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On the Relation between the Phonon Spectrum and the Specific Heat

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To the memory of Léon van Hove

Abstract

The relation between the phonon spectrum and the specific heat of solid crystals, obtained by solving a linear integral equation, is discussed. It is shown that the validity of the relation does not depend on the Riemann hypothesis contrary to the statement made by Dai et al. in a recent paper. A novel representation of the phonon spectrum is given in the form of a series involving the Möbius function. The importance of analytic properties and of van Hove singularities is pointed out.

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Recently, Dai et al. [1] have drawn attention to the fact that the phonon spectrum can be directly obtained from the measured lattice specific heat by solving a certain linear integral equation. Since the phonon spectrum is of key importance for understanding many properties of solids (e.g. thermodynamic properties, inelastic scattering of neutrons, superconductivity, correlations that may be responsible for high-T_c superconductivity), the solution proposed in ref. [1] deserves a thorough discussion.

In this letter I shall dwell on a few mathematical subtleties arising in solving the relevant integral equation. In particular, I shall point out that the uniqueness of the solution does not depend on the Riemann hypothesis, contrary to the statement made in ref. [1]. I shall give a representation of the phonon spectrum in the form of a series involving the Möbius function and shall propose a novel approach to the model building for the phonon spectrum and the specific heat. The discussion will follow ref. [1] using, however, a slightly different notation.

The normal modes of elastic vibrations of solid crystals (sound waves) can be considered as the energy levels of a system of phonons having energy $E = \hbar\omega$. The phonon spectrum $g(\omega)$ (phonon level density) is defined as the number of normal vibrations per unit frequency interval. Treating the phonon system as a Bose gas, the energy $\mathcal{U}(T)$ of a solid crystal at temperature T is given by

$$\mathcal{U}(T) = \int_0^\infty d\omega\, \mathcal{U}_{osc}(T,\omega) g(\omega) \ , \tag{1}$$

where

$$\mathcal{U}_{osc}(T,\omega) = \frac{\hbar\omega}{2}\, coth \left(\frac{\hbar\omega}{2k_B T}\right) \tag{2}$$

is the energy of a single harmonic oscillator with frequency ω. From $C_v(T) = (\partial\mathcal{U}/\partial T)_v$ one obtains for the lattice specific heat or thermal capacity

$$C_v(T) = \int_0^\infty d\omega\, C_v^E(\frac{\omega}{T}) g(\omega) \ , \tag{3}$$

where $C_v^E(\frac{\omega}{T})$ is the specific heat according to the Einstein model

$$C_v^E(\frac{\omega}{T}) = (\frac{\omega}{T})^2 \frac{e^{\omega/T}}{(e^{\omega/T}-1)^2} \ . \tag{4}$$

(From now on I set $\hbar = k_B = 1$). The basic relation (3) can be viewed as an integral equation which is of Fourier-convolution type if the following change of variables is performed : $T \to x = log(T/T_0)$, $-\infty < x < \infty$; $\omega \to y = log(\omega/T_0)$, $-\infty < y < \infty$; T_0 being an arbitrary temperature scale. Introducing the functions $h(x) = C_v(T_0 e^x)$ and $f(y) = T_0 e^y g(T_0 e^y)$, the integral equation reads

$$h(x) = \int_{-\infty}^{\infty} \frac{dy}{\sqrt{2\pi}}\, G(x-y) f(y) \,. \qquad (5)$$

Here the Jacobian of the transformation has been included in $f(y)$, and the integral kernel is given by

$$G(x) = \sqrt{2\pi} e^{-2x}\, \frac{exp(e^{-x})}{(exp(e^{-x})-1)^2} \,. \qquad (6)$$

Introducing the Fourier transform via

$$\tilde{h}(k) = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}}\, e^{ikx} h(x) \,, \qquad (7)$$

the formal solution of eq. (5) leads to the following integral representation of the phonon spectrum

$$\omega g(\omega) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} \left(\frac{T_0}{\omega}\right)^{ik} \frac{\tilde{h}(k)}{\tilde{G}(k)} \,. \qquad (8)$$

