

The Statistical Mechanical Resolution of a Thermodynamic "Paradox"¹

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We discuss a thermodynamic paradox suggested by Fallows and Greenleaf. Using quantum statistical mechanics, we analyze the problem in detail, showing why no paradox arises.

KEY WORDS: Second law; blackbody radiation; nonequilibrium statistical mechanics.

1. INTRODUCTION

Thermodynamics has outlived several proposed paradoxes. Most of them are violations of the second law, which states that the entropy of an isolated system never decreases. A corollary is that an isolated system initially at uniform temperature cannot evolve into a state of nonuniform temperature. In the spirit of thermodynamics, it is assumed that both the initial state and the final state are nearly at equilibrium. We examine here a paradox discussed by Fallows⁽¹⁾ and later revived by Greenleaf,⁽²⁾ which presumably violates the second law. It is of considerable interest, since it concerns the interaction of matter with radiation.

Let us consider the structure shown in Fig. 1. It consists of part of an ellipsoid with foci at *A* and *B*. Around *A*, part of a sphere is built, and the surfaces within the ellipsoid-sphere structure are removed. The interior surface of the structure is assumed to be perfectly reflecting. At some time blackbodies, at a common temperature *T*, are placed at *A* and *B*. They will

¹ This work was carried out some time ago, circulated as a MIT internal report, and has since enjoyed a modest popularity. We are pleased to publish it more broadly in this volume dedicated to the memory of such an outstanding researcher as Prof. P. Résibois. (MOS)

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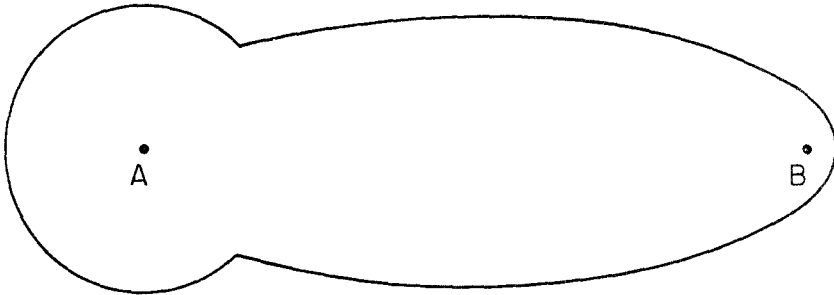


Fig. 1. Structure described in the text. A and B are foci of the ellipsoid; a sphere is built around A .

begin to radiate, and the radiation will be reflected by the walls of the cavity. Because of the geometry, most of the radiation leaving B will fall on A ; however, most of the radiation from A will be reflected back to A . This situation seems to lead to a paradox, since A apparently becomes warmer and B cooler. The system would then change from a state of uniform temperature to a state of nonuniform temperature.

We will see below why this argument is fallacious. When we follow the time development of the system on a microscopic level we find that A and B eventually reach equilibrium with the radiation. The entire system (bodies plus radiation) then has a single temperature, which is lower than the starting temperature because part of the energy is stored in the field. The relationship between our result and thermodynamics is as follows. Thermodynamics does not explain how a time-dependent system approaches equilibrium, nor whether equilibrium will even be reached. It makes no reference to time. However, it does say that if a system is in equilibrium, then the temperature is uniform. In our case this means that if there is an equilibrium solution, then the blackbodies and the radiation have a common temperature and each body emits radiation at the same rate as it absorbs it. Our solution, at equilibrium, is consistent with thermodynamics. In our formulation of the problem we have used a specific model of blackbodies which is sufficiently general for the problem at hand.

2. MODEL AND RESULTS

In this section we will briefly describe our model and the physics of the result.

A blackbody has atomic structure, and we can regard it as a collection of identical atoms. For our purposes, we will take each atom to have two energy levels: an excited state with energy ϵ_a and a ground state with

energy ϵ_b . If in a particular body the states have populations N_a and N_b , then the effective temperature is given by

$$\frac{N_a}{N_b} = \exp\left(-\frac{\epsilon_a - \epsilon_b}{kT}\right) \quad (1)$$

Radiation induces transitions between the two states. For the case of electric dipole radiation (to which we will restrict ourselves) there are two possible processes. (1) The radiation does work on the atom by inducing the transition $b \rightarrow a$, with the absorption of a photon. (2) The atom does work on the radiation by falling to its ground state ($a \rightarrow b$), with the stimulated emission of a photon. In addition, atoms in the upper state will decay spontaneously with a certain lifetime. Let us imagine that at $t = 0$ the blackbodies, with equal temperatures, are placed in the cavity. Some atoms will begin to decay spontaneously, and because of the geometry a greater intensity of radiation will fall on A than on B . Suppose for the moment that stimulated emission did not occur. Because the absorption rate would be greater at A than B , the proportion of excited atoms would increase in the former and decrease in latter. It follows that A would become hotter than B , and no equilibrium would be reached. But in fact the presence of stimulated emission guarantees that some of the radiation falling on A will cause transitions to the ground state, thus decreasing the proportion of excited atoms in A .

