

Upper and Lower Bounds to Rayleigh's Frequency for a Vibrating System

William J. Taylor

Citation: [The Journal of Chemical Physics](#) **14**, 570 (1946); doi: 10.1063/1.1724203

View online: <http://dx.doi.org/10.1063/1.1724203>

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i.e., neglecting the effect due to the superficies of the vibrating body.

Our having taken into account this effect^{1,2} leads to a calculation of the superficial density (in Gibbs's sense of the term) of the energy of natural vibrations. For the first of the above problems this superficial density gives a correct idea of the main features of the surface tension of metals. For the second problem a calculation of this kind results in establishing the dependence of the specific heat of dispersed bodies and the surface tension of solid bodies on the temperature. By considering the third problem along the same lines the surface tension of the radiation has been calculated.

While solving the first problem¹ it was essential to bear in mind that the electrons when fixed on the boundaries of the body cannot occupy energy levels with quantum numbers equaling zero. It was also important to estimate the error due to the substitution of the integration for a summation of the energy of natural vibrations. The latter process requires a determination of the number of whole points in the sphere. By effecting these calculations on the basis of Vinogradoff's paper³ we derived the following equation for the calculation of the surface tension of metals

$$\sigma = 56,400(\gamma/A)^{1/3} \text{ dyne} \cdot \text{cm}^{-1}, \quad (1)$$

where A is atomic weight and γ is density of the metal, $\text{g} \cdot \text{cm}^{-3}$.

A comparison with experimental data has shown that Eq. (1) expresses the order of magnitude and the dependence of the surface tension on the density of the electron gas.

An important factor in the solution of the second problem² is the fact that for an entirely free surface, account should be taken of the presence of the Rayleigh and transitional (from ordinary to Rayleigh) waves. This could be only done by considering a vector problem.

By making use of Lamb's⁴ solution of the problem of the vibrations of the infinite thin plate, we derived the following equation for the specific heat of a non-compressible solid body:

$$c_v = 9Nk \left[\frac{4}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{x}{e^x - 1} \right] + \frac{4.26 N^{2/3} k F^{2/3} l^{2/3}}{V^{2/3}} \left[\frac{6}{x^2} \int_0^x \frac{\xi^2 d\xi}{e^\xi - 1} - \frac{2x(e^x - 1) + x^2 e^x}{(e^x - 1)^2} \right] \quad (2)$$

which at low temperature passes into:

$$c_v = \frac{467.56}{V_m \cdot x^3} + \frac{61.3F}{V_m^{2/3} x^2 \cdot N_A^{1/3}} \quad (3)$$

In these equations N is the number of atoms contained in the body in question, with volume V , surface F , and length of edge of base l ; x and ξ have the same meaning as in the Debye theory: $x = h\nu_{mx}/kT$; $\xi = h\nu/kT$; V_m is molecular volume; N_A is Avogadro's number.

The first terms in Eqs. (2) and (3) are the usual expressions for the specific heat of a solid body according to the Debye theory. An estimation of the second term in Eq. (3) shows that a measurement of the specific heat of

dispersed bodies (catalysts and activated charcoal, for example) at low temperature may serve as a method for determining their specific surface. The difference in the specific heat of activated charcoal and graphite, for example, as established by Simon and Swain,⁵ corresponds to the specific surface of charcoal in its order of magnitude.

The authors wish to express their gratitude to Professor I. E. Tamm and Professor M. A. Leontovitch for a number of valuable suggestions made by them while discussing the results of the present investigation at the different stages of its progress.

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Upper and Lower Bounds to Rayleigh's Frequency for a Vibrating System

WILLIAM J. TAYLOR¹

National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

April 18, 1946

THE variation method of quantum mechanics has been extended by D. H. Weinstein² to yield upper and lower bounds for the eigenvalues of the wave equation. The method of Weinstein may be extended to the frequencies of a system of coupled harmonic oscillators. The characteristic equation of the system may be written as

$$V k_i = \lambda_i T k_i,$$

where V and T are the real symmetric potential and kinetic energy matrices, respectively, k_i is a real eigenvector (normal mode), and λ_i is the corresponding real positive eigenvalue ($\lambda_i = 4\pi^2 \nu_i^2$, where ν_i is the frequency). The secular equation for vibrations thus contains two non-commutable symmetric (real Hermitian) matrices, and in this respect differs from the wave equation of quantum mechanics, which contains a single Hermitian operator (the Hamiltonian). However the secular equation may be made isomorphic with the wave equation by transforming to a representation in which T is reduced to the unit matrix and V remains symmetric. The method of Weinstein may then be applied. Alternatively, the method with modifications may be applied directly to the secular equation in its original form. In either case the following result is obtained.