Since the last expression still involves the Fourier transform of the specific heat, it is tempting to insert (7) into (8) and to interchange the order of integrations yielding

$$\omega g(\omega) = \int_0^{\infty} \frac{dT}{T}\, C_v(T) H(log\, \frac{T}{\omega}), \qquad (9)$$

where $H(z)$ is given as the inverse Laplace transform

$$H(z) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} dk\, \frac{e^{kz}}{\tilde{G}(-ik)} \,. \qquad (10)$$

In order to give a mathematical meaning to eqs. (8-10), one has to investigate the analytic properties of the functions $1/\tilde{G}(k)$ and $\tilde{h}(k)$. In this letter I shall concentrate on the solution (8) and shall show that it is uniquely defined under very general physical assumptions on $C_v(T)$.

Making the substitution $e^{-x} = t$, one obtains for the Fourier transform of the kernel (6)

$$\tilde{G}(k) = \int_0^{\infty} dt\, t^{1-ik}\, \frac{e^t}{(e^t-1)^2} = \Gamma(2-ik)\zeta(1-ik) \,, \qquad (11)$$

where a well-known integral representation of the Riemann zeta-function $\zeta(z)$ has been used (see e.g. [2]). The above integral converges for $Re(1-ik) > 1$, and thus $\tilde{G}(k)$ is a holomorphic function in the upper half complex k-plane ($Imk > 0$). But $\Gamma(z)$ and $\zeta(z)$ are (after analytic continuation) meromorphic functions of z, and thus $\tilde{G}(k)$ is a well defined meromorphic function in the whole k-plane. Consequently, the relevant function $1/\tilde{G}(k)$ has an analytical continuation as a meromorphic function into the whole complex k-plane, which is, furthermore, holomorphic in the upper half-plane. The crucial question therefore is, whether $1/\tilde{G}(k)$ has singularities in the physical region, i.e. on the real line $Rek = 0$, which is the region of integration in the solution (8). Since $1/\Gamma(z)$ is an entire function, possible singularities can only arise from the zeros of $\zeta(z)$. Since the trivial (simple) zeros of $\zeta(z)$ located at $z = -2n(n = 1,2,3...)$ are exactly cancelled by the poles of the gamma function, we conclude that the only singularities of $1/\tilde{G}(k)$ are poles, which are confined to the critical strip $-1 \leq Imk \leq 0$ and are completely determined by the non-trivial zeros of the Riemann zeta-function. (There are an infinite number of non-trivial zeros).

Dai et al. [1] have drawn attention to a possible relation between the uniqueness of the solution (8) and the Riemann hypothesis. It is an old and very attractive idea, first put forward by Hilbert and Polya (independently) around 1915, that the Riemann zeros may have an eigenvalue interpretation which in turn would open the exciting possibility for a relation between the Riemann hypothesis and a problem in physics. As observed in [1], if the Riemann hypothesis is valid, all poles of $1/\tilde{G}(k)$ are lying on the critical line $Imk = -\frac{1}{2}$, and thus $1/\tilde{G}(k)$ is holomorphic in the plane $Imk > -\frac{1}{2}$, and the validity of the representation (8) for the phonon spectrum depends only on the physical properties of the measured specific heat.

I would like to point out that for the present problem one has not to rely on the validity of the Riemann hypothesis. The authors of ref. [1] assumed that the non-trivial zeros of $\zeta(z)$ may also occur on the boundary of the critical strip, $Rez = 1$, which exactly corresponds to the physical region, $Imk = 0$, in eq. (8). However, in their famous proofs of the prime-number theorem, Hadamard [3] and de la Vallée Poussin [4] proved independently in 1896 that $\zeta(z)$ has no zeros on the line $Rez = 1$ (which, by means of the functional equation for $\zeta(z)$, implies that there are also no zeros on the line $Rez = 0$. For an excellent review, see [5]). Thus the function $1/\tilde{G}(k)$ has all its poles in the strip $-1 < Imk < 0$, which means that it is holomorphic for $Imk \geq 0$, i.e. in the physical region it is completely free from singularities ; at $k = 0$ it has a simple zero,

