\mathbf{r}^2\rangle_{\rm cl} \ . \tag{3}$$

The expansion (1) is usually assumed at least asymptotically convergent.[5]

The Wigner method has been applied to introduce quantum corrections to equilibrium properties of fluid systems[6,7] while Fukuyama[8] has estimated the role of quantum fluctuations on melting temperature of the two-dimensional Wigner solid.

In this Rapid Communication we propose a different Wigner-like expansion for the partition function which we think particularly useful to study the properties of solids. Usually, for these systems the contribution to thermodynamics from small oscillations, with frequency ω_k, around the potential minima is the most relevant one at low temperatures. However, it is well known that a classical treatment of the statistical mechanics is totally inadequate to calculate some thermodynamic properties (e.g., specific heat). Therefore it is clear that, to obtain the correct behavior in the low-T limit, the contribution of the harmonic modes of frequencies ω_k has to be evaluated in the framework of quantum-statistical mechanics. While the quantum partition function of a system of free bosons can be calculated exactly, one has to resort to approximate methods in the presence of interaction terms. Here we propose a Wigner-like expansion only for the anharmonic part, while a correct quantum treatment of the statistical mechanics of the harmonic modes is preserved. This should allow us to broaden the range of temperatures for which the usual Wigner expansion is significant. However, the low-T limit is still unattainable by our treatment because it is semiclassical as far as the anharmonic part is concerned.

We consider the general expansion of the quantity

$$\frac{Z_q}{Z_{\rm cl}G} = 1+\hbar^2 Q_1+\hbar^4 Q_2+\cdots \ , \tag{4}$$

where G is the function which transforms the classical partition function $Z_{\rm cl}^H$ of an assembly of harmonic oscillators with frequencies ω_k into the corresponding *quantum* partition function Z_q^H

$$Z_{\rm cl}^H G = Z_q^H \ , \tag{5}$$

$$G = \exp\left\{\sum_k \left[-\tfrac{1}{2}\beta\hbar\omega_k + \ln\left(\frac{\beta\hbar\omega_k}{1-\exp(-\beta\hbar\omega_k)}\right)\right]\right\} \ . \tag{6}$$

In order to obtain the explicit expressions of the coefficients Q_i's in the expansion (4), we perform the Cauchy's division between the usual Wigner expansion for $Z_q/Z_{\rm cl}$ [Eq. (1)] and the expansion of the function G

$$G=1+\hbar^2C_1^H+\hbar^4C_2^H+\cdots \quad . \tag{7}$$

Because of the assumption about the asymptotic nature of expansions (1) and (7) and the properties of such series,[9] the expansion (4) is unique and at least asymptotically convergent. For the first Q_i's we find

$$Q_1=(C_1-C_1^H) \ , \tag{8a}$$

$$Q_2=(C_2-C_2^H)-C_1^H(C_1-C_1^H) \ . \tag{8b}$$

At this point we can give a generalized[9] asymptotic expansion for Z_q

$$Z_q=Z_{\rm cl}G(1+\hbar^2Q_1+\hbar^4Q_2+\cdots) \ . \tag{9}$$

The free energy per particle is then given by

$$N^{-1}F_q=N^{-1}F_q^H+N^{-1}F_{\rm cl}^A-\beta^{-1}\ln(1+\hbar^2Q_1+\cdots)^{1/N} \ , \tag{10}$$

where F_q^H is the free energy for a system of free bosons and $F_{\rm cl}^A$ is the classical contribution due to anharmonicity.

In order to clarify the improvement of our formulation with respect to the usual Wigner expansion we investigate the case of one-dimensional sine-Gordon (SG) model, where the effects of the anharmonic part are particularly important and where the calculation of the expansion coefficients can be done analytically. In the classical case it is well known that such a system bears soliton excitations in addition to the usual linear ones. The former are found to give a significant contribution to the classical statistical mechanics. In particular, they give rise to a Schottky-like peak in the specific heat versus temperature as shown by exact numerical calculations based on the transfer integral method.[10] This peak cannot be correctly reproduced in the framework of an ideal soliton gas phenomenology (valid for $k_BT \ll E_s$, energy of the static soliton) but requires to take account of soliton-soliton interaction.[11] The effect of quantum fluctuations has been included by Maki and Takayama,[12] who used the functional integral method. This semiclassical approach is not able to go beyond the ideal soliton gas approximation. A different approach to the quantum-statistical mechanics of the SG model has been proposed by Tsuzuki who used the coherent state representation of the density matrix. Taking into account the lowest quantum corrections in the displacive limit he obtained an approximate expression for the free energy valid beyond the ideal soliton gas regime.[13]

