PHYSICAL REVIEW A VOLUME 34, NUMBER 6 DECEMBER 1986

Entropy production in stopping atoms with laser light

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(Received 18 June 1986)

The production of entropy is analyzed for the stopping of a beam of atoms by momentum transfer from a counterpropagating laser beam. Expressions are given for the rate of entropy production in the photon beam and in the atomic beam. In the latter case, the kinetic entropy rate is computed from the compression of the velocity distribution function of the atoms under the radiation pressure. A thermodynamic analysis yields large irreversibilities in this process, because the total rate of entropy production due to absorption and emission of the photons is several orders of magnitude larger than the rate of entropy reduction in the atomic beam.

I. INTRODUCTION

This work was motivated by the active research being done[1–7] to stop and trap samples of very cold atoms. These atoms, introduced as beams, are irradiated in the low-frequency wing of a Doppler-broadened resonance line by a counterpropagating laser beam. The photons absorbed are, on average, reradiated in random directions, subject only to the usual conditions on polarization and propagation of fluorescence; the result is the net transfer of momentum from the photons to the beam. Therefore the atoms, which originally had an equilibrium velocity distribution with a high average kinetic energy, end up with a narrow velocity distribution and a low average kinetic energy. This narrowing (cf. Fig. 1) was first predicted by Letokhov[8] and extensive theoretical[9–19] and experimental work[20] followed, pursuing a variety of experimental methods and geometric configurations. Such cold samples are of interest in a wide range of studies into the properties of gases at low temperatures, and of atoms, for very-high-resolution spectroscopy. Experimental applications have been reviewed in the literature[21,22] and share as a common source a hypothesis due to Ashkin.[23]

In considering the cooling of gases by laser radiation, Hänsch and Schawlow[24] mentioned the production of entropy in scattered laser radiation. In addition to this effect, a change of entropy is also produced in the cooled gas due to the narrowing of the velocity distribution. Since the sample's volume in phase space decreases, its entropy decreases. This entropy change has to be brought about by a greater increase in the entropy of the photons, so long as the total process is spontaneous and irreversible. Here, we set out to investigate the relative contribution of each of these processes and the thermodynamic efficiency of the process as a whole, as a means of producing low-temperature atomic samples. In effect, we are estimating the performance of a laser-driven refrigerator. We take as our model the configuration used in the experiment described in Ref. 1, and use for our sample calculations parameters of the same order of magnitude as those used therein.

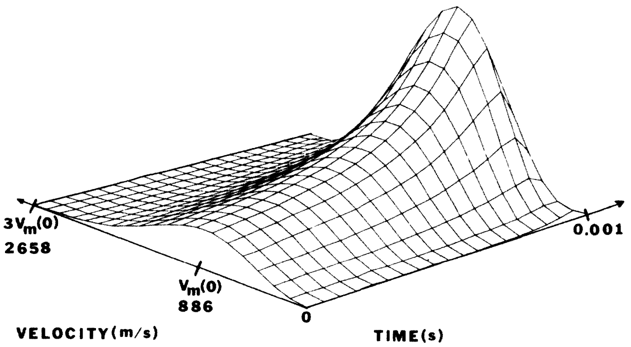

FIG. 1. Evolution of the internal velocity distribution. Velocity axis scales nonlinearly with time, but in the region shown the scaling is approximated by $v(t)=v(0)[1-999.26t]$.

II. CALCULATION OF ENTROPY CHANGE IN THE PHOTON BEAM

The photons of the refrigerator are initially in a circularly polarized, monochromatic, unidirectional, coherent beam; after absorption and emission the photons propagate incoherently as a $\sin^2\chi$ distribution, where χ is the azimuthal angle about the instantaneous axis of dipolar oscillation. Since the radiation is circularly polarized, the induced dipole rotates in a plane perpendicular to the laser wave vector; this produces an azimuthally radiated intensity distribution $\sigma(\hat{\mathbf{k}})=(3/16\pi)(1+\cos^2\theta)$ about the laser wave vector (cf. Appendix A). These changes imply that the entropy of the photons increases in the absorption-emission process. In order to calculate the entropy change it is necessary to use a combination of thermodynamics and information theory. In the experimental situation, there are, on average, N_α atoms which absorb and emit a photon of frequency ν_0 every two natural lifetimes τ. This implies a mean rate of energy change

$$\dot{E}_1=\frac{N_\alpha h\nu_0}{2\tau} \tag{1}$$

per unit time. This beam is focused at a distance R upon a projected area A_1, implying an energy flux

$$\Phi_1 = \frac{\dot{E}_1}{A_1} \tag{2}$$

about a sphere of radius R. After scattering, these photons still carry the same average energy flux, Φ_2, through a similar sphere centered about the atomic sample. However, an irreversibility has clearly occurred. This change is characterized by the difference of the entropy flux of the incoming beam, Ψ_1, and the outgoing beam, Ψ_2.

