

# Theory of Phonon-Terminated Optical Masers

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A simple dielectric theory is used to describe the operating properties of phonon-terminated masers of the type reported by Johnson, Dietz, and Guggenheim. Basic to this model is a broadband *gain characteristic* which describes the frequency-dependent gain of the active maser material as a function of the populations of metastable electronic levels and of the temperature or temperatures describing lattice vibrations. The power levels required to produce phonon saturation are estimated to be extremely high (typically,  $\sim 10^{10}$  W/cm<sup>2</sup> power output). Because phonon saturation does not ordinarily occur, a single-lattice temperature is generally sufficient. In that case, details of the electron-phonon coupling are unimportant, and the gain can be related by detailed balance to fluorescence and absorption spectra. Effects of phonon saturation are briefly discussed in the event that they might pertain to exceptional systems and because they give insight into the principles of operation of these masers.

## 1. INTRODUCTION

RECENTLY Johnson, Dietz, and Guggenheim<sup>1</sup> reported the successful pulsed operation of a new class of solid-state optical maser oscillators. Their optically excited masers operate in the fluorescence spectra of nickel and cobalt ions in fluorides. These spectra are qualitatively similar to fluorescence spectra in many other materials in that they contain strong sharp no-phonon (or "electronic") lines and broadband "vibrational structure" adjacent to the no-phonon lines on their low-frequency sides.<sup>2,3</sup> The vibrational structure results from electronic transitions which are accompanied by the simultaneous emission (or possibly at high temperatures, absorption) of one or more lattice phonons.<sup>4-7</sup> Previous solid-state optical masers have operated at sharp no-phonon lines<sup>8</sup>; the unusual feature of these new *phonon-terminated masers* is that they operate in the vibrational structure. They are potentially important in technology as the basic elements of very broadband optical amplifiers and of tunable oscillators.

In our discussion, based for definiteness upon the MgF<sub>2</sub>:Ni<sup>2+</sup> (1%) maser of Johnson *et al.*, we use the

fact that optical masers can be accurately described by a simple dielectric theory in which the active maser medium has a frequency-dependent gain or net negative absorption.<sup>9</sup> The most important properties of the material in a small macroscopic neighborhood of the space-time point  $(\mathbf{r}, t)$  are reflected in the *gain characteristic*  $g_\lambda(\mathbf{k}, \omega; \mathbf{r}, t)$ .<sup>10</sup> This function describes the gain per unit length at  $(\mathbf{r}, t)$  for radiation having the frequency  $\omega$ , a wave vector parallel to the unit vector  $\mathbf{k}$ , and the polarization index  $\lambda$ . The index  $\lambda$  specifies one of the two plane-wave solutions of Maxwell's equations appropriate to  $(\mathbf{k}, \omega)$ ; in degenerate cases it can alternatively describe plane or circular polarization. It is useful to write  $g_\lambda(\mathbf{k}, \omega; \mathbf{r}, t)$  as the difference

$$g_\lambda(\mathbf{k}, \omega; \mathbf{r}, t) = e_\lambda(\mathbf{k}, \omega; \mathbf{r}, t) - a_\lambda(\mathbf{k}, \omega; \mathbf{r}, t), \quad (1.1)$$

where  $a_\lambda(\mathbf{k}, \omega; \mathbf{r}, t)$  is an absorption coefficient of the pumped maser material and  $e_\lambda(\mathbf{k}, \omega; \mathbf{r}, t)$  is a corresponding stimulated-emission coefficient.

In phonon-terminated optical masers the most important saturation parameters at low power levels are the average temperature  $T(\mathbf{r}, t)$  of the lattice and the populations  $N_i(\mathbf{r}, t)$  of the metastable "electronic" levels.<sup>10</sup> It follows (Sec. 2) that, although lattice phonons clearly play an important role in phonon-terminated masers, we can predict many properties of  $g_\lambda(\mathbf{k}, \omega; \mathbf{r}, t)$  from low-intensity measurements of fluorescence and absorption spectra without having to consider the microscopic details of electron-phonon coupling or the form of the phonon spectrum. Detailed knowledge of phonon properties is only required for the computation at high power levels of line-shape saturation and "hole burning."<sup>11</sup>

In the following section we point out important rela-

<sup>1</sup> L. F. Johnson, R. E. Dietz, and H. J. Guggenheim, Phys. Rev. Letters **11**, 318 (1963).

<sup>2</sup> D. S. McClure, J. Chem. Phys. **36**, 2757 (1962); J. D. Axe and P. P. Sorokin, Phys. Rev. **130**, 945 (1963); G. Burns and M. I. Nathan, J. Appl. Phys. **34**, 703 (1963); M. D. Sturge, Phys. Rev. **130**, 639 (1963); D. B. Fitchen, R. H. Silsbee, T. A. Fulton, and E. L. Wolfe, Phys. Rev. Letters **11**, 275 (1963).

<sup>3</sup> R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters **8**, 391 (1962).

<sup>4</sup> E. O. Kane, Phys. Rev. **119**, 40 (1960); J. J. Hopfield, *Proceedings of the International Conference on Semiconductor Physics, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 75; E. D. Trifonov, Dokl. Akad. Nauk SSSR **147**, 826 (1962) [English transl.: Soviet Phys.—Dokl. **7**, 1105 (1963)].

<sup>5</sup> D. E. McCumber, J. Math. Phys. **5**, 221 (1964).

<sup>6</sup> D. E. McCumber, J. Math. Phys. **5**, 508 (1964).

<sup>7</sup> H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 75 (1941); C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962), Chap. 8 and references cited therein.

<sup>8</sup> Two articles which cite many examples are those of W. Kaiser, Phys. Status Solidi **2**, 1117 (1962); and L. F. Johnson, J. Appl. Phys. **34**, 897 (1963).

<sup>9</sup> A. L. Schawlow and C. H. Townes, Phys. Rev. **112**, 1940 (1958); W. G. Wagner and G. Birnbaum, J. Appl. Phys. **32**, 1185 (1961); D. E. McCumber, Phys. Rev. **130**, 675 (1963); E. I. Gordon, Bell System Tech. J. **43**, 507 (1964).

<sup>10</sup> Where they are not directly relevant to our discussion, we shall omit the indices  $(\mathbf{r}, t)$ .