We now present the application of our expansion to the SG system limiting ourselves to the lowest quantum correction. The Hamiltonian is

$$\mathscr{H}=Aa\sum_i\left[\frac{p_i^2}{2A^2}+\frac{1}{2}\frac{c_0^2}{a^2}(\phi_i-\phi_{i+1})^2+\omega_0^2(1-\cos\phi_i)\right] \ , \tag{11}$$

where A is a constant with dimensions of (energy) $\times$ (time)$^2\times$ (length)$^{-1}$, c_0 and ω_0 are characteristic velocity and frequency, respectively, a is the lattice constant, ϕ_i and p_i are canonical conjugate variables.

From Hamiltonian (11) C_1 turns out to be

$$C_1=-\frac{\beta^2N}{24}\left[2\frac{c_0^2}{a^2}+\omega_0^2\langle\cos\phi\rangle_{\rm cl}\right] \ . \tag{12}$$

In order to obtain C_1^H we expand the G function (6) in the $\hbar\to 0$ limit. The frequency ω_k is given by

$$\omega_k=[\omega_0^2+4(c_0^2/a^2)\sin^2(\tfrac{1}{2}ka)]^{1/2} \tag{13}$$

and finally we obtain

$$C_1^H=-\frac{\beta^2N}{24}\left[2\frac{c_0^2}{a^2}+\omega_0^2\right] \ . \tag{14}$$

Consequently the first coefficient of our expansion (9) is given by

$$Q_1=\frac{\beta^2N}{24}\omega_0^2(1-\langle\cos\phi\rangle_{\rm cl}) \ . \tag{15}$$

From Eq. (10) the free energy per particle at the lowest order in $\hbar$ is given by

$$N^{-1}F_q=N^{-1}(F_q^H+F_{\rm cl}^A+\Delta F_q) \ , \tag{16}$$

where

$$N^{-1}F_q^H=\beta^{-1}N^{-1}\sum_k\ln[2\sinh(\beta\hbar\omega_k)] \ . \tag{17}$$

Depending on temperature, we use the following expansion for $F_{\rm cl}^A$:[11] for low temperatures ($t=k_BT/E_s\lesssim\frac{1}{4}$)

$$F_{\rm cl}^A=NAa\omega_0^2\left[\sum_{n=2}a_nt^n-\tau_s(t)+\tau_{ss}(t)\right] \ , \tag{18}$$

where τ_s and τ_{ss} are the one and two-soliton contributions, respectively,

$$\tau_s(t)=16\sqrt{2/\pi}\,t^{1/2}\exp(-1/t)\left[1+\sum_{n=1}b_nt^n\right] \ , \tag{19}$$

$$\tau_{ss}(t)=\frac{64}{\pi}\exp(-2/t)\left[\ln\left(\frac{4\gamma}{t}\right)(1-\tfrac{5}{4}t-\tfrac{13}{32}t^2)-\tfrac{5}{4}t-\tfrac{1}{8}t^2\right] \ , \tag{20}$$

where $\ln\gamma=0.577$ is the Euler constant and the values of coefficients a_n and b_n are quoted in the original paper.[11] For high temperatures ($t\gtrsim\frac{1}{4}$) the anharmonic part takes the form

$$F_{\rm cl}^A=NAa\omega_0^2\left[1+\sum_{n=1}A_{2n-1}q^{2n-1}\right] \ , \tag{21}$$

where $q=1/(4t)^2$ and the coefficients A_{2n-1} are given in Refs. 13 and 14. The lowest quantum correction to the nonlinear part ΔF_q is

$$N^{-1}\Delta F_q=-\beta^{-1}\ln\left[1+\frac{\beta^2\hbar^2\omega_0^2}{24}(1-\langle\cos\phi\rangle_{\rm cl})\right] \ , \tag{22}$$

where

$$\langle\cos\phi\rangle_{\rm cl}=1-(AaN)^{-1}\frac{\partial F_{\rm cl}}{\partial(\omega_0^2)} \ . \tag{23}$$

It is interesting to compare our expansion with the usual

Wigner one (1). In the latter case one would obtain

$$N^{-1}\Delta F_q^w = -\beta^{-1}\ln\left[1-\frac{\beta^2\hbar^2\omega_0^2}{24}\left(\frac{2c_0^2}{\omega_0^2a^2}+\langle\cos\phi\rangle_{\rm cl}\right)\right] . \quad (24)$$

The conditions for which the $\hbar^2$ terms in (22) and (24) are much smaller than one are, respectively,

$$Q << \sqrt{12t} \ , \quad (25a)$$

$$QR << \sqrt{12}t \ , \quad (25b)$$

where we have defined $Q=\hbar\omega_0/E_s$ and $R=c_0/\omega_0 a$. Because in the displacive limit the soliton length $R >> 1$ and in the semiclassical approximation $Q << 1$, our expansion is significant down to temperatures lower than those of the Wigner expansion. Of course the limit $T\rightarrow 0$ is still beyond the validity range of our expansion, owing to its intrinsically semiclassical origin.