Parts of the subsequent calculation of the entropy flux were first done by Weinstein[25] and later reviewed by Landsberg and Tonge.[26] In considering the entropy of a gas of bosons, the normal procedure is to take the gas at equilibrium and obtain a maximal entropy. We are concerned, however, with a nonequilibrium particle picture of radiation. Two assumptions are made: (1) that the total probability $P(N_1, N_2, \ldots)$ of finding N_1 particles in a single-particle quantum state 1, N_2 particles in state 2, etc., is the product of the independent single state probabilities (an assumption that the intensity of the laser beam is not extremely high), and (2) that the marginal occupation probability of a particle in any quantum state j is independent of that state's already existing population. These assumptions allow straightforward derivation of the entropy

$$S = k_B \sum_j [(1+n_j)\ln(1+n_j) - n_j \ln n_j] \, , \tag{3}$$

where n_j is the mean occupation number of the state j. An entropy change computed from this equation would be due to changes in the populations of occupied states j. Reference 24 states that the expression derived above for the entropy is usually derived from equilibrium statistical mechanics,[27-29] but its use here without reference to equilibrium considerations presumes that it is of wider significance and represents a nonequilibrium entropy.

To replace the sum over states by an integral over frequencies, the density of states of the radiation crossing the element of surface dA enclosing the differential volume dV, under consideration, into a solid angle $d\Omega$ in the direction, making an angle ϕ, with the surface normal is required. See Fig. 2. The most convenient form of this quantity is

$$\frac{2dV\nu^2}{c^3} d\nu \, d\Omega \, ,$$

where the factor of 2 is due to the two independent polarizations.

This result and Eq. (3) allows calculation of the entropy as

$$S = \int \int \int s_\nu(\mathbf{k}) d\nu \, dV \, d\Omega \, , \tag{4}$$

where the entropy of unpolarized radiation in the translational state $\mathbf{k}$, per unit frequency, per unit solid angle of propagation is

$$s_\nu(\mathbf{k}) = 2k_B \nu^2 c^{-3} \{ [1+n_\nu(\hat{\mathbf{k}})] \ln[1+n_\nu(\hat{\mathbf{k}})] - n_\nu(\hat{\mathbf{k}}) \ln n_\nu(\hat{\mathbf{k}}) \} \, ,$$

where $n_\nu(\hat{\mathbf{k}})$ is the mean occupation number of the translational state $\mathbf{k}$ of frequency ν. The internal energy is

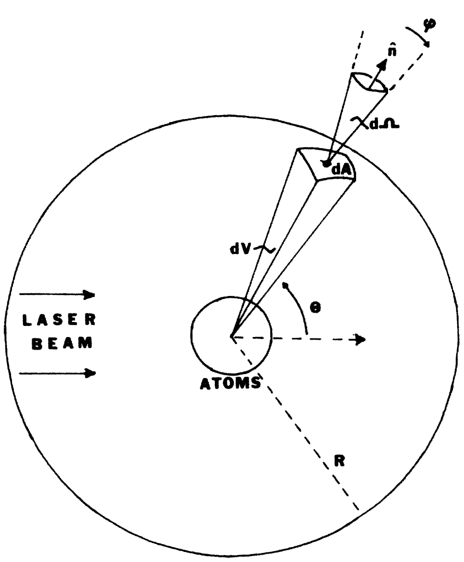

FIG. 2. Geometry of the scattering process.