<sup>11</sup> W. R. Bennett, Jr., Phys. Rev. **126**, 580 (1962); C. L. Tang and H. Statz, *ibid.* **128**, 1013 (1962); W. E. Lamb, Jr., Proceedings of the Third International Conference on Quantum Electronics, Paris, 1963 (to be published).

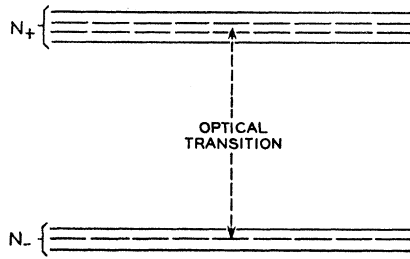


FIG. 1. Energy levels of a simple system having two optically separated multiplets. The total population densities within the two multiplets are, respectively,  $N_{\pm}$ .

tions connecting the emission and absorption coefficients  $e_{\lambda}(\mathbf{k}, \omega)$  and  $a_{\lambda}(\mathbf{k}, \omega)$  in Eq. (1.1), and we use those relations to indicate how useful information about  $g_{\lambda}(\mathbf{k}, \omega)$  can be inferred from fluorescence and absorption spectra. In Sec. 3 we use a fluorescence spectrum appropriate to the  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) maser of Johnson *et al.* to illustrate properties of a specific gain characteristic and to discuss threshold conditions for a prototype  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) maser.<sup>1</sup> In Sec. 4 we discuss the possibility of phonon saturation resulting from maser operation. We conclude that under ordinary circumstances saturation is extremely unlikely. Nevertheless, anticipating that phonon saturation might occur in some special circumstances, we consider qualitatively in Sec. 5 some effects of saturation on maser action. In the last section we briefly summarize our results.

## 2. RELATION OF THE GAIN CHARACTERISTIC TO FLUORESCENCE AND ABSORPTION SPECTRA

The direct measurement of the gain characteristic  $g_{\lambda}(\mathbf{k}, \omega)$  of an optically pumped material is at best difficult. It is therefore of considerable practical importance to relate the gain characteristic to more easily measurable fluorescence and absorption spectra.

In solids the spectra appropriate to radiative transitions between discrete electronic energy eigenstates of a localized impurity ion, for example, reflect the coupling of the impurity electrons to lattice vibrations.<sup>4-7</sup> These spectra generally display sharp no-phonon or "electronic" lines accompanied by adjacent broadband vibrational structure. The vibrational structure derives from transitions in which lattice phonons are emitted and/or absorbed simultaneously with the electronic transitions. At low temperatures, where only phonon emission is possible, the vibrational structure extends from the low-frequency side of the no-phonon line in emission and from the high-frequency side in absorption. In some special cases the spectrum in absorption may be the mirror image of that in emission, but in general these two spectra will be considerably different.<sup>12</sup> Nevertheless, at any given frequency<sup>13</sup> the absorption, stimulated-emission, and fluorescence spectra are connected by

<sup>12</sup> W. B. Fowler and D. L. Dexter, Phys. Rev. **128**, 2154 (1962).

<sup>13</sup> Fowler and Dexter, Ref. 12, compare properties at different frequencies.

detailed-balance relations. These are generalizations of well-known expressions connecting the Einstein  $A$  and  $B$  coefficients,<sup>14</sup> and they form the foundation of our present discussion.

Consider a simple model for an insulating crystal lightly doped with impurities in which the energy levels of the independent but phonon-perturbed impurities are grouped into two sets, as indicated in Fig. 1. Each set contains an energy spread of the order of the largest phonon energy ( $\sim 10^3 \text{ cm}^{-1}$ ), and the two sets are separated by an optical energy ( $\sim 10^4 \text{ cm}^{-1}$ ). The total populations per unit volume of the two sets are, respectively,  $N_{\pm}$ . Within the two sets we assume that the state populations are described by a single-lattice temperature  $T$ . We implicitly assume that the probability for radiationless transitions between the two sets of levels is negligible in a spontaneous-emission lifetime and that the time for thermal equilibration within each set is very short compared to that lifetime.

Let us consider for this simple model processes of radiative emission and absorption which involve the transfer of excitation from one set of levels in Fig. 1 to the other. Factoring the populations  $N_{\pm}$  from the coefficients in Eq. (1.1), we define absorption and stimulated-emission cross sections

$$\begin{aligned}\sigma_{a\lambda}(\mathbf{k}, \omega) &= a_{\lambda}(\mathbf{k}, \omega)/N_{-}, \\ \sigma_{e\lambda}(\mathbf{k}, \omega) &= e_{\lambda}(\mathbf{k}, \omega)/N_{+}.\end{aligned}\quad (2.1)$$

At any given frequency these cross sections are connected by the detailed-balance relation.<sup>15</sup>

$$\sigma_{a\lambda}(\mathbf{k}, \omega) = \sigma_{e\lambda}(\mathbf{k}, \omega) \exp[\hbar(\omega - \mu)/kT]. \quad (2.2)$$

Here  $\hbar\mu$  is a temperature-dependent excitation potential. It fixes the scale factor connecting the two spectral functions of Eq. (2.2). If  $F(N_{+}, N_{-}; T)$  is the free energy<sup>16</sup> of the system of Fig. 1, and if we define chemical potentials  $\hbar\mu_{\pm}$  such that<sup>17</sup>

$$\hbar\mu_{\pm}(N_{+}, N_{-}; T) \equiv \frac{\partial}{\partial N_{\pm}} F(N_{+}, N_{-}; T), \quad (2.3)$$

then

$$\begin{aligned}\hbar\mu &= \hbar(\mu_{+} - \mu_{-}) \\ &= F(N_{+}+1, N_{-}; T) - F(N_{+}, N_{-}+1; T).\end{aligned}\quad (2.4)$$

That is,  $\hbar\mu$  is the net free energy required to excite one impurity ion while maintaining the initial lattice temperature  $T$ . Equivalently,  $\exp(-\hbar\mu/kT)$  equals the ratio  $N_{+}^0/N_{-}^0$  where  $N_{\pm}^0$  are the populations  $N_{\pm}$  at

<sup>14</sup> D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353.

<sup>15</sup> Cf. Secs. 2 of the two articles cited in Refs. 5 and 6. Also, A. Einstein, Z. Physik **18**, 121 (1917).