Our calculation relates the number of excited atoms at A and at B to the number of photons in the cavity. Let n_a^A be the number of excited atoms at A ; n_b^A the number of nonexcited atoms at A , $= 1 - n_a^A$; and N the number of photons. Quantities n_a^B and n_b^B are defined similarly. We finally obtain rate equations of the form

$$\dot{n}_a^A(t) = -\omega_A [N(t) + 1] n_a^A(t) + \omega_A N(t) n_b^A(t) \quad (2a)$$

$$\dot{n}_a^B(t) = -\omega_B [N(t) + 1] n_a^B(t) + \omega_B N(t) n_b^B(t) \quad (2b)$$

where ω_A and ω_B are certain frequencies. It turns out that as $t \rightarrow \infty$ the solution becomes simply the time-dependent solution, viz.

$$n_a^A / n_b^A = n_a^B / n_b^B = N / (N + 1) \quad (3)$$

This implies that the blackbodies come to the same temperature. Note, though, that they approach the common temperature at different rates.

If we had taken only absorption into account, then the factors in (2a) and (2b) proportional to $N(t) + 1$ would have been absent. No meaningful rate equations would have resulted.

Having given the general idea of our treatment, we now proceed with the actual calculations.

3. DETAILS OF THE MODEL

The system described consists of atoms and the radiation field. The only role of the mirror system is to define a cavity with a certain collection of normal modes. In practice, these are difficult to determine, but there is no need to calculate them. Since the coupling between different modes (via interaction with the atomic systems) is weak, we can concentrate on a single mode. If its frequency is ν , then the Hamiltonian of the radiation field is

$$H_F = \hbar\nu a^\dagger a \quad (4)$$

and the electric field operator is

$$E(x) = \epsilon(x)(a + a^\dagger) \quad (5)$$

where $\epsilon(x)$ is a numerical function of x . In the electric dipole approximation, the interaction between an atom at x and the radiation field is

$$V(x) = ex_{\text{op}}E(x) \quad (6)$$

Let us label the states of the atom-radiation system by $|\alpha, n\rangle$, where α denotes the state of the atom (a or b , i.e., the excited state or the ground state) and n is the photon occupation number. We will restrict ourselves to energy-conserving transitions, so that the only relevant matrix elements of V are

$$\langle a n | V | b n + 1 \rangle = ex_{ab}\epsilon(x)(n + 1)^{1/2} \quad (7a)$$

$$\langle b n | V | a n - 1 \rangle = ex_{ab}\epsilon(x)n^{1/2} \quad (7b)$$

Here x_{ab} is the real dipole moment $\langle a | x_{\text{op}} | b \rangle$.

From these results it is clear that the interaction can effectively be taken as

$$V = g(x)(\sigma^+ a + \sigma a^\dagger) \quad (8)$$

where the raising and lower operators

$$\sigma^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \sigma = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (9)$$

operate on the atomic states

$$|a\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |b\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (10)$$

The coupling is

$$g(x) = ex_{ab}\epsilon(x)$$

Generalizing this treatment to the problem of atoms placed at A and

B , we obtain

$$\begin{aligned} V &= V_A + V_B \\ &= g_A(\sigma_A^+ a + \sigma_A a^+) + g_B(\sigma_B^+ a + \sigma_B a^+) \end{aligned} \quad (11)$$

where

$$g_A = g(x_A) \quad (12a)$$

$$g_B = g(x_B) \quad (12b)$$

The geometry of the system requires that $g_A > g_B$. In the actual problem there are many atoms at A and many at B . However, for our purposes we can consider only a single atom at each position and, when necessary, scale the appropriate results. This means that we consider photon-mediated interactions between atoms at A and B but neglect interactions among atoms within A or B . Equivalently, we can take all the atoms at A (or B) to behave in the same way. The essential features of the problem are contained in this model.