$$\frac{1}{\widetilde{G}(k)} = -ik + O(k^2) \; . \tag{12}$$

The above mentioned properties of $1/\zeta(z)$ are nicely reflected on the fact [5] that the Dirichlet series

$$\frac{1}{\zeta(z)} = \sum_{n=1}^{\infty} \frac{\mu(n)}{n^z} \tag{13}$$

converges for $Re z \geq 1$, including all points on the line $Re z = 1$; in particular

$$\sum_{n=1}^{\infty} \frac{\mu(n)}{n} = 0, \qquad \sum_{n=1}^{\infty} \frac{\mu(n) log\, n}{n} = -1 \tag{14}$$

due to the simple pole (with residue 1) of $\zeta(z)$ at $z = 1$. (If the Riemann hypothesis holds, eq. (13) is true for every z with $Re z > \frac{1}{2}$). Here $\mu(n)$ is the Möbius function defined by

$$\mu(n) = \begin{cases} 1 & if\ n = 1 \\ (-1)^{\ell} & if\ n\ is\ the\ product \\ & of\ \ell\ distinct\ primes \\ 0 & if\ n\ is\ divisible\ by \\ & a\ square\ > 1. \end{cases}$$

With (13) one obtains the following series expansion, valid for $Imk \geq 0$

$$\frac{1}{\widetilde{G}(k)} = \sum_{n=1}^{\infty} \frac{\mu(n)}{n} \frac{n^{ik}}{\Gamma(2-ik)} \; . \tag{15}$$

The series (15) is, however, not absolutely convergent for $Imk = 0$, which is explicitly seen from the relation

$$\sum_{n=1}^{\infty} \frac{|\,\mu(n)\,|}{n^z} = \frac{\zeta(z)}{\zeta(2z)} \; , \tag{16}$$

which (after analytic continuation) produces a pole at $z = 1$; thus (16) is only convergent for $Re z > 1$.

To complete the uniqueness proof of the solution (8), one has to discuss the analytic properties of $\widetilde{h}(k)$. Assuming that $C_v(T)$ vanishes as T^d at low temperatures (d is the dimension of the lattice) and obeys Dulong-Petit's law in the high-temperature limit, implies

$$h(x) = \begin{cases} A\, e^{-d|x|} + o(e^{-d|x|}), x \to -\infty \\ C_v(\infty) + o(1), x \to +\infty. \end{cases} \tag{17}$$

From the asymptotic behaviour (17) one infers that $\widetilde{h}(k)$ is holomorphic in the strip $0 < Imk < d$ in the upper half complex k-plane, but that it is singular in the physical region. However, such a behaviour is very familiar from many branches of physics, e.g. classical and relativistic dispersion theory (Kramers-Kronig relation, fixed-t dispersion relations for pion-nucleon scattering), where the analyticity in the upper half-plane is a consequence of causality. The well-known trick to get around this problem is to define the physical value as the boundary value obtained by approaching the real axis from above, i.e. $k \to k + i\epsilon$, $\epsilon > 0$. I am thus led to define the unique solution of the integral equation (5) by

$$\omega g(\omega) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} \left(\frac{T_0}{\omega}\right)^{ik} \frac{\widetilde{h}(k+i\epsilon)}{\widetilde{G}(k)} \tag{18}$$

(the limit $\epsilon \to 0$ being understood, and all integrals being interpreted as distributions). That the limit $\epsilon \to 0$ is well defined, is seen as follows. From the asymptotic condition (17) one easily derives

$$\widetilde{h}(k+i\epsilon) = \frac{C_v(\infty)}{\sqrt{2\pi}} \frac{i}{k+i\epsilon} - \frac{A}{\sqrt{2\pi}} \frac{i}{k-id} + R(k), \tag{19}$$

where the function $R(k)$ is holomorphic for $0 \leq Imk \leq d$. (Here I assume that the nonleading terms in (17) are well behaved). Taking (12) into account yields the finite limit

$$\widetilde{f}(0) = \lim_{k \to 0} \frac{\widetilde{h}(k+i\epsilon)}{\widetilde{G}(k)} = \frac{C_v(\infty)}{\sqrt{2\pi}} \; , \tag{20}$$

which shows explicitly that the integrand of eq. (18) is nonsingular. The finiteness of $\widetilde{f}(0)$ exemplified by eq. (20) has a simple physical interpretation.Looking at

$$C_v(\infty) = \sqrt{2\pi}\; \widetilde{f}(0) = \int_{-\infty}^{\infty} dy\; f(y) = \int_0^{\infty} d\omega\; g(\omega) \tag{21}$$

we see that it is nothing but the correct normalization of the phonon spectrum $g(\omega)$ with $C_v(\infty)$ being the total number of vibrations in agreement with Dulong-Petit's law.