<sup>16</sup> By definition,  $F(N_{+}, N_{-}; T) = -kT \ln \{\text{tr}_{N_{\pm}}[\exp(-H/kT)]\}$ , where the trace is over all states of the Hamiltonian  $H$  with populations  $N_{\pm}$ .

<sup>17</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 69.

thermal equilibrium of the unpumped material. In the limit of zero temperature for general systems and at arbitrary temperatures for simple "mirror-image" two-level impurity systems  $\mu$  equals the frequency  $\omega_0$  of the no-phonon line; in that case  $(\omega - \mu) = (\omega - \omega_0)$  is the frequency measured from the no-phonon line. We assume that in other cases  $\exp(\hbar\mu/kT)$  can be estimated to sufficient accuracy; a 20% error is not intolerable for many purposes.

Using Eqs. (2.1) and (2.2) in Eq. (1.1), we obtain for the system of Fig. 1:

$$g_\lambda(\mathbf{k}, \omega) = \sigma_{e\lambda}(\mathbf{k}, \omega) \{N_+ - N_- \exp[\hbar(\omega - \mu)/kT]\} \quad (2.5a)$$

$$= \sigma_{a\lambda}(\mathbf{k}, \omega) \{N_+ \exp[-\hbar(\omega - \mu)/kT] - N_-\}. \quad (2.5b)$$

Although either of these expressions could be used to determine  $g_\lambda(\mathbf{k}, \omega)$ , Eq. (2.5a) is of greater practical importance because in the high-gain regions of the vibrational structure the absorption cross section  $\sigma_{a\lambda}(\mathbf{k}, \omega)$  is generally too small and too rapidly changing to be easily measured, whereas the stimulated-emission cross section  $\sigma_{e\lambda}(\mathbf{k}, \omega)$  can be readily inferred from the fluorescence spectrum.

To relate  $\sigma_{e\lambda}(\mathbf{k}, \omega)$  to the fluorescence spectrum, we introduce a dimensionless function  $f_\lambda(\mathbf{k}, \omega)$  such that  $f_\lambda(\mathbf{k}, \omega)d\Omega_{k\lambda}$  is the average intensity in photons/sec per unit frequency interval of  $\lambda$ -polarized frequency- $\omega$  radiation spontaneously emitted into the solid angle  $d\Omega_{k\lambda}$  from each excited fluorescent center. If  $\tau$  is the spontaneous-emission lifetime of a center, then

$$\frac{1}{\tau} = \sum_\lambda \int_{4\pi} d\Omega_{k\lambda} \int_0^\infty \frac{d\omega}{2\pi} f_\lambda(\mathbf{k}, \omega). \quad (2.6)$$

From trivial generalizations of expressions derived by Dexter<sup>18</sup> it follows that

$$\sigma_{e\lambda}(\mathbf{k}, \omega) = f_\lambda(\mathbf{k}, \omega) [2\pi c / \omega n_\lambda(\mathbf{k}, \omega)]^2, \quad (2.7)$$

where  $n_\lambda(\mathbf{k}, \omega)$  is the index of refraction of the maser material. Equations (2.2) and (2.7) are the basic equations of our analysis.

Using Eq. (2.7) with Eq. (2.5), we obtain

$$g_\lambda(\mathbf{k}, \omega) = \{N_+ - N_- \exp[\hbar(\omega - \mu)/kT]\} f_\lambda(\mathbf{k}, \omega) \times [2\pi c / \omega n_\lambda(\mathbf{k}, \omega)]^2, \quad (2.8)$$

an expression for the gain characteristic in terms of the experimentally measurable fluorescence spectrum. If the absolute strength of the function  $f_\lambda(\mathbf{k}, \omega)$  is not measured directly, it can be estimated through Eq. (2.6) from the spontaneous-emission lifetime or it can be determined from a single-frequency calibration measurement of  $g_\lambda(\mathbf{k}, \omega)$  with known electronic populations  $N_\pm$ . In ground-state systems the simplest technique

<sup>18</sup> Reference 14, Eqs. (2.1) and (2.2). With  $S_{mk}^a(E)$  replaced by  $S_{mk}^e(E)$  Dexter's  $\sigma_{mk}(E = \hbar\omega)$  becomes our  $\sigma_{e\lambda}(\mathbf{k}, \omega)$ . The connection between his  $w_{mk}(E)$  and our  $f_\lambda(\mathbf{k}, \omega)$  is  $w_{mk}(E = \hbar\omega) = (2\pi\hbar)^{-1} \sum_\lambda \int d\Omega_{k\lambda} f_\lambda(\mathbf{k}, \omega)$ .

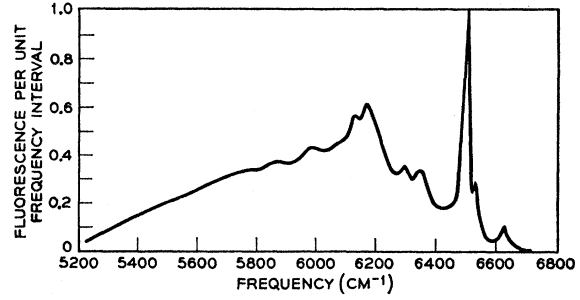


Fig. 2. Spectrum  $f_\pi(\omega)$  of  $\pi$ -polarized fluorescence in photons/sec per unit frequency interval for  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) at 77°K. The sharp peaks at 6502  $\text{cm}^{-1}$  and above derive from no-phonon or purely electronic transitions; the structure at lower frequencies derives from transitions in which lattice vibrations are simultaneously excited (phonon emission).

will usually be an unpumped ( $N_+ \approx 0$ ) absorption measurement in an electronic line strong both in emission and absorption.

Equation (2.8) applies to the simple system of Fig. 1. Systems of physical interest may have more than two important sets of metastable levels. If we indicate the various levels by Latin indices, then the appropriate generalizations of Eqs. (2.2) and (2.8) are

$$\sigma_{a\lambda}(\mathbf{k}, \omega)_{ij} = \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} \exp[\hbar(\omega - \mu_{ji})/kT] \quad (2.9)$$

and

$$g_\lambda(\mathbf{k}, \omega) = \sum_{j>i} [N_j \sigma_{e\lambda}(\mathbf{k}, \omega)_{ji} - N_i \sigma_{a\lambda}(\mathbf{k}, \omega)_{ij}] = \sum_{j>i} \{N_j - N_i \exp[\hbar(\omega - \mu_{ji})/kT]\} \times f_\lambda(\mathbf{k}, \omega)_{ji} [2\pi c / \omega n_\lambda(\mathbf{k}, \omega)]^2. \quad (2.10)$$

As before, we have assumed that within each metastable set the populations are characterized by the single-lattice temperature  $T$ . The  $\hbar\mu_{ji} = \hbar(\mu_j - \mu_i)$  are excitation potentials; the chemical potentials  $\hbar\mu_j$  are defined as in Eq. (2.3). In the general case, the experimental determination of the separate functions  $f_\lambda(\mathbf{k}, \omega)_{ji}$  may require considerable ingenuity.