The simplest choice for the Hamiltonian of body A is

$$H_A = \epsilon_a \sigma_A^+ \sigma_A + \epsilon_b \sigma_A \sigma_A^+ \quad (13)$$

and similarly for B . However, the atoms are bound into a crystal of some kind, and their energy levels will be perturbed by phonon processes. We can account stochastically for this effect by adding to ϵ_a and ϵ_b random functions of time, $f_a(t)$ and $f_b(t)$. Statistically independent functions are used for the two bodies. Results obtained from the modified Hamiltonian must then be averaged over an ensemble of random functions. We will choose $f_a(t)$ and $f_b(t)$ to have zero average value, and certain other properties will be explained in the actual calculation. It might seem that these functions add an unnecessary complication to the problem, but actually they simplify it, since they eliminate correlations between the two blackbodies. The net effect is that the interaction of A with the radiation is statistically independent of the interaction of B with the radiation. Thus

$$H_A = [\epsilon_a + f_a^A(t)] \sigma_A^+ \sigma_A + [\epsilon_b + f_b^B(t)] \sigma_A \sigma_A^+ \quad (14a)$$

$$H_B = \text{same, with } A \leftrightarrow B \quad (14b)$$

and finally the entire model Hamiltonian is

$$H = H_F + H_A + H_B + V \quad (15)$$

Within the framework of statistical mechanics, we need not solve for the eigenstates of H . Instead, we consider a collection of states $|1\rangle, |2\rangle, \dots$ and suppose that the system has probabilities p_1, p_2, \dots , respectively, of being in these states. (The states $\{|n\rangle\}$ need not be eigenstates of H .) The

probabilities must satisfy

$$p_n \geq 0 \quad (16a)$$

$$\sum_n p_n = 1 \quad (16b)$$

If O is an operator, then its statistical average value is

$$\langle O \rangle = \sum_n p_n \langle n | O | n \rangle \quad (17)$$

which can be written as a trace

$$\langle O \rangle = \text{Tr } \rho O \quad (18)$$

where ρ is the density operator

$$\rho = \sum_n p_n |n\rangle \langle n| \quad (19)$$

Alternatively, the probability that the system is in some state $|\Psi\rangle$ is simply

$$P\Psi = \sum_n p_n |\langle \Psi | n \rangle|^2 = \langle \Psi | \rho | \Psi \rangle \quad (20)$$

Thus the object of interest is ρ . We can find it by solving its equation of motion, which follows from (19):

$$\dot{\rho} = -(i/\hbar)[H, \rho] \quad (21)$$

Of course the initial conditions must be satisfied.

In our particular problem, we will always work with a specific representation of ρ in which the matrix elements are $\langle \alpha_A \alpha_B n | \rho | \alpha'_A \alpha'_B n' \rangle$. Here α_A and α'_A represent states of an atom at A (either a or b); similarly, α_B and α'_B refer to an atom at B . The photon occupation numbers are n and n' . The probability that an atom at A is in its excited state, regardless of the state of B and the field, is

$$\rho_{aa} = (\text{Tr}_B \text{Tr}_F \rho)_{aa} \quad (22a)$$

$$= \sum_n |\langle aan | \rho | aan \rangle + \langle abn | \rho | abn \rangle| \quad (22b)$$

$$= 1 - \rho_{bb} \quad (22c)$$

Clearly ρ_{aa} and ρ_{bb} are the fractions of excited and ground-state atoms at A , so that

$$\frac{\rho_{aa}}{\rho_{bb}} = \exp\left(-\frac{\epsilon_a - \epsilon_b}{kt}\right) \quad (23)$$

Similar formulas apply for the atoms at B . The average number of photons in the cavity is

$$N = \sum_n n (\text{Tr}_A \text{Tr}_B \rho)_{nn} \quad (24)$$

At $t = 0$ the density matrix factorizes; that is, $\rho(0)$ has the form

$$\begin{aligned} & \langle \alpha_A \alpha_B n | \rho(0) | \alpha'_A \alpha'_B n' \rangle \\ & = \langle \alpha_A | \rho_A(0) | \alpha'_A \rangle \langle \alpha_B | \rho_B(0) | \alpha'_B \rangle \langle n | \rho_F(0) | n' \rangle \end{aligned} \quad (25)$$

It is also diagonal, with $\rho_A(0)$ and $\rho_B(0)$ giving thermal populations at the initial temperature. No photons are present.

4. THE RATE EQUATIONS

First we find the equation of motion for ρ_{aa} , the fraction of excited atoms at A . We use

$$\dot{\rho}_{a,a} = -(i/\hbar) \text{Tr}_F \text{Tr}_B [H, \rho]_{a,a} \quad (26)$$

The only part of H which makes a contribution is V_A , and the result is

$$\dot{\rho}_{a,a} = -i \frac{g_A}{\hbar} \sum_n (n+1)^{1/2} \rho_{bn+1,an} + \text{c. c.} \quad (27)$$