$$U = \int \int \int u_\nu(\mathbf{k}) d\nu \, dV \, d\Omega \, , \tag{5}$$

with

$$u_\nu(\mathbf{k}) = u_\nu \sigma(\hat{\mathbf{k}}) = 2\nu^2 (h\nu) c^{-3} n_\nu \sigma(\hat{\mathbf{k}}) \, ,$$

analogous to $s_\nu(\mathbf{k})$ and where n_ν is the mean occupation number of a translational state with frequency ν. These two occupation numbers are related through the radiation distribution as

$$n_\nu(\hat{\mathbf{k}}) = n_\nu \sigma(\hat{\mathbf{k}}) \, .$$

In the situation under consideration, as in all efficiency analyses, we have already noted that we require energy and entropy fluxes. These quantities are

$$\Phi(\mathbf{k}) = \int \int K_\nu(\mathbf{k}) \cos\phi \, d\nu \, d\Omega \, , \tag{6}$$

$$K_\nu(\mathbf{k}) = c u_\nu(\mathbf{k}) = 2h\nu^3 c^{-2} n_\nu(\hat{\mathbf{k}}) \, ,$$

$$\Psi(\mathbf{k}) = \int \int L_\nu(\mathbf{k}) \cos\phi \, d\nu \, d\Omega \, , \tag{7}$$

$$L_\nu(\mathbf{k}) = c s_\nu(\mathbf{k}) = 2k_B \nu^2 c^{-2} \{ [1+n_\nu(\hat{\mathbf{k}})] \ln[1+n_\nu(\hat{\mathbf{k}})] - n_\nu(\hat{\mathbf{k}}) \ln n_\nu(\hat{\mathbf{k}}) \} \, .$$

As originally named by Planck,[27] $K_\nu(\mathbf{k})$ and $L_\nu(\mathbf{k})$ are called the spectral energy radiance and the spectral entropy radiance. In the special case where $K_\nu(\mathbf{k})$ and $L_\nu(\mathbf{k})$ are independent of direction within $d\Omega$,

$$\Phi(\mathbf{k}) = B \int K_\nu(\mathbf{k}) d\nu \, , \tag{8}$$

$$\Psi(\mathbf{k}) = B \int L_\nu(\mathbf{k}) d\nu \, , \tag{9}$$

with

$$B=\int \cos\phi\, d\Omega=\int_0^{\varphi} 2\pi\, d\phi \cos\phi \sin\phi=\pi \sin^2\varphi \ ,$$

where φ is the half-angle of the cone subtending the source at the receiver. Note that we are assuming that the atoms are inside a small volume which subtends the angle φ on the surface of a sphere of radius R. If we use the same average K_ν in both cases, then we can obtain the same radiated power with the isotropic radiation distribution

$$\sigma(\hat{\mathbf{k}})=\frac{1}{4\pi} \ ,$$

and the rotating dipole radiation distribution

$$\sigma(\hat{\mathbf{k}})=\frac{3}{16\pi}(1+\cos^2\theta) \ .$$

Now we apply these results to a laser beam which is monochromatic at a frequency ν_1 with a frequency spread $\Delta\nu$. Integration of (8) and (9) gives

$$\Phi(\mathbf{k})=2Bh\nu_1^3 c^{-2}\bar{n}_\nu(\hat{\mathbf{k}})\Delta\nu \tag{10}$$

and

$$\Psi(\mathbf{k})=2Bk_B\nu_1^2 c^{-2}\{[1+\bar{n}_\nu(\hat{\mathbf{k}})]\ln[1+\bar{n}_\nu(\hat{\mathbf{k}})] \\ -\bar{n}_\nu(\hat{\mathbf{k}})\ln\bar{n}_\nu(\hat{\mathbf{k}})\}\Delta\nu \ , \tag{11}$$

where $\bar{n}_\nu(\hat{\mathbf{k}})$ is the average occupation number of the translational mode $\mathbf{k}$ in the frequency range $\Delta\nu$. With these expressions we can now calculate the rate of entropy change of the radiation. This, however, only takes into account the contribution that the change of direction makes to the total entropy change. We have pointed out the loss of coherence of the radiation field; this additional contribution will be taken into account later.