The preceding results apply to phonon-terminated masers for which the lattice phonons are characterized by a single lattice temperature  $T$ . This is always the case at the maser oscillation threshold (and below) and, as we indicate in Sec. 4, usually considerably beyond that threshold. Electronic saturation is reflected in the populations  $N_i$ , which at any instant are determined by the excitation or "pumping" mechanism of the maser and by the various relaxation processes (including stimulated emission).<sup>11,19</sup>

### 3. THRESHOLD PROPERTIES OF A MASER OSCILLATOR

To indicate how the threshold properties of a phonon-terminated-maser oscillator relate to  $g_\lambda(\mathbf{k}, \omega)$ , we con-

<sup>19</sup> H. Statz and G. de Mars, in *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960), p. 530.

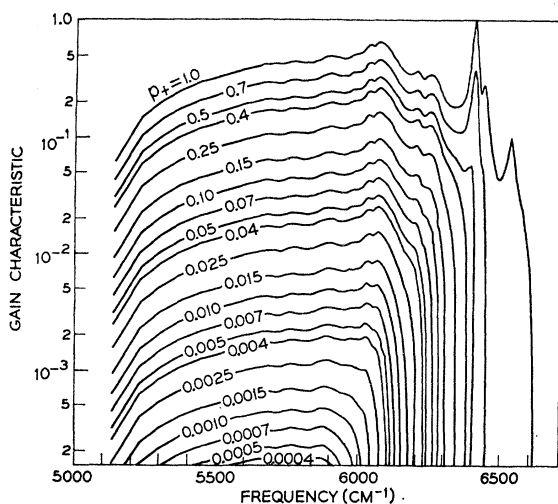


FIG. 3. Gain characteristic  $g_{\pi}(\omega)$  appropriate to the 77°K  $\pi$ -fluorescence spectrum of Fig. 2. The curves are calculated from Eq. (2.8) with  $\mu = \omega_0$  (no-phonon) = 6502  $\text{cm}^{-1}$  and for different values of the population ratio  $p_+ = N_+ / (N_+ + N_-)$ . The normalization for  $p_+ = 1.0$  is arbitrary.

sider in some detail a  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) maser similar to that constructed by Johnson *et al.*<sup>1</sup> This is a system for which the two-level model of Fig. 1 and Eq. (2.8) obtains.

We assume for our analysis that the crystal orientation is such that with polarization-selective cavity reflectors the relevant fluorescence spectrum is the  $\pi$ -polarized (electric vector parallel to the crystal axis) spectrum  $f_{\pi}(\omega)$  shown for 77°K in Fig. 2. Assuming that impurity levels other than the ground-state and excited-state maser levels are negligibly occupied (so that  $N_+ + N_-$  is constant) and that the excitation potential  $\mu$  in Eq. (2.8) equals the frequency  $\omega_0 = 6502 \text{ cm}^{-1}$  of the no-phonon line, we can use Eq. (2.8) with the spectrum of Fig. 2 to compute the gain characteristic  $g_{\pi}(\omega)$  for different values of the ratio  $p_+ \equiv N_+ / (N_+ + N_-)$ . The results are shown for the regions of positive gain on the semilog plot of Fig. 3.

If the total cavity losses (determined predominately by the reflectors at the cavity ends) are characterized for  $\pi$ -polarized radiation of frequency  $\omega$  by the function  $l_{\pi}(\omega) \geq 0$  and if  $L$  is the effective length of the gain region, then the condition for maser oscillation is nominally the condition that at some frequency

$$Lg_{\pi}(\omega) = l_{\pi}(\omega). \quad (3.1)$$

Because the gain characteristic  $g_{\pi}(\omega)$  shown in Fig. 3 is positive over an extensive frequency region, frequency-selective reflectors which have a sharp reflection maximum [minimum in  $l_{\pi}(\omega)$ ] where they are tuned can (in principle) be used to adjust the oscillation frequency over a very wide range.<sup>20</sup> Correspondingly, a suitably

<sup>20</sup> Versatile prism tuning techniques are described by A. L. Bloom, *Appl. Phys. Letters* 2, 101 (1963), and A. D. White and J. D. Rigden, *ibid.* 2, 211 (1963).

constructed phonon-terminated maser could be used as a very broadband optical amplifier.

For any given loss  $l_{\pi}(\omega)$  the electronic populations  $N_{\pm}$  will saturate under oscillation conditions at those values for which the gain characteristic  $g_{\pi}(\omega)$  just touches from below the locus  $l_{\pi}(\omega)/L$  of the effective loss per unit length. The oscillator operating frequency  $\omega_{\pi}[l_{\pi}(\omega)]$ , a functional of the effective loss  $l_{\pi}(\omega)$ , equals the frequency of the point of contact. These facts can be used to derive practical graphical techniques (to be discussed in a subsequent article) for the determination of oscillator properties from curves of  $g_{\pi}(\omega)$  and  $l_{\pi}(\omega)$ .

In the event that  $l_{\pi}(\omega) = l_{\pi}$ , a frequency-independent constant, the operating frequency of the maser is that frequency for which with suitable excitation  $p_+$  the gain characteristic has its maximum value  $g_{\pi}(\text{max}) = l_{\pi}/L$ . In Fig. 4 we have plotted this frequency  $\omega_{\pi}(\text{max})$  as a function of  $g_{\pi}(\text{max})$ . Points for this plot were obtained from plots of  $g_{\pi}(\text{max})$  versus  $p_+$  and  $\omega_{\pi}(\text{max})$  versus  $p_+$  computed from curves of the type shown in Fig. 3. Notice from Fig. 4 that, as  $g_{\pi}(\text{max})$  decreases,  $\omega_{\pi}(\text{max})$  shifts monotonically to lower frequencies.

