Discontinuity of vibrational and translational temperatures in a system with fast-particle sources

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The possibility of separating the vibrational and translational temperatures from each other by disturbing the Maxwellian velocity distribution in the far energy region is discussed for a system consisting of a small admixture of heavy diatomic molecules (harmonic oscillators constituting a small impurity in a light gas). It is shown that a fast-particle source which produces particles with energies E_0 [$\exp(-E_0/kT) \ll 1$, $E_0 > \hbar\omega$] is capable of producing a finite deviation of the vibrational temperature from the translational temperature.

Modern molecular lasers based on vibrational-rotational transitions operate under substantially nonequilibrium conditions, when the translational and vibrational temperatures are "broken." Such a break is achieved either as a result of pumping into the vibrational degrees of freedom (in a discharge or during a chemical reaction), or as a result of chilling the translational degrees of freedom (gas-dynamical method). In thd present paper we propose to use for the realization of the separation of the temperatures a new method based on the perturbation of the Maxwellian distribution over the translational degrees of freedom in the far energy region[1,2]. The physical mechanism underlying the formation of the gap between the vibrational and translational temperatures in a gaseous molecular system with a non-Maxwellian distribution consists in the following. Under equilibrium conditions, a Maxwellian distribution over the translational degrees of freedom leads to the formation of an equilibrium Boltzmann distribution with a vibrational temperature equal to the temperature of the translational motion (the gas temperature). There is then established a dynamical equilibrium, i.e., the energy flux from the translational into the vibrational degrees of freedom due to activating collisions is equal to the reverse flux from the vibrational into the translational degrees of freedom caused by deactivating collisions. Practically all the molecules can participate in deactivating collisions, while only the molecules whose relative kinetic energy is higher than the activation energy (e.g., the energy of the vibrational quantum) can participate in activating collisions. At low gas temperatures, only the "tail" of the Maxwellian distribution participates in the activation. Let us suppose that we have by some means violated the Maxwellian distribution at the tail. In itself, this violation may be insignificant, since the tail of the distribution contains a small fraction of the total number of particles and, therefore, finite perturbations at the tail of the distribution curve will practically not change the mean translational-energy reserve and the distribution in the vicinity of the mean thermal velocity, i.e., they will not change the translational temperature and the mean energy flux due to the deactivating collisions. However, finite perturbations at the "tail" of the distribution will lead to finite variations in the energy flux getting into the vibrational degrees of freedom as a result of the increase in the number of activating collisions. To the dynamical equilibrium in this case will correspond conditions under which the vibrational temperature is higher than the gas temperature. We can form by such means a gap between the vibrational and gas temperatures. Let us estimate the order of magnitude of this gap.

Let us, for simplicity, consider a mixture consisting of a small admixture of heavy diatomic molecules (mass M) in a constant-temperature bath formed by a light gas (molecular mass m) in which the same sort of particles are produced. The vibrational relaxation of the heavy diatomic molecules, which will henceforth be regarded as harmonic oscillators, is described by equations of the form[3]

$$\frac{dx_n}{dt} = ZP_{10}\left\{(n+1)x_{n+1} - \left[(n+1)\frac{P_{01}}{P_{10}} + n\right]x_n + n\frac{P_{01}}{P_{10}}x_{n-1}\right\}, \quad n = 0, 1, 2, \ldots, \tag{1}$$

where x_n is the population per unit volume of the n-th vibrational level of the molecules, Z is the number of collisions per unit time of a molecule M with the surrounding atoms m,

$$P_{ij}(T) = \int_0^\infty p_{ij}(v) f(v) v\, dv \Big/ \int_0^\infty f(v) v\, dv \tag{2}$$

is the probability of a vibrational transition (i → j) in one collision, and f(v) is the velocity distribution function for the particles of the constant-temperature bath. If a fast-particle source operates in the system, then the velocity distribution f(v) of the particles will not be Maxwellian. The distributions f(v) in such systems have been thoroughly studied in[4]. If by change the fast-particle source produces the same type of particles as the atoms of the constant-temperature bath, then the distribution f(v) has the form

$$\begin{aligned} f_-(x)\,dx &= [\rho + J(x)(x - {}^3/_2)]f^0(x)\,dx + \tilde{N}\tau_0\delta(x - x_0)\,dx, \quad x \leqslant x_0, \\ f_+(x)\,dx &= [\rho + J(x_0)(x - {}^3/_2)]f^0(x)\,dx + \tilde{N}\tau_0\delta(x - x_0)\,dx, \quad x > x_0, \end{aligned} \tag{3}$$

where $x = mv^2/2kT$, $x_0 = E_0/kT$; $\tilde{N}$, m, and E_0 are respectively the number, mass, and energy of the particles produced by the source in a unit volume per unit time, ρ is the particle-number density of the monatomic gas, $f^0(x)$ is the Maxwellian distribution normalized to unity, and τ_0 is the mean free time of a particle with energy E_0 in the monatomic gas.