The symbol at the right means "complex conjugate." Note that

$$(\rho_{bn+1,an})^* = \rho_{an,bn+1} \quad (28)$$

Similarly, we can calculate $\dot{\rho}_{bn+1,an}$, using

$$\dot{\rho}_{bn+1,an} = -(i/\hbar) \text{Tr}_F [H, \rho]_{bn+1,an} \quad (29)$$

We relegate the details of the reduction of (29) to Appendix A. When the resulting expression is integrated and inserted into (27), we find

$$\begin{aligned} \dot{\rho}_{a,a}(t) = & - \left(\frac{g_A}{\hbar} \right)^2 \int_0^t dt' \exp[i\Delta(t-t') + i\phi_A(t,t')] \\ & \times \left[\sum_n (n+1) \rho_{an,an}(t') - \sum_n n \rho_{bn,bn}(t') \right] \\ & - \frac{g_A g_B}{\hbar^2} \int_0^t dt' \{ \exp[i\Delta(t-t') + i\phi_A(t,t')] \} \rho_{ba,ab}(t') \\ & + \text{c. c.} \end{aligned} \quad (30)$$

where

$$\Delta = \frac{1}{\hbar} (\epsilon_a - \epsilon_b) - \nu \quad (31a)$$

$$\phi_A(t_2, t_1) = \frac{1}{\hbar} \int_{t_1}^{t_2} dt' [f_a^A(t') - f_b^A(t')] \quad (31b)$$

Details are contained in Appendix A.

The term proportional to g_A^2 looks desirable, since it makes (30) have roughly the form of a rate equation. Forgetting for the moment the dependence on n , we see that $\dot{\rho}_{a,a}$ is related to $\rho_{a,a}$ and $\rho_{b,b}$. This is certainly

an expected result. But the term contains an integral, so $\dot{\rho}_{a,a}$ depends on the history of $\rho_{a,a}$ and $\rho_{b,b}$, not simply on their instantaneous values. This will be discussed below. Atoms at B make their presence known via the term proportional to $g_A g_B$, since $\rho_{ba,ab}$ contains correlations between the populations at A and B . We would expect, however, that if the energy levels are perturbed sufficiently randomly, and if the fluctuations at A and B are independent, then this term should average to zero. To a good approximation, this is actually the case, provided that we make certain reasonable assumptions about the fluctuations. The averaging procedure is carried out in Appendix A. Our treatment of the fluctuations pays another dividend: it erases the system's memory by removing the integrals in (30). The resulting rate equation contains no explicit reference to the past. Physically, it is believable that a system subject to random forces should behave this way. After the smoke clears we are left with

$$\dot{\rho}_{a,a}(t) = -\omega_1 \sum_n (n+1) \rho_{an,an}(t) + \omega_1 \sum_n n \rho_{bn,bn}(t) \quad (32)$$

where ω_1 is proportional to g_A^2 .

Now we consider the sums in the equation above. Our aim is to show that diagonal elements of the density matrix factorize in some approximation, e.g., that $\rho_{an,an} \approx \rho_{a,a} \rho_{n,n}$. Then the sums over n will be related to the average number of photons in the cavity. It is intuitive that part of the density matrix should factorize. Initially ρ factorizes, and as time goes on the interaction $V_A + V_B$ mixes the atomic and radiation coordinates, causing ρ not to factorize. However, if the interaction is sufficiently gentle, then we expect parts of ρ to be almost factorizable. It turns out that

$$\rho_{an,an} = \rho_{a,a} \rho_{n,n} + O(g^2) \quad (33)$$

The symbol $O(g^2)$ denotes terms proportional to g_A^2 , g_B^2 , or $g_A g_B$ (and higher powers). This property is proved in Appendix B. Generally the coupling of atoms to radiation is weak enough so that we can neglect the higher order terms. Equation (32) then becomes a simple rate equation:

$$\dot{\rho}_{a,a}(t) = -\omega_1 [N(t) + 1] \rho_{a,a}(t) + \omega_1 N(t) \rho_{b,b}(t) \quad (34)$$

where $N(t)$ is the average number of photons, Eq. (24). By symmetry the rate equation for an atom at B has the same form, with ω_1 replaced by ω_2 , which is proportional to g_B^2 .

In order to solve (34) we have to calculate $N(t)$. This is easily done by the methods above, and the result is

$$\dot{N}(t) = -\dot{\rho}_{a,a}^A(t) - \dot{\rho}_{a,a}^B(t) \quad (35a)$$

or

$$N(t) = \rho_{a,a}^A(0) - \rho_{a,a}^A(t) + \rho_{a,a}^B(0) - \rho_{a,a}^B(t) \quad (35b)$$

since there are no photons present at $t = 0$. Here $\rho_{a,a}^A$ is the same as the previous $\rho_{a,a}$ and $\rho_{b,b}^B$ is the corresponding quantity for an atom at B . In detail

$$\rho^A = \text{Tr}_B \text{Tr}_F \rho \quad (36a)$$

$$\rho^B = \text{Tr}_A \text{Tr}_F \rho \quad (36b)$$

So far our calculation concerns a single atom at A and a single atom at B . More realistically, there should be M atoms at each site. To take this circumstances into account we need only scale $N(t)$ by M and interpret $\rho_{a,a}^A$ as the fraction of excited atoms at A , and similarly for $\rho_{a,a}^B$.