Eq. (19) reveals clearly the physical meaning of the nearest singularities of $\widetilde{h}(k)$. The simple pole at $k = 0$ is equivalent to Dulong-Petit's law, whereas the simple pole at $k = id$ reflects the dimension d of the crystal lattice and is responsible for the correct low-temperature behaviour of the specific heat.

It is obvious from eq. (7) that the $i\epsilon$−rule used in eq. (18) is equivalent to the replacement $h(x) \to h(x)e^{-\epsilon x}$, which in turn means that instead of $C_v(T)$ one considers the reduced heat capacity $C_v(T)/T^\epsilon$, which vanishes in the high-temperature limit. This can be generalized by considering $C_v(T)/T^s$, where s is an arbitrary real parameter satisfying $0 < s < d$. This s−regularization has been used first by Montroll [6] (for the special value $s = 1$) and recently by Dai et al. [1]. By shifting the contour of integration in eq. (8) from the real line to the contour C, where C is the straight line from $-\infty + is$ to $+\infty + is$ (the shift being allowed, since the integrand is holomorphic in the strip $0 < Imk < d$), one obtains for the phonon spectrum

$$\omega g(\omega) = \left(\frac{\omega}{T_0}\right)^s \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} \left(\frac{T_0}{\omega}\right)^{ik} \frac{\widetilde{h}(k+is)}{\Gamma(2+s-ik)\zeta(1+s-ik)} . \tag{22}$$

(Note that there is a misprint in the corresponding eq. (28) of ref. [1]; the factor $(\hbar\omega/T_0)^{ik-s}$ should read $(\hbar\omega/T_0)^{ik+s}$). Eq. (22) holds for finite s-values, without the need to perform a limit, as long as $0 < s < d$; in the limit $s = \epsilon \to 0$, it becomes identical to eq. (18).

Inserting the Dirichlet series (13) into (22) and interchanging integration and summation, which is justified for $s > 0$, I arrive at the following representation of the phonon spectrum in the form of a series

$$\omega g(\omega) = \left(\frac{\omega}{T_0}\right)^s \sum_{n=1}^{\infty} \frac{\mu(n)}{n^{1+s}}\, a\left(\frac{nT_0}{\omega}\right) , \tag{23}$$

where the function $a(z)$ is given by

$$a(z) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}}\, z^{ik}\, \frac{\widetilde{h}(k+is)}{\Gamma(2+s-ik)} . \tag{24}$$

Here the Riemann zeta-function has been eliminated, and one is left only with the gamma function which is easy to handle in numerical calculations.

I have shown above that the Riemann hypothesis is not required to prove the uniqueness of the solution (8). Indeed, the only singularity in the physical region is the pole of $\widetilde{h}(k)$ at $k = 0$ as demanded by Dulong-Petit's law, but this is exactly cancelled by the zero of $1/\zeta(z)$ at $z = 1$ (see eq. (12)). Nevertheless, it is interesting to enquire about a possible rôle of the Riemann zeros in eq. (18). For example, one may be tempted to interpret the poles in $1/\widetilde{G}(k)$, caused by the

