

If we now calculate the rate of change of the mean energy of the oscillators [by multiplying the i th equation in (4) by i and summing], we find that the terms involving transfer of vibrational energy from one oscillator to another contribute nothing, and we obtain a simple linear differential equation for the relaxation of the mean energy;

$$d\langle\epsilon\rangle/d\tau = s e^{-\theta} - (1 - e^{-\theta}) \langle\epsilon\rangle, \quad (5)$$

where $\tau = aMt$ and $\langle\epsilon\rangle = \sum_{i=0}^{\infty} i A_i$. The solution to this equation is

$$\langle\epsilon\rangle = [s e^{-\theta} / (1 - e^{-\theta})] \{1 - \exp[-(1 - e^{-\theta})\tau]\} + \langle\epsilon_0\rangle \exp[-(1 - e^{-\theta})\tau], \quad (6)$$

where $\langle\epsilon_0\rangle$ is the initial mean energy. This result is a simple extension of Montroll and Shuler's⁶ Eq. (1.18), and is a special case of a problem discussed in reference 1(c).

We may readily investigate the case in which interaction with the heat-bath molecules M can be ignored, so that $\langle\epsilon\rangle(t) = \langle\epsilon_0\rangle$. Noting that $\sum_{j=0}^{\infty} j A_j = \langle\epsilon\rangle$ and that $\sum_{j=0}^{\infty} A_j = 1$ (assuming unit total concentration of A), we obtain from Eq. (4) the following result:

$$dA_i/dt = \alpha \langle\epsilon_0\rangle + s \left\{ (i+1) A_{i+1} + (i+s-1) \times \frac{\langle\epsilon_0\rangle}{\langle\epsilon_0\rangle + s} A_{i-1} - \left[i + (i+s) \frac{\langle\epsilon_0\rangle}{\langle\epsilon_0\rangle + s} \right] A_i \right\}. \quad (7)$$

This is identical in form to the equation obtained^{1k} describing the relaxation of $[s]$ oscillators in contact with a heat bath at a temperature defined by $e^{-\theta} = \langle\epsilon_0\rangle / (\langle\epsilon_0\rangle + s)$. The equations can be solved in exactly the same way as was used in reference 1(k), a method used earlier by Montroll and Shuler.⁶

One may then take expression (6) for $\langle\epsilon\rangle$, substitute it for $\langle\epsilon_0\rangle$ in Eq. (7), and then substitute the right-hand side of this result in Eqs. (4) in place of the four summations. This converts (4) into a system of first-order, homogeneous, linear differential equations. Unfortunately, the coefficients depend on the time in a moderately complex way, so that this linearization of the nonlinear problem does not lead to simpler machine computation than would result from using Eqs. (4) as is.

Equations (4) were therefore programmed for numerical integration by the Heun-Euler method,⁷ and the various examples were computed. As checks on rounding off and truncation errors, we computed $\sum_i A_i$, which should be unity, and $\sum_i i A_i$, which was then compared with the value of the energy computed by Eq. (6). These results enabled us to determine how

small we needed to make the time intervals Δt in the numerical integration, and how many levels we needed to include to avoid having molecules "piling up" at the top level during the relaxation; inspection of the A_i also was used to avoid this last source of error.

One other point must be made before discussing our results. One can readily verify that substitution of

$$(1 - e^{-\theta})^{s-1} g_s(i) e^{-i\theta}, \quad g_s(i) = (i+s-1)! / (s-1)! i!,$$

for A_i (with similar expressions for A_j , etc.) causes the four summations in Eqs. (4) to cancel out identically, no matter what value of θ is used. Therefore, after the distribution A_i has once become of Boltzmann type, the system will continue to relax to equilibrium through a series of Boltzmann distributions in exactly the same way as does a similar system in which the only mode of energy transfer is to and from the heat bath. This latter problem has been studied in detail.^{1k,6} It was therefore necessary for us to carry out our integrations only until a Boltzmann distribution (at a temperature generally quite different from that of the heat bath) was reached; the remainder of the relaxation could yield nothing not already understood.

The calculation above of the mean energy of the system showed that the transfer of quanta among the molecules of interest had no effect on the relaxation of the mean energy. As one would expect, however, the mean-square energy $\langle\epsilon^2\rangle = \sum_i i^2 A_i$ does depend on the efficiency of this mode of energy transfer. If one multiplies Eqs. (4) by i^2 , sums, uses the definitions of $\langle\epsilon\rangle$ and $\langle\epsilon^2\rangle$, and inserts the expression (6) for $\langle\epsilon\rangle$, one

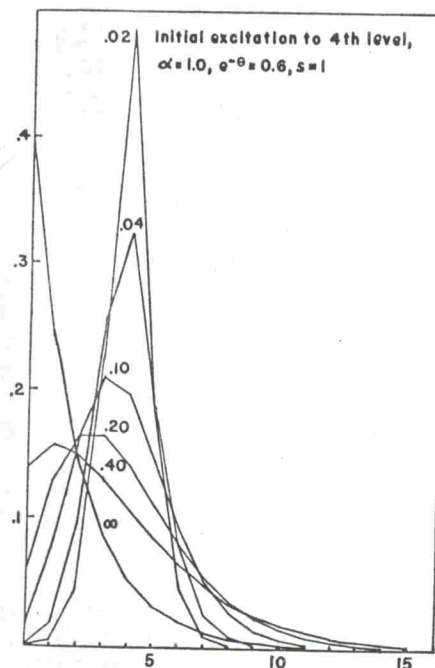


FIG. 1. Plots of $A_n / \sum_i A_i$ vs n . The dimensionless time (aMt) elapsed since initial excitation is indicated by each plot.

⁶ E. W. Montroll and K. E. Shuler, *J. Chem. Phys.* **26**, 454 (1957).

⁷ See, for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1956), 2nd ed., Sec. 13.17.