The distribution (3) was obtained for δ-function sources that produce particles with energy E_0. The distribution of the sources in the system is assumed to be isotropic. The above-described distribution differs from the Maxwellian distribution by the presence of a δ-function correction and of a term proportional to J(x), where

$$J(x) = \rho\beta\left(\frac{8}{e}\right)^{1/2}\left(x - \frac{3}{2}\right)\int_\eta^{x+1/2} \frac{e^t}{(t^2 - 2t)^2}\, dt.$$

In J(x), the quantity β is the dimensionless power of the source ($\beta = \tilde{N}\tau_0/\rho$) and is assumed to be small ($\beta \ll 1$) in deriving (2). The constant η is chosen from the condition $(\eta^2 - 2\eta)^2 \sim 1$[4].

If the energy of the particles produced by the source is less than the vibrational quantum energy ($E_0 < \hbar\omega$) (this case was first considered in[3,4]), then, as has been shown in[1,2], the vibrational temperature will differ insignificantly from the translational temperature. The reason for this is that the δ-function source appreciably disturbs the equilibrium distribution function in the energy region $E < E_0$, while the number of fast particles (with energy $E > \hbar\omega$) participating in the oscillation excitation is relatively small and rapidly decreases (according to an exponential law) with increasing energy. In this connection, it is advisable to consider another case: $E_0 > \hbar\omega$.

Let us assume that the source strength is such that the vibrational relaxation time $\tau_{VT} \sim 1/ZP_{10}$ turns out to be considerably shorter than the characteristic time $\tau_S \sim \rho/\tilde{N}$ of the source, i.e., $\tau_{VT} \ll \tau_S$. In this case in the time scale t satisfying the condition $T_{VT} \ll t \ll \tau_S$, we can assume that the vibrational relaxation is complete at each moment of time and consider at that same moment of time the quasi-stationary, vibrational-energy distribution, determined by the translational-energy distribution.

This distribution is obtained from the Eqs. (1), in which the derivatives dx_n/dt for the instants $t \gg \tau_{VT}$ can be assumed to be equal to zero (a condition signifying the completion of the vibrational relaxation). The distribution has the form

$$x_n / x_{n-1} = P_{01}(T) / P_{10}(T). \tag{4}$$

The probabilities $P_{ij}(T)$ are determined from the general formula (2). Let us change in (2) from integration with respect to velocity to integration with respect to the dimensionless energy $x = mv^2/2kT$ and substitute into it the distribution f(v) in the form (3). We obtain in that case

$$P_{10}(T) = P_{10}^{(0)}(T) + M_{10} + \frac{1}{\xi}\int_0^{\hbar\omega/kT} J(x)\left(x - \frac{3}{2}\right) f^0(x)\, p_{10}(Ax^{1/2})\, Ax^{1/2}dx$$
$$+ \frac{1}{\xi}\, p_{10}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0, \tag{5}$$

$$P_{01}(T) = P_{01}^{(0)}(T) + M_{01} + \frac{1}{\xi}\, p_{01}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0.$$

In the relations (5), $P_{ij}^{(0)}(T)$ are the probabilities $p_{ij}(v)$ averaged over the Maxwellian distribution $f^{(0)}(x)$,

$$\xi = \int_0^\infty v f(v)\, dv, \qquad A = (2kT/m)^{1/2},$$

$$M_{ik} = \frac{1}{\xi}\Big[\int_{\hbar\omega/kT}^{x_0} J(x)\left(x - \frac{3}{2}\right) f^0(x)\, p_{ik}(Ax^{1/2})\, Ax^{1/2}dx$$
$$+ \int_{x_0}^{\infty} J(x_0)\left(x - \frac{3}{2}\right) f^0(x)\, p_{ik}(Ax^{1/2})\, Ax^{1/2}dx\Big].$$