As in thermodynamics, a "flux"[26] or "radiation"[30] temperature can be defined as the ratio of the rate of energy transfer to the rate of entropy transfer:

$$T_F=\left[\frac{\dot{E}}{\dot{S}}\right]=\left[\frac{\Phi}{\Psi}\right] \ . \tag{12}$$

T_F is not always an absolute thermodynamic temperature[26] defined as

$$T_A\equiv\left[\frac{\partial S}{\partial U}\right]_V \ . \tag{13}$$

For near-monochromatic radiation

$$\frac{1}{T_A}=\left[\frac{d\Psi}{d\Phi}\right]=\left[\frac{d\Psi/d\bar{n}_\nu}{d\Phi/d\bar{n}_\nu}\right]=\frac{k}{h\nu_0}\ln(1+\bar{n}_\nu^{-1}) \ , \tag{14}$$

and therefore

$$\bar{n}_\nu=\left[\frac{1}{\exp\left[\dfrac{h\nu_0}{kT_A}\right]}\right] \ . \tag{15}$$

This expression for $\bar{n}_\nu$ relates the temperature to K_ν through Eq. (6) giving the Planck formula

$$K_\nu=\frac{h\nu^3}{c^2}\left[\frac{1}{\exp\left[\dfrac{h\nu}{kT_A}\right]}\right] \ . \tag{16}$$

That is, T_A can be identified as the temperature of a blackbody emitting the same intensity in the same narrow frequency range as the near-monochromatic radiator. In this context, T_A has also been called a "brightness temperature"[26] or an "effective temperature."[25,26] For the near-monochromatic case T_A and T_F are related by

$$\frac{1}{T_F}=\frac{1}{T_A}-\frac{k}{h\nu_0}\left[\exp\left(\frac{h\nu_0}{kT_A}\right)-1\right] \\ \times\ln\left[1-\exp\left(-\frac{h\nu_0}{kT_A}\right)\right] \ . \tag{17}$$

Even though temperatures are not necessary in entropic considerations, the above differences are essential in calculating availabilities or efficiencies.

III. CALCULATION OF ENTROPY CHANGE IN THE ATOMIC BEAM

The sample of hot atoms undergoes a narrowing of its velocity distribution under the constant radiation pressure of the laser beam. The energy and entropy removed are carried away completely by reradiation, because collisional contributions are negligible at the low pressures of the beam experiments. In this section it will be necessary to assume knowledge of the internal state of the atom and of its coupling to the radiation field, even though knowledge of the velocity distribution of the atoms is sufficient to obtain the entropy change.

A. Equilibrium considerations

First, we take the process as the cooling of an equilibrium sample of atoms of an ideal gas and use the initial and final temperatures to calculate the entropy change. The entropy change calculated from the partition function (e.g., the Sackur-Tetrode equation) necessarily is the same as the thermodynamically calculated change

$$\Delta S_{\rm th}=1.5k_B\ln\left[\frac{T_f}{T_i}\right] \ , \tag{18}$$

where the subscripts f and i indicate final and initial temperatures. It is also clear that this result has to serve as an upper limit to the entropy change because the equilibrium-to-equilibrium process produces the maximum entropy reduction.

If a variable x can assume discrete values $\{x_1,x_2,\ldots\}$ and be assigned corresponding probabilities $\{p_1,p_2,\ldots\}$ of assuming those values, then the information theoretic entropy[31,32] is

$$S_I=-k_B\sum_{i=1}^{N}p_i\ln p_i \ . \tag{19}$$

Jaynes[33] warns of the dangers of using the continuous analogue. In our case, we are restricting ourselves to a

Boltzmann gas, hence the entropy of a given state is

$$S_I=-k_B\int w(p)\ln\left[\frac{w(p)}{w_0(p)}\right]dp=H_B=H_G=S_{\text{th}}\ . \tag{20}$$

where $w(p)$ is the momentum (or velocity) distribution function, and H_B and H_G are, respectively, the Boltzmann and Gibbs H's, to be defined below. We consider a monoatomic fluid of M particles and take the ensemble to be defined by the M-particle distribution function, or Liouville function, $W_M(x_1,p_1;x_2,p_2;\ldots;x_M,p_M)$ which gives the probability density in the full phase space of the system. The Gibbs H is

$$H_G=\int W_M\ln W_M d\Gamma\ , \tag{21}$$

where $d\Gamma=d^3x_1\ldots d^3p_M$. The corresponding Boltzmann H is

$$H_B=M\int w_1\ln w_1 d\Gamma_1\ , \tag{22}$$

where the single-particle probability density

$$w_1(x_1,p_1;t)=\int W_M d\Gamma_{-1}\ , \tag{23}$$

and $d\Gamma_{-1}=d^3x_2,\ldots,d^3p_M$ is the phase-space volume element of all particles except one. In equilibrium considerations, we normally choose the state 0 [cf. Eq. (20)] as that which has zero entropy; in nonequilibrium considerations, we choose the state 0 as that to which the nonequilibrium state would tend if the constraints keeping it away from equilibrium were lifted. Since absolute entropies have no significance except in the context of third-law applications and can only be introduced through statistical thermodynamic or quantum theoretic concepts,[34] this choice of reference state amounts to choosing a convenient origin for the entropy.