5. ANALYSIS

To simplify the notation we define

$$x(t) = \rho_{aa}^A(t) \quad (37a)$$

$$y(t) = \rho_{aa}^B(t) \quad (37b)$$

The initial condition that the temperatures of A and B are equal implies that $x(0) = y(0) = x_0$ (with $0 < x_0 < \frac{1}{2}$). Thus the basic equations become

$$\dot{x}/\omega_1 = 2x^2 + 2xy - x(4x_0 + 2) - y + 2x_0 \quad (38a)$$

$$\dot{y}/\omega^2 = 2y^2 + 2xy - y(4x_0 + 2) - x + 2x_0 \quad (38b)$$

These coupled nonlinear equations describe the evolution of the system.

If the system reaches equilibrium, then x and y asymptotically become constant for large t . It is therefore of interest to check that (38a) and (38b) have sensible time-dependent solutions, x_{eq} and y_{eq} . A short calculation shows that

$$x_{\text{eq}} = y_{\text{eq}} = \frac{1}{8} \left[4x_0 + 3 \pm (16x_0^2 - 8x_0 + 9)^{1/2} \right] \quad (39)$$

The first equality is certainly expected, since it ensures that A and B have the same temperature. This is a property which the equilibrium solution must have. The upper and lower signs correspond to the following ranges of x_{eq} :

$$+ : \quad \frac{3}{4} < x_{\text{eq}} < 1 \quad (40a)$$

$$- : \quad 0 < x_{\text{eq}} < \frac{2}{3}x_0 \quad (40b)$$

and to keep the temperature positive, we must choose the latter. The inequality (40b) simply reflects the fact that a portion of the energy is stored in the radiation field. A further property of the time-dependent solution is that it is stable under small perturbations in x and y . To see this,

let

$$x(t) = x_{\text{eq}} + x_1(t) \quad (41a)$$

$$y(t) = x_{\text{eq}} + y_1(t) \quad (41b)$$

with x_1 and y_1 small compared to x_{eq} . Neglecting nonlinear terms in (38a) and (38b), we find that both x_1 and y_1 satisfy

$$\ddot{x}_1 + 2c_1\dot{x}_1 + c_2^2x_1 = 0 \quad (42)$$

where c_1 and c_2 are positive frequencies with $c_1 > c_2$. As expected, the solutions to (42) are damped in time.

Evidently the time-dependent solution (39) has all the properties which are expected of the true equilibrium solution. It is now our aim to show that the system actually evolves into this state as t goes to infinity.

First we note that x_0 is typically small compared to unity. For example, if $\epsilon_a - \epsilon_b = 1$ eV and initially $T = 3000$ K, then $x_0 = 0.018$. So to a good approximation the nonlinear terms in (38a) and (38b) can be neglected. When this is done we obtain

$$x(t) = \frac{2}{3}x_0 + \frac{x_0}{\alpha_+ - \alpha_-} \left[\left(\omega_1 - \frac{1}{3}\alpha_- \right) e^{-\alpha_+ t} - \left(\omega_1 - \frac{1}{3}\alpha_+ \right) e^{-\alpha_- t} \right] \quad (43a)$$

$$y(t) = \text{same, with } \omega_1 \Leftrightarrow \omega_2 \quad (43b)$$

where

$$\alpha_{\pm} = (2x_0 + 1)(\omega_1 + \omega_2) \pm \left[(2x_0 + 1)^2(\omega_1 + \omega_2)^2 - (16x_0 + 3)\omega_1\omega_2 \right]^{1/2} \quad (44)$$

(The quantity within the radical is always positive.) The asymptotic value of x and y agrees in the linear approximation with the previously calculated x_{eq} . It is instructive to examine the nonequilibrium properties of this solution. Since $\omega_1 > \omega_2$ we have $x(t) < y(t)$. Therefore in the interval $0 < t < \infty$, A is actually cooler than B . This surprising result could not easily be predicted from a casual examination of the problem. It emphasizes the fact that because of stimulated emission, a stronger coupling to the radiation field does not necessarily lead to a higher temperature.