For the relations $P_{01}(T)/P_{10}(T)$, we have from (5)

$$\frac{P_{01}(T)}{P_{10}(T)} = \frac{P_{01}^{(0)}(T)}{P_{10}^{(0)}(T)}\,\frac{1 + \mathcal{A}}{1 + e^{-\hbar\omega/kT}(\mathcal{A} + \mathcal{B})} \approx e^{-\hbar\omega/kT}\mathcal{A} \equiv e^{-\hbar\omega/kT}(1 + \eta);$$
$$\mathcal{A} = 1 + \frac{M_{01} + \xi^{-1}p_{01}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0}{P_{01}^{(0)}(T)}, \tag{6}$$
$$\mathcal{B} = \frac{1}{P_{01}^{(0)}(T)\,\xi}\int_0^{\hbar\omega/kT} J(x)\left(x - \frac{3}{2}\right) f^0(x)\, p_{10}(Ax^{1/2})\, Ax^{1/2}dx.$$

In writing down (6), we used the detailed-balancing equation and took account of the fact that the second term in the denominator is small.

Let us estimate the order of magnitude of η under the condition that $E_0 > \hbar\omega$. The probabilities $p_{ik}(v)$ entering into (5) and (6) are usually computed in the semiclassical approximation and have the form[3,5]

$$p_{ik}(v) = \frac{\mu}{m}\,\frac{8\pi^2\omega\lambda^2\mu}{\hbar\alpha^2}\, e^{-a/x^{1/2}}\,\mathscr{E}_\pm(x),$$
$$\mathscr{E}_\pm(x) = \exp\left\{\pm\frac{\pi\omega}{\alpha m}\,\frac{\hbar\omega}{A^3x^{3/2}}\right\}, \tag{7}$$

where $a = 2\pi\omega/\alpha A$, α is the parameter of the exponential intermolecular-interaction potential, having the form $V(r) \sim e^{-\alpha r}$. The quantity α is, as a rule, not known exactly. Below we shall take the approximate value[3] $\alpha \approx (2 - 5) \times 10^8\ \text{cm}^{-1}$.

The dependence on $x = v^2/A^2$ of the second exponential factor $\mathscr{E}_\pm$ in the expression (7) for the $p_{ik}(Ax^{1/2})$ is weak and, therefore, in evaluating the integrals containing the $p_{ik}(Ax^{1/2})$, we can take this factor outside the integral sign, taking its value at the "midway" points ($\bar{x}$ and $\bar{\bar{x}}$). Taking account of the foregoing, we can write

$$M_{01} \approx \xi^{-1}\mathscr{E}_-(\bar{x}_0)\, w_1 + \xi^{-1}\mathscr{E}_-(\bar{\bar{x}}_0)\, w_2,$$
$$\xi^{-1}p_{01}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0 \approx \xi^{-1}\mathscr{E}_-(x_0)\, w_3. \tag{8}$$

In (8), we have introduced the following notations:

$$w_1 = \int_{\hbar\omega/kT}^{x_0} J(x)(x - {}^3/_2) f^0(x)\, p_{01}^{(0)}(Ax^{1/2})\, Ax^{1/2}dx,$$
$$w_2 = \int_{x_0}^{\infty} J(x_0)(x - {}^3/_2) f^0(x)\, p_{01}^{(0)}(Ax^{1/2})\, Ax^{1/2}dx, \tag{9}$$
$$w_3 = p_{01}^{(0)}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0.$$

The numerical estimate of η requires the computation of w_i, where i = 1, 2, 3. Let us consider a CO − He mixture, assuming (see[6]) that $\hbar\omega_{CO}/kT \sim 10$. The choice of $x_0 = E_0/kT$ is specified, first, by the condition $E_0 > \hbar\omega$, which yields $x_0 > 10$, and, secondly, by the condition of adiabaticity of the collisions: $v < 2\pi\omega/\alpha$. Choosing $x_0 \approx 100$, we satisfy (as can easily be verified) both requirements and therefore have a right to use for $x \sim 100$ the semiclassical expressions (7) for the probabilities. For the quantity a defined in (7), we choose $a \approx 60$. It should be noted that because of the uncertainty about α, the quantity a is also indeterminate and, depending on the choice of α, it can vary from ~ 30 to ~ 80 (at 200–400°K); the choice $a \approx 80$ can then change the final estimate for η by an order of magnitude.