The state of a system is assumed to be described by the phase-space distribution function $w(\Gamma)=w(x,y,z,p_x,p_y,p_z)$; the entropy of a nonequilibrium state is calculated, with respect to an equilibrium state described by $w_0(\Gamma)$, by integrating Eq. (20) over all phase-space volume elements

$$d\Gamma=dx\,dy\,dz\,dp_x dp_y dp_z\ .$$

If the only difference between the final and initial states (from a Lagrangian system of reference) is a change along the p_z coordinate, then the change in entropy is[34]

$$\Delta S=\int dp_z w(p_z)\ln\left[\frac{w(p_z)}{w_0(p_z)}\right]\ , \tag{24}$$

since all terms of the form $\int d\xi\, w(\xi)$ and $\int d\xi\, w(\xi)\ln[w(\xi)/w_0(\xi)]$ are zero for $\xi=\{x,y,z,p_x,p_y\}$. The Euler relation for the entropy $S(U,V,p_z)$ as a function of the internal energy U, the volume V, and the internal coordinate p_z is given in Ref. 34. This entropy difference should more properly be referred to as the kinetic entropy difference.

If we want to calculate the total entropy change for a process taking a system from an equilibrium state 1 to a nonequilibrium state 3 that would relax to an equilibrium state 2 without external constraints, then we apply

$$\begin{aligned}\Delta S&=(S_3-S_2)+(S_2-S_1)\\&=-k_B\int dv\, w_3(v)\ln\left[\frac{w_3(v)}{w_1(v)}\right]+\frac{k_B}{2}\ln\left[\frac{T_2}{T_1}\right]\ .\end{aligned} \tag{25}$$

The missing factor of 3 in the second term is due to the fact that we are considering one-dimensional cooling [cf. Eq. (18)]. Since T is proportional to v_m^2, the square of the velocity at the maximum of the velocity distribution function, this equation becomes

$$\Delta S=k_B\ln\left[\frac{v_{m2}}{v_{m1}}\right]-k_B\int dv\, w_3(v)\ln\left[\frac{w_3(v)}{w_1(v)}\right]\ . \tag{26}$$

Figure 3 illustrates how this calculation is performed.

B. Exact treatment and calculations

The average velocity in the atomic beam decreases linearly in time according to Newton's second law and ultimately can be reversed; the evolution of the internal velocity distribution relative to this average velocity has to be computed. A distribution function that followed the real time-dependent behavior of the system would determine the true entropy change in the sample, and could be compared with the entropy change in the beam of photons. This function can be obtained as the solution of a nonlinear, partial differential equation governing the change in time of the velocity distribution function of the atoms traveling in a particular direction, opposed by a counterpropagating laser beam that narrows the distribution, which in turn broadens due to diffusion (a Fokker-Planck equation[35]). This diffusion equation cannot be obtained from a macroscopic treatment of the problem because the translational motion of the atoms is quantized on a time scale smaller than the time scale during which the stopping process takes place. The atoms are subjected to an average force which is the gradient of the product of the electromagnetic field intensity and the average dipole moment. The quantized behavior of the dipole moment produces fluctuations in the force. These fluctuations produce uncertainties in the momentum of the order of the momentum transferred to the atoms in the time scale discussed above. One must therefore look to a quantum-mechanical treatment to obtain this equation. Since most electro-optic phenomena, resonance fluorescence being one, do not require quantization of the field, it is not necessary to quantize the radiation field[36] but it is necessary to recognize the discrete changes of the translational motion of the atoms.[9]