This shift in  $\omega_{\pi}(\text{max})$  can be understood from Eq. (2.8) if we observe that  $g_{\pi}(\text{max})$  is itself a monotonically increasing function of  $p_+ = N_+ / (N_+ + N_-)$ . For  $\hbar(\mu - \omega) \gg kT$  the factor  $\exp[\hbar(\omega - \mu)/kT]$  in Eq. (2.8) is small. If in that case  $N_+ \approx N_-$ , the absorption ( $N_-$ ) term in Eq. (2.8) will be much smaller than the emission ( $N_+$ ) term. However, if  $N_+ \ll N_-$ , there two terms can be of comparable magnitude even if  $\exp[\hbar(\omega - \mu)/kT]$  is small. That is, even though the absorption in the low-frequency vibrational structure is small, the stimulated emission for  $p_+ \ll 1$  may be comparably small. As  $p_+$

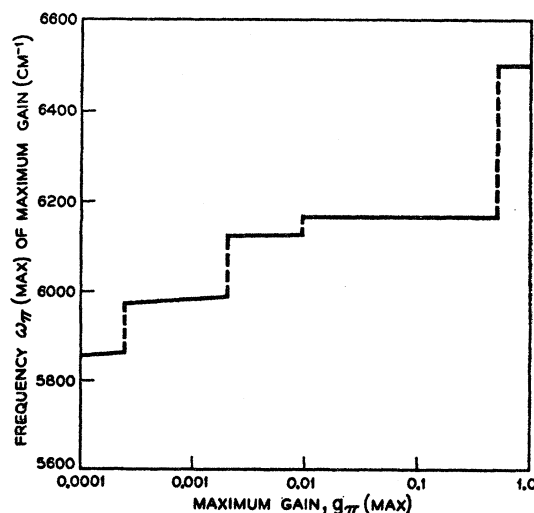


FIG. 4. Frequency  $\omega_{\pi}(\text{max})$  of maximum gain  $g_{\pi}(\text{max})$  as a function of that gain for the  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) system at 77°K for which Fig. 3 obtains. The dashed lines connect the curve at those points where the maximum gain shifts discontinuously from peak to peak in the vibrational structure or from the no-phonon line. These discontinuities gradually disappear as the sample temperature is raised and the gain characteristic becomes smoother.

decreases, the region where these weak absorption effects are significant will shift to lower frequencies. The crossover point of zero gain is the frequency  $\omega_{co} = \mu + (kT/\hbar) \ln(N_+/N_-) \rightarrow -\infty$  as  $N_+ \rightarrow 0$ . These remarks are particularly relevant to masers for which the losses ( $l_+$ ) are small, because their threshold populations  $N_+$  will also be small.

Even though the strength of the no-phonon line in Fig. 2 is greater than that of the vibrational structure, we see in Fig. 4 that the frequency of maximum gain is at the no-phonon line only for large excitations  $p_+$ . If  $\mu$  is approximately equal to the frequency of the no-phonon line, it follows from Eq. (2.8) that oscillation can occur in that line only if the electronic populations have actually been inverted ( $N_+ > N_-$ ) and then only if the peak gain ( $g_e$ ) in the electronic line with *all* ions excited ( $p_+ = 1$ ) exceeds the corresponding peak gain ( $g_v$ ) in the vibrational structure. In Table I we have indicated for different peak values ( $g_e, g_v$ ) of the totally excited ( $p_+ = 1$ ) gain and for arbitrary cavity loss per unit length  $l$  whether the maser will operate at the no-phonon line or in the vibrational structure. In making the table, we assumed that in the vibrational region of interest  $\exp[\hbar(\omega - \mu)/kT] = 0$ . The  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) system operates with  $g_e \geq g_v$  and  $g_e g_v / (2g_e - g_v) > l$ ; the well-known dilute-ruby optical maser operates with  $g_e \geq g_v$  and  $g_e g_v / (2g_e - g_v) < l$ . We believe that many more systems than those already reported will operate as phonon-terminated masers. The principal reason why such operation has not been frequently observed is that researchers have neglected broadband materials in favor of materials having sharp no-phonon lines and weak vibrational structure (high no-phonon quantum efficiency).

#### 4. PHONON SATURATION

In the preceding sections we developed a phenomenological theory based to a large extent upon the assumption

TABLE I. Nature of maser oscillation in a ground-state electronic system of the type  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) for different relative strengths of electronic line and vibrational structure.

Peak strengths <sup>a</sup>	Maser action		Population ratio at threshold <sup>b</sup>
	Electronic line	Vibration structure	
(a) $g_e < g_v$ :			
$g_v < l$	...	...	No maser action
$g_v > l$	...	x	$p_+ = l/g_v$
(b) $g_e \geq g_v$ :			
$g_e < l$	...	...	No maser action
$g_e g_v / (2g_e - g_v) > l$	...	x	$p_+ = l/g_v$
$g_e g_v / (2g_e - g_v) = l$	x	x	$p_+ = g_e / (2g_e - g_v)$
$g_e g_v / (2g_e - g_v) < l$	x	...	$p_+ = (l + g_e) / 2g_e$

<sup>a</sup> The constants  $g_e, g_v$  are, respectively, the peak values at the electronic line and in the vibrational structure of the gain characteristic with all ions excited ( $p_+ = 1$ ).

<sup>b</sup> Threshold values of  $p_+ = N_+ / (N_+ + N_-)$  are calculated from Eqs. (2.5) and (3.1) with  $\omega = \mu$  at the no-phonon line and  $\exp[\hbar(\omega - \mu)/kT] = 0$  in the vibrational structure.

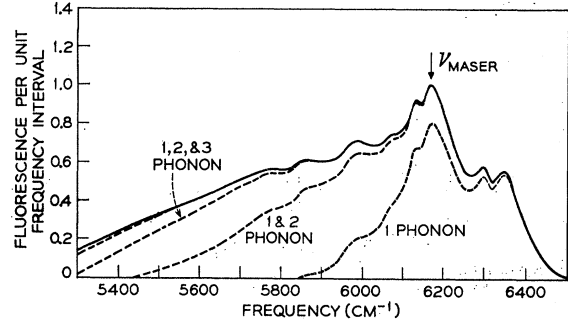


FIG. 5. Role of multiphonon processes in the vibrational structure of Fig. 2 for  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) at 77°K. The dashed curves indicate the structure that results from single-phonon processes, single plus double-phonon processes, etc. The envelope gives the measured curve of Fig. 2. The location of the maser oscillations observed by Johnson *et al.* (Ref. 1) is indicated by the heavy arrow.

tion that at any point the lattice is described by a single temperature  $T(\mathbf{r}, t)$ . In contrast, we permitted the electronic populations  $N_i$  to saturate at values different from their thermal-equilibrium values. In this and the next sections we estimate the power levels required for phonon saturation and very briefly consider the effects of such saturation on  $g_\lambda(\mathbf{k}, \omega)$ .