Taking account of the fact that $x_0 \approx 100$, $\hbar\omega/kT \approx 10$, and $a \approx 60$, we can, by integrating (9), easily obtain the following relations between the w_i's:

$$w_3 \approx 5{,}5 \cdot 10^3 w_1, \quad w_1 \gg w_2; \qquad w_1 = \frac{\mu}{m}\,\frac{8\pi^2\omega\lambda^2\mu}{\hbar\alpha^2}\,\frac{\tilde{N}}{\rho d^2}\,\frac{1}{\pi\sqrt{e}} \cdot 9.7 \cdot 10^{-6}. \tag{10}$$

Since the values of the exponential factors in (8) do not differ very much from unity, we can infer from (10) the validity of the following expression for η defined in (6):

$$\eta = \frac{p_{01}(Ax_0^{1/2})\, Ax_0^{1/2}\tilde{N}\tau_0}{\xi P_{01}^{(0)}(T)} \approx \frac{w_1}{\xi P_{01}^{(0)}(T)} \cdot 4.9 \cdot 10^3. \tag{11}$$

For $\mathcal{E}$, we have in order of magnitude

$$\xi = \int_0^\infty v f(v)\, dv \sim (1 - 2)\rho A/2\sqrt{\pi}.$$

If we take account of the fact that for CO − He collisions

$$\frac{\mu}{m}\,\frac{8\pi^2\omega\lambda^2\mu}{\hbar\alpha^2} \sim (46 - 290),$$

then after substituting these values into (11), we obtain

$$\eta \approx \frac{\tilde{N}}{\rho^2 d^2}\,\frac{1}{AP_{01}^{(0)}(T)} \cdot (0.75 - 4.75),$$

where d is the particle diameter (in the hard-sphere model[4]). The condition $\tau_{VT} \ll \tau_S$ allows us to write $\tilde{N}/\rho^2 d^2 \ll AP_{10}(T)\sqrt{8\pi}$. For the estimates, let us take $\tau_{VT}/\tau_S \sim 10^{-2}$. Then $\eta \approx e^{+\hbar\omega/kT}(0.04-0.24)$. In that case it follows from (4) that

$$x_n / x_{n-1} \sim (0.04 \div 0.24). \tag{12}$$

Such relative-population values for CO correspond to a vibrational temperature $T_{vib} \sim 1000-3000°K$ (at gas temperatures of $\sim 200-400°K$). It should be noted that when the distirbution in the constant-temperature bath is Maxwellian, the relative CO populations at the same gas temperatures are given by $x_n/x_{n-1} = e^{-\hbar\omega/kT} \sim 10^{-5}$.

It is worth estimating the source strength $\tilde{N}$ necessary for the observation of the indicated effect. If we assume the gas pressure to be equal to 10 Torr, then we have for the density ρ_0 (at 250°K) the value $\rho_0 \approx 3.9 \times 10^{17}\ \text{cm}^{-3}$. The collision rate Z at such densities is $Z \approx 2.8 \times 10^7\ \text{sec}^{-1}$. In order for the requirement $\tau_{VT} \sim 10^{-2}\tau_S$ to be fulfilled, it is necessary to impose on $\tilde{N}$ the condition $\tilde{N} \sim 10^{-2}\ \rho_0 Z P_{10}$. The latter yields for $\tilde{N}$ the following estimate: $\tilde{N} \sim 10^{15}\ \text{cm}^{-3} \times \text{sec}^{-1}$ (for $P_{10} \sim 10^{-7}$).

Thus, in a system with a δ-function fast-particle source (for which $E_0 > \hbar\omega$) there gets established a quasistationary vibrational-energy distribution, which (for harmonic oscillators) corresponds to a vibrational temperature considerably exceeding the temperature of the translational degrees of freedom.

Two possible applications of the obtained results can be pointed out. The first one is the control of chemical reactions. If the chemical reactions proceed with the participation of vibrationally excited molecules, then we can, by varying the fast-particle source strength, vary the vibrational temperature and, consequently, the reaction rate. Secondly, it can be employed as one of the methods for bringing about partial vibrational-rotational population inversion. Although the relative population values obtained in (12) above are not yet sufficient for the realization of generation in CO[7], the above-described temperature separation mechanism can nevertheless be recommended as a method for pumping the vibrational degrees of freedom in conjunction with other known methods.

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