Riemann zeros, as resonances. I will argue, however, that the Riemann zeros do not play such a spectacular rôle in the present problem. Our argument is based on the observation that the Riemann zeta-function enters via the Fourier transform of the kernel $G(x)$, which is essentially the Einstein specific heat given in eq. (4). The latter displays, however, no striking structure which could be traced back to the Riemann zeros. Taking as an example the two well-known models for the specific heat, the Einstein and Debye model, it turns out that $\widetilde{h}(k)$ is exactly proportional to $\widetilde{G}(k)$ and thus the zeta-function drops out completely in the relevant ratio $\widetilde{f}(k) = \widetilde{h}(k)/\widetilde{G}(k)$. Explicitly, one obtains ($d = 3$)

$$\widetilde{f}^E(k) = \frac{3N}{\sqrt{2\pi}} \left(\frac{\omega_E}{T_0}\right)^{ik} \tag{25}$$

$$\widetilde{f}^D(k) = \frac{3N}{\sqrt{2\pi}} \left(\frac{\omega_D}{T_0}\right)^{ik} \frac{3}{3+ik} . \tag{26}$$

Here I have assumed that the crystal has 3N independent normal modes of vibration ; ω_E and ω_D denote the Einstein and Debye frequency, respectively. (Note that the term −3 in the bracket of eq. (34) in ref. [1] has the wrong sign).

Rewriting eq. (18) in the following form

$$\omega g(\omega) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} \left(\frac{T_0}{\omega}\right)^{ik} \widetilde{f}(k), \tag{27}$$

I can summarize our findings as follows : the phonon spectrum $g(\omega)$ is determined by eq. (27), where $\widetilde{f}(k)$ has the following properties:

i) $\widetilde{f}(-k) = \widetilde{f}(k)^*$,

ii) $\widetilde{f}(k)$ is a holomorphic function of k in the strip $0 \le Imk < d$,

iii) $\widetilde{f}(k)$ has a simple pole at $k = id$ with residue $\frac{-iA}{\sqrt{2\pi}(d+1)!\zeta(d+1)}$,

iv) $\widetilde{f}(k)$ takes at $k = 0$ the value $\widetilde{f}(0) = \frac{C_v(\infty)}{\sqrt{2\pi}}$.

These results shed a new light on the structure of the two familiar models cited in eqs. (25) and (26). From the point of view of the analytic structure of $\widetilde{f}(k)$, the Einstein model is the simplest one, since it assumes that $\widetilde{f}(k)$ is not only holomorphic in the strip $0 \le Imk < d$, but even an entire function. It is as if the Einstein model corresponds to the limit $d \to \infty$, i.e. the pole at $k = id$ is considered to be far away and thus can be neglected. The Debye model, on the other hand, appears to be the simplest model respecting all the above mentioned properties i)-iv) by assuming that $\tilde{f}(k)$ is a meromorphic function in the whole k-plane having its only pole at $k = id (d = 3$ in eq. (26)). There is no doubt that these properties are responsible for the great success of the Debye model.

It is suggestive to generalize the Ansätze (25, 26) to the following Ansatz

$$\tilde{f}(k) = \frac{C_v(\infty)}{\sqrt{2\pi}} \left(\frac{\omega_0}{T_0}\right)^{ik} \tilde{Q}(k) , \tag{28}$$

where the function $\tilde{Q}(k)$ is meromorphic in the strip $0 \leq Imk \leq d$ with a simple pole at $k = id$ and satisfies $\tilde{Q}(-k) = \tilde{Q}(k)^*$, $\tilde{Q}(O) = 1$. (The last two properties ensure that $g(\omega)$ is real and satisfies the correct normalization (21)). The frequency ω_0 is a free parameter. The corresponding phonon spectrum is given by

$$\omega g(\omega) = \frac{C_v(\infty)}{\sqrt{2\pi}} \; Q(log \frac{\omega_0}{\omega}) , \tag{29}$$

while the heat capacity is obtained as the Fourier transform of the function

$$\tilde{h}(k) = \frac{C_v(\infty)}{\sqrt{2\pi}} \left(\frac{\omega_0}{T_0}\right)^{ik} \Gamma(2 - ik)\zeta(1 - ik)\tilde{Q}(k) . \tag{30}$$