The vibrational structure in Fig. 2 results from those photon-emitting electronic transitions in the  $\text{Ni}^{2+}$  ion which are accompanied by the simultaneous emission (and/or absorption) of one or more lattice phonons. Using a theory of vibrational structure developed elsewhere,<sup>5</sup> we estimate that in the vibrational structure of Fig. 2 multiphonon processes have the relevance indicated in Fig. 5.<sup>21,22</sup> Notice that over a large spectral region much of the intensity derives from processes involving more than one phonon.<sup>23</sup>

If  $\omega_0$  is the frequency of the no-phonon line, the strength of the one-phonon component of  $\omega$  reflects the density of phonon modes at frequency  $|\omega - \omega_0|$ , their electronic couplings, and their average populations. More precisely, the contribution of any particular phonon mode is proportional to the population of that mode in phonon absorption and to one plus that population in phonon emission. Multiphonon contributions are proportional to convolutions of the one-phonon spectrum. At low temperatures the phonon populations

<sup>21</sup> To obtain Fig. 5, we assumed that the only energy dependence of Eq. (2.1), Ref. 14, is that explicitly shown. We then used an electronic computer to fit the spectral function  $S_{mk}(E = \hbar\omega)$  derived from that equation and Fig. 2 (compare footnote 18) to the Fourier transform of a function having the structure indicated in Eq. (1.4a), Ref. 5. The  $n$ -phonon contribution to Fig. 5 derives from the  $n$ th-order term of the power-series expansion of the last exponential in Eq. (1.4a), Ref. 5.

<sup>22</sup> The width of the no-phonon line (shown in Fig. 2 but not in Fig. 5) results principally from phonon scattering processes different from the phonon emission and absorption processes relevant to the vibrational structure. Cf. D. E. McCumber and M. D. Sturge, *J. Appl. Phys.* **34**, 1682 (1963); and D. E. McCumber, *Phys. Rev.* **133**, A163 (1964).

<sup>23</sup> Roughly, if  $\theta_D$  is the Debye temperature of the host lattice, one-phonon processes only contribute at frequencies within  $\Delta\omega = k\theta_D/\hbar$  of the no-phonon line.

are small and the spectra derive exclusively from phonon emission.

If for a fixed average lattice temperature  $T$  we wish to modify  $g_\lambda(\mathbf{k}, \omega)$  at some particular frequency  $\omega$  by modifying phonon populations, we must change the average population of all phonon modes which significantly contribute to the fluorescence  $f_\lambda(\mathbf{k}, \omega)$  at  $\omega$ . For the one-phonon fluorescence the density of such phonons depends primarily upon the density of strongly coupled phonon modes at  $|\omega - \omega_0|$  and upon the phonon linewidth. For the multiphonon components many different regions of the one-phonon spectrum contribute at any given multiphonon frequency. As a consequence the multiphonon components are generally much more difficult to saturate than is the one-phonon fluorescence. An exception occurs when the one-phonon spectrum is very sharply peaked at a particular optical-phonon band. In that case the multiphonon components display similar but slightly broadened peaks which are superimposed upon a broad unsaturable background and which sample a limited region of the one-phonon spectrum near the sharp peak.<sup>3</sup>

In what follows we consider a maser which operates at a peak in the gain curve associated exclusively with the emission of single phonons from a sharp optical-phonon band.<sup>24</sup> The resulting estimate of the power level required for significant phonon saturation will approximately apply to sharp peaks in the multiphonon fluorescence, but it will considerably underestimate the power level required to saturate the smooth multiphonon background.

To determine the conditions for phonon saturation, we must first determine the number of phonon modes which contribute significantly to the one-phonon gain characteristic at the maser frequency. Because the width of the maser line is negligible in comparison with the phonon linewidths, the number of coupled modes is roughly equal to the number of phonon modes whose frequencies lie within a phonon half-width of the maser frequency. For the reasons we indicate below the volume density  $n_c$  of such coupled modes can be adequately approximated either by the volume density  $n_i$  of impurity ions or by  $n_u/Q_{pn}$ , the volume density  $n_u$  of unit cells divided by the phonon quality factor  $Q_{pn}$ . The first estimate ( $n_c \approx n_i$ ) obtains in lightly doped materials if the lattice vibrations of interest are completely localized at the impurity sites.<sup>25</sup> In that case there will be one significantly coupled mode from each site; the modes from different sites will have identical frequencies. If the impurity density is high or if the

relevant phonons are not localized but extend over many sites as in an ordinary optical band, an accurate estimate of  $n_c$  would involve the ratio of the phonon line width to the width of the optical band. A lower bound on  $n_c$  may be obtained without this detailed information if we assume that the phonons at frequency  $\omega_{pn}$  have widths  $\omega_{pn}/Q_{pn}$  and that the mode density is greater than would obtain if the optical-band modes ( $n_u$  in number) are uniformly spread over the full frequency range  $0 \leq \omega \leq \omega_{pn}$ .<sup>24</sup> With these assumptions it follows that  $n_c > n_u/Q_{pn}$ . In  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) with  $Q_{pn} \lesssim 10^3$  these two estimates of  $n_c$  are not significantly different because  $n_i = 2.9 \times 10^{20}$  ions/cc and  $n_u = 1.45 \times 10^{22}$  cells/cc.