First, the two-level atom interacting with the classical field is considered and the equations of motion of the four relevant amplitudes of the wave function are determined in the interaction representation.[37] These equations are needed to obtain the equation of motion of the density matrix $\rho(\mathbf{r}_1,\mathbf{r}_2,t)$, the master equation:

$$i\frac{\partial\rho}{\partial t}=(\mathscr{H}_1-\mathscr{H}_2^*)\rho-i\Gamma\rho\ . \tag{27}$$

The density matrix depends on the coordinate of the atom's center of mass, r_1 and r_2, at different times t_1 and t_2. The Hamiltonian $\mathscr{H}$ is

$$\mathscr{H}=\mathscr{H}_0-\frac{\hbar^2}{2m}\nabla^2+\mathscr{V}\ , \tag{28}$$

where $\mathscr{H}_0$ is the internal Hamiltonian, $-(\hbar^2/2m)\nabla^2$ is the translational Hamiltonian, and $\mathscr{V}$ the dipole field interaction Hamiltonian. Γ is the phenomenological relaxation operator. The density matrix can be transformed[9] from the internal coordinates of the center of mass $(\mathbf{r}_1,\mathbf{r}_2)$ to the coordinates $(\mathbf{r}=\mathbf{r}_1+\mathbf{r}_2/2,\ \mathbf{x}=\mathbf{r}_1-\mathbf{r}_2)$. These coordinates are used to introduce the Wigner density function:

$$\rho(\mathbf{p},\mathbf{r},t)=\frac{1}{(2\pi\hbar)^3}\int e^{-i\mathbf{p}\cdot\mathbf{x}/\hbar}\rho\left[\mathbf{r}-\frac{\mathbf{x}}{2},\mathbf{r}+\frac{\mathbf{x}}{2},t\right]dx\ , \tag{29}$$

in terms of which Eq. (27) can be written as a system of integro-differential equations. The quantization of the center-of-mass coordinates is clearly seen upon expansion of the field in terms of plane waves and substitution of

$$\mathscr{V}(\mathbf{r},t)=\int \mathscr{V}(\mathbf{k},t)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}\ , \tag{30}$$

in the integro-differential equations obtained from the Wigner density function. The electromagnetic field connects states differing in momentum by an amount proportional to the photon momentum $\hbar\mathbf{k}$. Substitution of the field into these equations and the assumption that the rotating-wave approximation is valid results in equations that do not contain rapidly oscillating terms. The elements of $\rho(\mathbf{p},\mathbf{r},t)$ can be combined to form Bloch variables[38] and to obtain an equation of motion for the trace of ρ. The longitudinal velocity distribution function is then

$$w(v_l,t)=\int \rho(\mathbf{v},\mathbf{r},t)d\mathbf{v}_{\mathrm{nl}}d\mathbf{r}\ , \tag{31}$$

where the integral is performed over the nonlongitudinal velocity components $\mathbf{v}_{\mathrm{nl}}$ and over the position vector $\mathbf{r}$. The longitudinal subscript l is assumed implicit from now on. Restriction to the time regime discussed above leads to the following equation for the velocity distribution function:[19]

$$\frac{\partial w(v,t)}{\partial t}=-\frac{\partial[A(v)w(v,t)]}{\partial v}+\frac{\partial^2[D(v)w(v,t)]}{\partial v^2}\ , \tag{32}$$

where

$$A=\frac{-G}{[1+G+(v+\delta)^2]}$$

is the atomic deceleration due to the light pressure force and

$$D=\frac{2\epsilon X G}{[1+G+(v+\delta)^2]}$$

is the atomic velocity diffusion coefficient in the longitudinal velocity space. The equation is written in dimensionless variables t and v; their dimensional forms are t/kv_r and $\tau v/k$, respectively; $k=|\mathbf{k}|$. v_r is the recoil velocity $\hbar k/m$. The following dimensionless parameters were also introduced: the saturation parameter

$$G=\left[\frac{1}{2}\right]\left[\frac{\mu E_0\tau}{\hbar}\right]^2,$$

the detuning

$$\delta=\Upsilon\tau\ ,$$

and the parameter

$$\epsilon=\frac{kv_r\tau}{2}\ll 1\ .$$

Here μ is the atomic transition dipole moment, and $\Upsilon=\omega-\omega_0$ is the field frequency detuning with respect to the atomic transition frequency ω_0. The parameter ϵ compares the time scale of the translational motion of the atoms with the time scale of reradiation of the photons or the time scale of interaction with the field.