A potential generalization of the Debye model could be characterized by a function $\tilde{Q}(k)$ which has in addition to the above properties poles located at $Imk > d$ and /or $Imk < 0$. (For example, since the low-temperature behaviour of a three-dimensional crystal is well described by the asymptotic series $C_v(T) \sim \sum_{n=0}^{\infty} b_n \, T^{3+2n}$, one expects an infinite series of poles at $k = (3 + 2n)i$, n=0,1,2...). In this context the so-called van Hove singularities could play an important rôle. It is known since a long time from studies of simple models, which allow an exact computation of the phonon spectrum, that $g(\omega)$ can develop singularities. In 1953 it was shown by van Hove [7] that $g(\omega)$ of a general crystal contains a finite number of singularities due to the periodic structure. The van Hove singularities are singular points ω_c in the neighbourhood of which $g(\omega)$ has one of the two forms (see also [8])

$$g(\omega) = g(\omega_c) + \begin{cases} B \mid \omega_c - \omega \mid^{1/2} + O(\mid \omega_c - \omega \mid) \; for \; \omega < \omega_c \\ O(\mid \omega - \omega_c \mid) \; for \; \omega > \omega_c \end{cases} \tag{31}$$

or the same with $\omega < \omega_c$ and $\omega > \omega_c$ interchanged. (The constant B can have either sign; it is usually negative for $\omega_c < \omega_{max}$). It seems likely that the singular behaviour (31) forces $\tilde{f}(k)$ (or $\tilde{Q}(k)$ in the Ansatz (28)) to have in addition to poles also cuts in the complex k-plane. To my knowledge, a systematic study, starting from the analytic properties in the k-plane and deriving from them the phonon spectrum and the specific heat, has not yet been performed. As an ultimate goal, one would like to derive the analytic properties from a fundamental theory like e.g. the Born-Karman theory for crystal dynamics.

Studying the analytic properties of $g(\omega)$ one should also keep in mind that the phonon spectrum can be directly measured in neutron scattering. As shown by Placzek and van Hove [8], the differential cross section for incoherent scattering of neutrons on a crystal is directly proportional to $g(E)$, where E is the energy of the outgoing neutron.

Finally, I would like to mention that the solution of linear integral equations of type (5) has extensively been discussed in the mathematical literature using two-sided Laplace transforms (see e.g. [9]). (The latter are, of course, directly related to the Fourier transform (7) used here). For a certain class of integral kernels, the solution can be expressed in terms of a differential operator of infinite order [9,10] using Wiener's operational calculus [11]. It would be extremely interesting to investigate whether these results can be generalized to integral kernels of the type (11). Let us also mention that the original integral equation (3) with the kernel given by (4) can be directly solved (without change of variables) by means of a Mellin transformation since (3) is of Mellin-convolution type. With respect to the physical literature, it seems that Bauer was the first to study an inversion problem similar to the one posed by eq. (3). In two papers [12] he studied an inversion formula that expresses $g(\omega)$ in terms of the partition function $Z(T)$ and which is the solution of an integral equation analogous to eq. (3). Somewhat later, Montroll [6] gave an inversion formula for eq. (3) which corresponds to the choice $s = 1$ in eq. (22).

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REFERENCES

[1] X. Dai, X. Xu and J. Dai, Phys. Lett. **A147** (1990) 445.

[2] W. Magnus, F. Oberhettinger and R.P. Soni, Formulas and Theorems for the Special Functions of Mathematical Physics, Third edition (Springer, Berlin, Heidelberg, New York, 1966).

[3] J. Hadamard, Bull. Soc. Math.. France **24** (1896) 199.

[4] C.J. de la Vallée Poussin, Ann. Soc. Sci. Bruxelles **20** (1896) 183.

[5] E.C. Titchmarsh, The Theory of the Riemann Zeta-Function (Oxford University Press, 1951).

[6] E.W. Montroll, J. Chem. Phys. **10** (1942) 218.

[7] L. Van Hove, Phys. Rev. **89** (1953) 1189.

[8] G. Placzek and L. van Hove, Phys. Rev. **93** (1954) 1207.

[9] G. Doetsch, Handbuch der Laplace Transformation, Bd.III (Birkhäuser, Basel, Stuttgart, 1956).

[10] D.V. Widder, Duke Math. J. **14** (1947) 217; Am. Math. Monthly **58** (1951) 179.

[11] N. Wiener, Math. Annalen **95** (1925) 557.

[12] S. Bauer, J. Chem. Phys. **6** (1938); ibid. **7** (1939) 1097.