Phonon saturation will be important when the volume density  $n_{pn}$  of maser-generated optical phonons is greater than or comparable to the density  $n_c$  of coupled phonon modes—that is, when  $\tilde{n} \equiv n_{pn}/n_c \gtrsim 1$ . Let  $n_{pt}$  be the volume density of maser photons within the maser cavity. Let  $(\tau_{pn}, \tau_{pt})$ ,  $(\omega_{pn}, \omega_{pt})$ , and  $(Q_{pn}, Q_{pt})$  be respectively the (phonon, photon) cavity lifetimes, angular frequencies, and cavity quality factors. If one phonon is generated for each maser photon, the volume density  $n_{pn}$  of maser-generated phonons will be

$$n_{pn} = \frac{\tau_{pn}}{\tau_{pt}} n_{pt} = \frac{Q_{pn} \omega_{pt}}{Q_{pt} \omega_{pn}} n_{pt}. \quad (4.2)$$

If  $\mathcal{T}$  is the fraction of incident power transmitted by one of the end reflectors of the optical cavity, if  $P$  is the power output through that reflector in watts, and if  $A$  is the cross-sectional area of the output beam in  $\text{cm}^2$ , then the volume density  $n_{pt}$  of maser photons within the cavity is

$$n_{pt} = 2 \times 10^7 P / (A \mathcal{T} c \hbar \omega_{pt}). \quad (4.3)$$

Using this expression with Eq. (4.2), we find that in terms of the maser output power the saturation parameter  $\tilde{n} \equiv n_{pn}/n_c$

$$\tilde{n} = \frac{3.36 \times 10^{12} Q_{pn} P}{n_c Q_{pt} \mathcal{T} \hat{\nu}_{pn} A}, \quad (4.4)$$

where  $\hat{\nu}_{pn} = \omega_{pn}/2\pi c$  is the phonon frequency in wave numbers ( $\text{cm}^{-1}$ ).

Using Eq. (4.4), we may estimate the power output  $P/A$  in  $\text{W}/\text{cm}^2$  required from the  $\text{MgF}_2:\text{Ni}^{2+}$  (1%) maser in order that  $\tilde{n} = 1$ . To a sufficient accuracy we take  $\mathcal{T} = 0.01$ ,  $Q_{pt} = 10^5$ ,  $\hat{\nu}_{pn} = 340 \text{ cm}^{-1}$ , and  $n_c = n_i = 2.9 \times 10^{20} \text{ cm}^{-3}$ . Under favorable circumstances  $Q_{pn}$  might be as high as  $10^3$ .<sup>26</sup> These numbers give  $\tilde{n} = 1$  when  $P/A = 3 \times 10^{10} \text{ W}/\text{cm}^2$ , an extremely large power output. We conclude that the shape of the gain curve will not be modified by phonon saturation at the usual power levels of maser operation.

## 5. EFFECTS OF PHONON BUILD-UP ON MASER ACTION

Although the remarks of the preceding section preclude phonon saturation under ordinary circumstances,

<sup>26</sup> P. G. Klemens, *Phys. Rev.* **122**, 443 (1961).

<sup>24</sup> Phonon bottlenecks in microwave systems are associated with long-lived low-frequency acoustic phonons in an energy region where the density of phonon states is low. In the optical-maser systems of interest here such phonons will never be important. The peaks in the vibrational structure derive from higher energy regions of the phonon spectrum for which the density of states is high.

<sup>25</sup> A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), Chap. 5, especially Secs. 5 and 6.

it is conceivable that under very special circumstances (for which  $Q_{pn}$  is abnormally high and  $\omega_{pn}$  low) phonon saturation might be important. In this section we briefly consider how phonon build-up affects the gain characteristic.

For simplicity we assume that the fluorescence spectrum consists exclusively of sharp lines which for a given impurity ion derive from  $m$ -phonon ( $m \geq 0$ ) processes involving a single frequency- $\tilde{\omega}$  mode of lattice vibration localized at the impurity.<sup>25</sup> Such local modes would be expected to interact strongly with the impurity ion and potentially to have the high  $Q$ 's necessary for saturation.<sup>26</sup> We also assume that the populations of these modes are described by a canonical ensemble at a temperature  $\bar{T}$  different from the average lattice temperature  $T$  and related to the average local-mode population  $\bar{n}$  by

$$\bar{n} = [\exp(\hbar\omega/k\bar{T}) - 1]^{-1}. \quad (5.1)$$

Equations (2.8) and (2.10) still obtain if we replace  $T$  by  $\bar{T}$ .

Because  $f_\lambda(\mathbf{k}, \omega)_{ji} \geq 0$  in Eq. (2.10), the sign of  $g_\lambda(\mathbf{k}, \omega)$  at any particular (relevant) frequency is determined by the signs of the factors

$$S(\omega)_{ji} = \{N_j - N_i \exp[\hbar(\omega - \mu_{ji})/kT]\}, \quad j > i. \quad (5.2)$$

If for some reason the average local-mode population  $\bar{n}$  increases to a value much greater than unity, the effective temperature  $\bar{T}$  will increase correspondingly:

$$\bar{T} = \bar{n} \frac{\hbar\omega}{k} \left\{ 1 + \frac{1}{2\bar{n}} - \frac{1}{12\bar{n}^2} + \dots \right\}. \quad (5.3)$$

It follows that in the limit of large  $\bar{n}$

$$S(\omega)_{ji} = N_j - N_i - N_i \frac{(\omega - \mu_{ji})}{\bar{n}\omega} \left\{ 1 - \frac{1}{2\bar{n}} + \dots \right\} \rightarrow N_j - N_i. \quad (5.4)$$

It is a general result that in the limit of high-phonon temperatures (or, equivalently, large average populations) the sign of the gain is determined by the electronic population inversions  $\{N_j - N_i\}$ . At lower temperatures the factor  $\exp[\hbar(\omega - \mu_{ji})/kT]$  in Eq. (2.10) reduces the absorption in the low-frequency vibrational tail<sup>27</sup> ( $\omega < \mu_{ji}$ ) so that in that tail the maser operates as an excited-state system even though at the no-phonon electronic line it might operate as a ground-state system.<sup>28</sup>

<sup>27</sup> A "cold" lattice cannot supply the energy deficit ( $\mu_{ji} - \omega$ ) for a low-frequency photon ( $\omega < \mu_{ji}$ ) to excite the electronic state  $j$  from the state  $i$ . In a "hot" lattice numerous phonons are available to supply the required energy.

<sup>28</sup> By a "ground-state system" we mean a maser for which the terminal electronic state is the ground state (or a thermally populated state near the ground state) of the impurity ion. An "excited-state system" is one for which the terminal state lies appreciably above the ground state and is not ordinarily populated. (In the literature these are sometimes called three-level and four-level systems, respectively. The "extra" level is an auxiliary level used in the excitation process.)