From Eq. (16) it is possible to calculate the thermodynamic quantities for the SG model. In particular the specific heat per particle

$$C=-T\frac{\partial^2(F/N)}{\partial T^2}$$

is given by the sum of three contributions.

(i) The quantum harmonic part

$$C_q^H = N^{-1}\sum_k x_k^2\exp(x_k)[\exp(x_k)-1]^{-2} \quad (26)$$

with

$$x_k=(Q/T)[1+2R^2(1-\cos k)]^{1/2} \ .$$

(ii) The classical anharmonic part

$$C_{\rm cl}^A=\begin{cases}\Delta C_{sw}+C_s+C_{ss}, & t<\frac{1}{4} \quad (27a)\\ -\frac{1}{4RT}\sum_{n=1}A_{2n-1}(8n^2-6n+1)q^{2n-1}, & t<\frac{1}{4} \quad (27b)\end{cases}$$

where ΔC_{sw} is the contribution due to the interactions among linear modes, C_s the contribution from the ideal gas of solitons, and C_{ss} is due to the interaction between two solitons. The explicit expressions are given in Ref. 11.

(iii) The lowest quantum correction for the anharmonic part

$$\Delta C_q=\frac{Q^2}{24}\left\{\frac{2}{t^2}(1-\langle\cos\phi\rangle_{\rm cl})+\frac{2}{t}\frac{\partial}{\partial t}\langle\cos\phi\rangle_{\rm cl}-\frac{\partial^2}{\partial t^2}\langle\cos\phi\rangle_{\rm cl}\right\} . \quad (28)$$

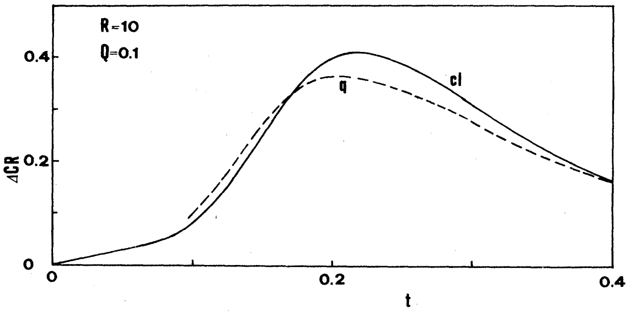

FIG. 1. Nonlinear contribution to the specific heat ΔCR vs reduced temperature t for $R=10$ and $Q=0.1$. Full line: classical result; dashed line: quantum result.

In Fig. 1 we report the nonlinear contribution to the specific heat $\Delta CR=(C_{\rm cl}^A+\Delta C_q)R$ vs t for $R=10$ and $Q=0.1$, together with the classical result. The quantum corrections have the effect of lowering the peak height by 10%–15% with respect to the classical result. Also the temperature at which the peak occurs is reduced. The curves in Fig. 1 have been obtained matching the low- and high-temperature expansions for the classical quantities $C_{\rm cl}^A$ and $\langle\cos\phi\rangle_{\rm cl}$.

It is worthwhile to compare our results for ΔC with those of Tsuzuki.[13] Generally he obtains quantum corrections much larger than ours, for example, a reduction of about 20% in the peak height for $R=10$ and $Q=0.01$, while, with the same parameters our theory gives results for ΔCR which are undistinguishable from the classical ones. The amount of the quantum corrections found by Tsuzuki appears to be excessive for this low value of Q. This parameter is related to the parameter g^2 in the quantum SG field theory,[12] $g^2\hbar=8Q$, and from Maki's theory[12] it is known that at low temperatures a system with $g^2\hbar=0.08$ is substantially classical.

In conclusion, for the specific heat of the SG model we find that the greatest correction to the classical result is due, for low values of Q $(Q<0.1)$, to the harmonic part, while the nonlinear contribution seems not to be very sensitive to quantum effects. This result is in agreement with the conclusions of Imada, Hida, and Ishikawa,[15] who calculated the specific heat of the quantum SG model through the equivalence with the massive Thirring model.

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