At least one eigenvalue, λ_i , lies within the range

$$\mu_1 \pm (\mu_2 - \mu_1)^{1/2},$$

where

$$\mu_1 = (k' V k) / (k' T k),$$

$$\mu_2 = ((V k)' T^{-1} (V k)) / (k' T k).$$

k is an arbitrary (variation) vector. Primed and unprimed vectors are row and column vectors, respectively. $\mu_1 = 4\pi^2 \nu^2$, where ν is the frequency of the system when it is forced by means of constraints to vibrate in a non-normal mode k .³ μ_1 and μ_2 are positive or zero. If k is an eigenvector, k_i , $\mu_1 = \lambda_i$, and $(\mu_2 - \mu_1)^{1/2} = 0$. If k is not an eigenvector,

$(\mu_2 - \mu_1^2) > 0$. Therefore, at least in principle, the minimization of $(\mu_2 - \mu_1^2)$ provides a method of obtaining all the eigenvalues and eigenvectors.

G. Kron⁴ has recently made use of Rayleigh's estimate of the frequency in connection with electric circuit models for the vibration of polyatomic molecules.

¹ Research Associate on the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons," at the National Bureau of Standards.

² D. H. Weinstein, *Proc. Nat. Acad. Sci.* **20**, 529 (1934); J. K. L. MacDonald, *Phys. Rev.* **46**, 828 (1934).

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The Preparation of Mixed Thallium Bromide-Iodide for Infra-Red Transmission

O. F. TUTTLE AND P. H. EGLI

Naval Research Laboratory, Washington, D. C.

July 25, 1946

MIXED thallium bromide-iodide crystals were synthesized in Germany for use in military infra-red optical instruments. Superior chemical and mechanical stability and the increased range of infra-red transmission of these crystals make them appear promising for a variety of infra-red applications.

The composition of the material was reported in a foreign technical mission report by Dr. Wallace Brode, but the method of preparation was not discussed. Crystals of 42 mole percent TlBr-58 mole percent TlI, having properties similar to those reported for the German material, have been synthesized at the Naval Research Laboratory by crystallization from a melt of the same composition.

Transmission measurements of a plate of the material 2 mm thick over the spectral range 0.5 to 14 μ were kindly furnished by Dr. J. A. Sanderson of this laboratory. The observed transmission rose rapidly from approximately 0 percent at 0.5 μ to 50 percent at 1 μ and to approximately 67 percent from 10 to 14 μ . Although precise transmission measurements have not been performed beyond 14 μ on the present specimens, the German results reported by Brode showed constant transmission factors of about 67 percent from 2 μ to 30 μ with transmission decreasing at longer wavelengths to zero percent at 70 μ . The light loss is caused

largely by reflection, since the index of refraction of the crystal is nearly 2.4 at 10 μ .

The crystals were grown from a melt using a modification of the technique developed by Bridgman¹ for growing single crystals of metals. The furnace is a vertical tubular resistance type similar to that used by Stockbarger² for growing single crystals of lithium fluoride. The upper section and the lower section are separated by an insulating baffle, and the temperature in the two sections is independently controlled, the baffle serving to increase the gradient in the region where growth takes place.

A mixture of the desired composition is melted in a cylindrical platinum or Pyrex crucible with a conical bottom, for which an angle of 60° has been found satisfactory. A single crystal will result provided only one nucleus is formed in the tip of the crucible; or if several nuclei form, if only one is favorably oriented to grow along the axis of the crucible.

The growth process is controlled by the temperature gradient maintained, and the rate at which the crucible is lowered through the furnace. For homogeneous growth, relatively free of strains, a sharp temperature difference is needed, and the rate of passage through the gradient must be sufficiently slow that crystallization takes place at the point of the temperature gradient in a plane across the whole surface of the solid-melt interface. Too rapid lowering causes crystallization to proceed up the sides of the boule leaving the center molten, and results in multi-crystalline formation. For this material the temperature in the upper section of the furnace is held at approximately 470°C with variations of 5°C not noticeably affecting the quality of the crystal. No heat is used in the lower section of the furnace which is open at the bottom. A lowering rate of 7 hours per inch has given excellent crystals one inch in diameter, and 32 hours per inch has proved satisfactory for two-inch diameters.

The system TlBr-TlI is characterized by a complete solid solution with a minimum temperature at a composition close to 50 mole percent. The region of minimum temperature is relatively broad, and the properties of the crystal appear not to change rapidly with small changes in composition. With sufficiently pure material, single crystals form very readily.

¹ P. W. Bridgman, *Proc. Am. Acad. Sci.* **60**, 305 (1925).

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