It remains to briefly consider the effect on maser action of an increase in phonon temperature when the electronic populations are actually inverted. There are two cases to consider, the case of allowed transitions in which the vibrational structure borrows its intensity from the no-phonon line and the case of vibrationally assisted transitions in which the vibrational structure borrows its intensity from distant electronic states.<sup>4-7</sup> (In the latter case the no-phonon line is not enhanced.) In the former case phonons typically mix and shift closely spaced electronic states belonging to the same multiplet; in the latter case phonons mix distant "allowed" states into the original "forbidden" or "weakly allowed" electronic state. Selection rules can sometimes prevent the same phonon from taking part in both mechanisms.

Of these two cases the first is theoretically more tractable.<sup>4-6</sup> Increasing the phonon temperature  $\bar{T}$  will increase the strength of high-order multiphonon components and thereby spread the spectrum over a greater frequency range. Because the phonon interactions do not modify the total integrated intensity of the spectrum, there will be a compensating decrease in the peak intensity of lines involving only a few or no phonons. Since the maser presumably was initially operating on a strong "few phonon" line, we conclude that maser action will be *impeded* by a population build-up in those phonon modes whose associated vibrational structure borrows its spectral intensity from the no-phonon line.

Vibrational structure which derives its spectral intensity from distant electronic states is difficult to treat in detail when the phonon temperature (or effective coupling strength) is high. However, from the low-order results which have been derived,<sup>6,7</sup> we conclude that up to moderately large populations, an increase in phonon population will *enhance* maser operation by increasing the phonon-induced coupling to the "allowed" electronic states and by increasing thereby the gain at operating frequencies in the vibrational structure. This enhancement will be most apparent in systems for which selection rules either preclude a no-phonon line or prohibit these same phonons from generating vibrational structure which borrows its intensity from the no-phonon line.

## 6. DISCUSSION AND CONCLUSIONS

A simple dielectric model based upon a broadband gain characteristic  $g_\lambda(\mathbf{k}, \omega)$  is sufficient to describe the operating properties of phonon-terminated masers of the type reported by Johnson, Dietz, and Guggenheim.<sup>1</sup> The function  $g_\lambda(\mathbf{k}, \omega)$  depends upon populations of metastable electronic levels and upon the temperature or temperatures describing lattice vibrations. Ordinarily phonon saturation is not important, and a single-lattice temperature is sufficient. In that case the gain characteristic can be related to observable fluorescence and absorption spectra through the equations of Sec. 2.

For most systems prohibitively high operating power levels are required to modify the gain characteristic by phonon saturation. In those exceptional systems where phonon  $Q$ 's might be high enough to permit saturation at reasonable power levels, increases in phonon populations tend to transform the phonon-terminated maser into a ground-state maser. Depending upon whether the particular phonons are such that their vibrational structure borrows its intensity from distant electronic states or from the no-phonon line and provided the electronic populations are actually inverted, increases in phonon population can increase or decrease the

amplitude of the gain characteristic at the operating frequency. Systems of both types will be very interesting to study, if it should prove possible to locate materials with saturable phonons.

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### Ground-State Occupancy of an Ideal Bose-Einstein Gas Confined to a Finite Volume\*

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The number of particles in the ground state has been computed as a function of temperature for an ideal Bose-Einstein gas confined to a box of finite volume by evaluating the discrete sum over states on a computer. Large deviations from London's bulk-gas result are found when the length of the box is much greater than its width for the range of dimensions investigated here. It is shown that the deviations occur because in this limit the system tends to behave like a one-dimensional system.

#### I. INTRODUCTION

IT has been suggested<sup>1</sup> that the superfluid properties of liquid He<sup>4</sup> may be qualitatively understood by treating the fluid as a gas of noninteracting bosons. In the ideal-gas approximation the superfluid component is assumed to consist of the particles in the ground state, which is macroscopically occupied for temperatures below a critical temperature  $T_c$ .

Measurements of the temperature of the lambda point  $T_\lambda$  of liquid He<sup>4</sup> confined to fine pores have been performed.<sup>2</sup> A severe depression of  $T_\lambda$  was observed when the fluid was confined to pores of 40–50 Å diameter. In one case  $T_\lambda$  was depressed from the bulk value of 2.18–1.36°K in a sample consisting of pores of diameter 43 Å.

We have calculated the number of particles in the ground state as a function of temperature for an ideal Bose-Einstein gas confined to a container of width  $D$  and length  $L$ , where  $L$  ranges from 200–5000 Å and  $D$  is in the range of 10–100 Å in order to see if the ideal Bose-Einstein gas model is able to offer a qualitative understanding of the above mentioned depression of  $T_\lambda$ .

#### II. GENERAL DISCUSSION

Consider a system of  $n$  noninteracting bosons of spin zero and mass  $m$ . We assume the particles are confined to a box of length  $L$  and square cross section, where  $D$  is the length of a side of the square. The allowed single-particle energy levels are

$$E_{n_1 n_2 n_3} = \frac{\hbar^2}{2m} \left[ \left( \frac{n_1 \pi}{D} \right)^2 + \left( \frac{n_2 \pi}{D} \right)^2 + \left( \frac{n_3 \pi}{L} \right)^2 \right],$$

where  $n_1$ ,  $n_2$  and  $n_3$  range over the positive integers. The mean number of particles in the state  $(n_1, n_2, n_3)$  is

$$N_{n_1 n_2 n_3} = \left[ \exp \left( \frac{E_{n_1 n_2 n_3} - \mu}{kT} \right) - 1 \right]^{-1},$$

where  $\mu$  is the chemical potential,  $k$  is Boltzmann's constant and  $T$  is the temperature in degrees Kelvin. The chemical potential  $\mu$  is determined from

$$N = \sum_{n_1, n_2, n_3=1}^{\infty} N_{n_1 n_2 n_3} = \sum_{n_1, n_2, n_3=1}^{\infty} \left[ \exp \left( \frac{E_{n_1 n_2 n_3} - \mu}{kT} \right) - 1 \right]^{-1}. \quad (1)$$

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<sup>1</sup> F. London, *Phys. Rev.* **54**, 947 (1938).

<sup>2</sup> K. R. Atkins, H. Seki, and E. U. Condon, *Phys. Rev.* **102**, 582 (1956).