From the expression for α_{\pm} one can show that if x_0 is chosen sufficiently small, then

$$\frac{1}{3}\alpha_- < \omega_2 < \frac{1}{2}(\omega_1 + \omega_2) < \frac{1}{3}\alpha_+ < \omega_1 \quad (45)$$

This implies that $y(t) < 0$ and $\ddot{y}(t) > 0$, with the result that y decreases

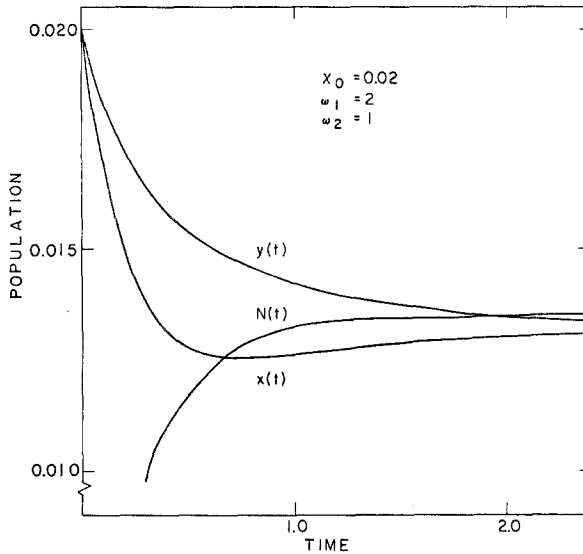


Fig. 2. Behavior of x , y , and N in the linear approximation. Here x , y , and N stand for the fraction of excited atoms at A , the fraction of excited atoms at B , and the number of photons (scaled by the number of atoms at A and B). The units of ω_1 , ω_2 , and time are arbitrary.

smoothly from x_0 to its limit $2x_0/3$. On the other hand, x has a minimum at a single time t' , and \dot{x} has a maximum at a later time t'' . So x passes through $2x_0/3$, reaches a minimum, and then asymptotically approaches $2x_0/3$ from below. In the case of N we obtain $\dot{N} > 0$ and $\dot{N} < 0$, which imply that N increases smoothly to its limit. Figure 2 illustrates the behavior of x , y , and N . It should be noted that the restriction to small x_0 [in order for (45) to hold] is in the spirit of the linear approximations which we have made.

When the nonlinear terms in (38a) and (38b) cannot be neglected, the analysis is much more difficult. No exact solution is immediately apparent. We have numerically integrated the equations, using values of x_0 large enough to make the nonlinearities important. We find that the solutions asymptotically approach the time-dependent predictions. Thus the system reaches equilibrium. The qualitative behavior of the solutions closely resembles that of the linearized solutions. That is, y and N are monotonic without wiggles, and x passes through a minimum before it reaches the asymptotic region. For sufficiently large t it is easy to fit the solutions to an exponential, and in this way a relaxation time can be determined. Sample solutions are illustrated in Fig. 3.

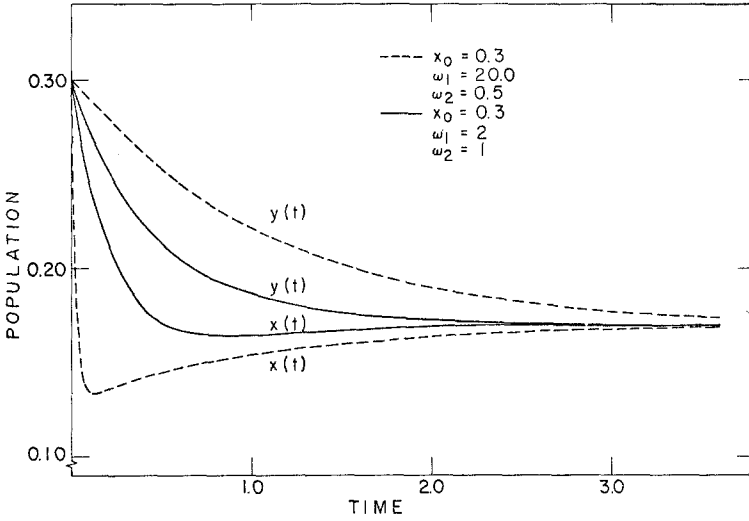


Fig. 3. Behavior of x , y , and N in the nonlinear regime. The units of ω_1 , ω_2 , and time are arbitrary.

APPENDIX A

We want to reduce the expression

$$\dot{\rho}_{bn+1,an}(t) = -(i/\hbar) \text{Tr}_F[H, \rho]_{bn+1,an} \quad (\text{A1})$$

All parts of H except H_B contribute to the right-hand side. A straightforward calculation shows that

$$\begin{aligned} \dot{\rho}_{bn+1,an}(t) &= \frac{i}{\hbar} [\hbar\Delta + f_a^A(t) - f_b^A(t)] \rho_{bn+1,an}(t) \\ &\quad - \frac{ig_A}{\hbar} (n+1)^{1/2} [\rho_{an,an}(t) - \rho_{bn+1,bn+1}(t)] \\ &\quad - \frac{ig_B}{\hbar} (n+1)^{1/2} [\rho_{ban,abn}(t) - \rho_{ban+1,abn+1}(t)] \\ &\quad - \frac{ig_B}{\hbar} [(n+2)^{1/2} \rho_{bbn+2,aan}(t) - n^{1/2} \rho_{bbn+1,aan-1}] \end{aligned} \quad (\text{A2})$$

The integrated form of (A2) is simply

$$\begin{aligned} \rho_{bn+1,an}(t) = & \int_0^t dr' \{ \exp[i\Delta(t-t') + i\phi_A(t,t')] \} \\ & \times \left\{ \frac{ig_A}{\hbar} (n+1)^{1/2} [\rho_{an,an}(t) - \rho_{bn+1,bn+1}(t')] \right. \\ & - \frac{ig_B}{\hbar} (n+1)^{1/2} [\rho_{ban,abn}(t') - \rho_{ban+1,abn+1}(t')] \\ & \left. - \frac{ig_B}{\hbar} [(n+2)^{1/2} \rho_{bbn+2,aan}(t') - n^{1/2} \rho_{bbn+1,aan-1}(t')] \right\} \quad (A3) \end{aligned}$$

We have defined ϕ_A in the text. Inserting (A3) into (27), we obtain

$$\begin{aligned} \dot{\rho}_{a,a}(t) = & \int_0^t dt' \{ \exp[i\Delta(t-t') + i\phi_A(t,t')] \} \\ & \times \left(- \left(\frac{g_A}{\hbar} \right)^2 \sum_n (n+1) [\rho_{an,an}(t') - \rho_{bn+1,bn+1}(t')] \right. \\ & - \frac{g_A g_B}{\hbar^2} \sum_n \{ [(n+2)(n+1)]^{1/2} \rho_{bbn+2,aan}(t') \\ & - [(n+1)n]^{1/2} \rho_{bbn+1,aan-1}(t') \} \\ & \left. - \frac{g_A g_B}{\hbar^2} \sum_n (n+1) [\rho_{ban,abn}(t') - \rho_{ban+1,abn+1}(t')] \right) \\ & + \text{c. c.} \quad (A4) \end{aligned}$$

The second sum above is identically zero, while the third sum is nothing but $\rho_{ba,ab}(t')$ in disguise. Hence we obtain (30).

At this point we wish to average (30) over an appropriate ensemble of random functions. This can be done approximately after we identify the strongest dependence of the right-hand side on ϕ_A and ϕ_B . It is easy to see that $[H_A + H_B, \rho]_{an,an} = 0$, so that

$$\dot{\rho}_{an,an} = - (i/\hbar) [V, \rho]_{an,an} \quad (A5)$$

Hence $\rho_{an,an}$ has no explicit dependence on ϕ_A and ϕ_B , to order g_A (or g_B). The same result holds for $\rho_{bn,bn}$. On the other hand,

$$\begin{aligned} \dot{\rho}_{ba,ab}(t) \\ = \frac{1}{\hbar} \{ [f_a^A(t) - f_b^A(t)] - [f_a^B(t) - f_b^B(t)] \} \rho_{ba,ab}(t) + A(t) \quad (A6) \end{aligned}$$

where $A(t)$ contains terms proportional to g_A or g_B . So we have

$$\begin{aligned} \frac{\partial}{\partial t} \{ \rho_{ba,ab}(t) \exp[-i\phi_A(t,0) + i\phi_B(t,0)] \} \\ = A(t) \exp[-i\phi_A(t,0) + i\phi_B(t,0)] \end{aligned} \quad (\text{A7})$$

The dominant dependence of $\rho_{ba,ab}$ on the ϕ 's is thereby transformed away. (This procedure is equivalent to transforming to an interaction picture.) In (30) we can make the replacement

$$\rho_{ba,ab}(t') = \{ \exp[i\phi_A(t',0) - i\phi_B(t',0)] \} \tilde{\rho}_{ba,ab}(t') \quad (\text{A8})$$

where now $\tilde{\rho}$ does not depend strongly on the ϕ 's. The properly averaged form of (30) is then

$$\begin{aligned} \dot{\rho}_{a,a}(t) = & - \left(\frac{g_A}{\hbar} \right)^2 \int_0^t dt' \exp[i\Delta(t-t')] \\ & \times \langle \exp[-i\phi_A(t,t')] \rangle S(t') \\ & - \frac{g_A g_B}{\hbar^2} \int_0^t dt' \exp[i\Delta(t-t')] \\ & \times \langle \exp[i\phi_A(t,0)] \rangle \langle \exp[-i\phi_B(t',0)] \rangle \tilde{\rho}_{ba,ab}(t') \\ & + \text{c. c.} \end{aligned} \quad (\text{A9})$$

where

$$S(t) = \sum_n (n+1) \rho_{an,an}(t) - \sum_n n \rho_{bn,bn}(t) \quad (\text{A10})$$

The second average factorizes because fluctuations at A and B are independent.

It is known that perturbations caused by phonon interactions are adequately described by Gaussian statistics. In this case we have the result

$$\begin{aligned} \langle \exp \left[\pm i \int_{t_1}^{t_2} dt F(t) \right] \rangle \\ = \exp \left(- \frac{1}{2} \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt' \langle F(t) F(t') \rangle \right) \end{aligned} \quad (\text{A11})$$

provided that $\langle F(t) \rangle = 0$. If in addition $F(t)$ fluctuates so rapidly that its autocorrelation vanishes at different times, we can take

$$\langle F(t) F(t') \rangle = 2\gamma \delta(t-t') \quad (\text{A12})$$

This is a satisfactory approximation for our purposes. When the averaging procedure is applied to (A9) (with the energy splittings taken as the

stochastic functions) the result is

$$\begin{aligned} \dot{\rho}_{a,a}(t) = & - \left(\frac{g_A}{\hbar} \right)^2 \int_0^t dt' \{ \exp[i\Delta(t-t') - \gamma_A(t-t')] \} S(t') \\ & - \frac{g_A g_B}{\hbar^2} \int_0^t dt' \\ & \times \{ \exp[i\Delta(t-t') - \gamma_A t - \gamma_B t'] \} \tilde{\rho}_{ba,ab}(t') + \text{c.c.} \quad (\text{A13}) \end{aligned}$$

Now we assume that the correlations in each atom are damped out quickly with respect to the time scale of physical interest. The exponentials then act as delta functions, and we get

$$\begin{aligned} \dot{\rho}_{a,a}(t) = & - \frac{1}{\gamma_A} \left(\frac{g_A}{\hbar} \right)^2 S(t) \\ & - \frac{1}{\gamma_B} \frac{g_A g_B}{\hbar^2} [\exp(i\Delta t - \gamma_A t)] \tilde{\rho}_{ba,ab}(0) + \text{c.c.} \quad (\text{A14}) \end{aligned}$$

Thus the net effect of the averaging is to cause the diagonal terms to be evaluated at time t and the off-diagonal terms to be evaluated at $t = 0$. The latter vanish because there are no initial correlations. Equation (A14) becomes

$$\dot{\rho}_{a,a} = - \frac{2}{\gamma_A} \left(\frac{g_A}{\hbar} \right)^2 \left[\sum_n (n+1) \rho_{an,an} - \sum_n n \rho_{bn,bn} \right] \quad (\text{A15})$$

as asserted in the text.

APPENDIX B

In order to prove the factorizability property, it is most convenient to work in an interaction picture given by

$$\bar{\rho}(t) = U(t)\rho(t)U^{-1}(t) \quad (\text{B1})$$

where

$$U(t) \exp \frac{i}{\hbar} \left\{ H_F t + \int_0^t dt' [H_A(t') + H_B(t')] \right\} \quad (\text{B2})$$

As usual, H_F , H_A , and H_B are in the Schrödinger picture; the sole time dependence is contained in the energy level fluctuations. We can easily show that

$$\dot{\bar{\rho}}(t) = -(i/\hbar) [\bar{V}(t), \bar{\rho}(t)] \quad (\text{B3})$$

where

$$\bar{V}(t) = U(t)VU^{-1}(t) \quad (\text{B4})$$

Integrating (B3) and iterating it once, we obtain

$$\begin{aligned} \bar{\rho}(t) = & \rho(0) - \frac{i}{\hbar} \int_0^t dt' [\bar{V}(t_1), \rho(0)] \\ & + \left(\frac{i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 [\bar{V}(t_1), [\bar{V}(t_2), \bar{\rho}(t_2)]] \end{aligned} \quad (\text{B5})$$

When we take a diagonal matrix element of this equation, we find that the second term on the right-hand side vanishes. This happens because $\rho(0)$ is diagonal. Also, the diagonal elements of $\bar{\rho}$ are the same as the diagonal elements of ρ . Therefore in the case of diagonal matrix elements we have

$$\rho(t) = \rho(0) + O(g^2) \quad (\text{B6})$$

with $O(g^2)$ as explained in the text.

Now ρ can always be written as the sum of a factorized part and a correction:

$$\rho(t) = \rho_A(t)\rho_B(t)\rho_F(t) + \sigma(t) \quad (\text{B7})$$

Specializing to a diagonal matrix element, we find

$$\begin{aligned} & \rho(0) + O(g^2) \\ & = [\rho_A(0) + O(g^2)][\rho_B(0) + O(g^2)][\rho_F(0) + O(g^2)] + \sigma(t) \end{aligned} \quad (\text{B8})$$

Since $\rho(0) = \rho_A(0)\rho_B(0)\rho_F(0)$, it follows that the diagonal elements of $\sigma(t)$ are of order g^2 . Hence we obtain (33).

REFERENCES

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