Equation (20) can be solved analytically if the diffusive part is neglected. By the method of characteristics,[39] with the initial condition that the atoms have an equilibrium distribution

$$w(v,0)=\left[\frac{4}{\sqrt{\pi}v_m^3}\right]v^3\exp\left[-\left[\frac{v}{v_m}\right]^2\right]\Theta(v)\ , \tag{33}$$

where $\Theta(v)$ is the Heaviside function, the solution is found to be

$$w(v,t)=\left[\frac{4}{\sqrt{\pi}v_m^3}\right]\left[\frac{1+G+(v+\delta)^2}{1+G+[\alpha(v,t)+\beta(v,t)]^2}\right]\times\exp\left[-\left[\frac{\alpha(v,t)+\beta(v,t)-\delta}{v_m}\right]^2\right]\times\Theta(\alpha(v,t)+\beta(v,t)-\delta)\ , \tag{34}$$

where

$$\alpha(v,t)=[\sqrt{q(v,t)}+\eta(v,t)]^{1/3}\ ,$$

$$\beta(v,t)=-[\sqrt{q(v,t)}-\eta(v,t)]^{1/3}\ ,$$

$$q(v,t)=(1+G)^3+\eta(v,t)^2\ ,$$

$$\eta(v,t)=0.5(v+\delta)^3+1.5(1+G)(v+\delta)+1.5Gt\ .$$

Here, $v_m=\sqrt{2k_BT/m}=\sqrt{\pi}\bar{v}/2$ is the velocity at the maximum of the velocity distribution, where $\bar{v}$ is the average velocity and T is the temperature. The distribution for the case where diffusion was not neglected was determined numerically by using a forward differences method to determine the evolution of the initial condition, Eq. (33), according to the governing equation (32).

IV. RESULTS

To calculate the entropy using Eq. (26), we numerically integrated the distribution function up to $3\bar{v}$ since this will cover 99.96% of the area under the curve $w(v,t)$ at any given time. Of course, at time $t=0$ both the entropy calculated from equilibrium considerations, and the entropy calculated from Eq. (34) were equal (-61.0796 J/K mole).

TABLE I. Results.

Run	G	δ	ΔS (J/K—one mole basis)
1	6.425	-0.169	-61.0644
2	6.425	-0.3384	-61.0641
3	6.625	-5.0	-61.0561
4	40.0	-0.169	-61.0024
5	0.0	-0.169	-61.0792
6	6.425	0.0	-61.0647

Photons

ΔS	4.73×10^{11} J/K (one mole basis)

At any time t, the former provides a lower bound to the entropy change, while the latter provides an upper bound. This is so because an equilibrium-to-equilibrium calculation provides maximal entropy change. Table I illustrates that the bounds are quite tight. At later times, as the distribution deviates from the equilibrium distribution, the entropy calculated is less than the equilibrium entropy at the corresponding temperature as defined by the average kinetic energy. Even though the model including the diffusion gives a distribution function with characteristics quite distinct from the model neglecting diffusion, the entropy differences are not substantial. The difference is a slightly broader profile shifted to higher velocities. The tight bounds substantiate this result. It is also apparent that detuning too far away from the absorption line requires an increase in the rate of entropy production per unit of momentum transferred. In this situation, the atoms interact with only a fraction of the available photons. Increasing the saturation parameter requires a decrease in the rate of entropy production per unit of momentum transferred because the atoms are interacting with a stronger field which has more available energy to slow them down. In both these cases we require that the final state be reached within the allotted time. The total time of the process (still in dimensionless units) is

$$\Delta t=\frac{(\overline{v}_{\text{initial}}-\overline{v}_{\text{final}})}{v_r} . \tag{35}$$

Choosing a transition at higher frequency ν_0 would provide more stopping power to the atoms, bringing them to a stop in a shorter period of time. Since τ, ν_0, and μ are related, G is likely to change with ν_0, changing the rate of entropy production. The photon beam makes a positive contribution to the entropy change from the ν^2 term in Eq. (11) and a negative contribution to the entropy change from the smaller Δt term in the following equation. The net change for the photons will increase proportionally to the frequency. The situation for the atoms will depend on the particular experimental conditions.

The change of entropy of the photons is

$$\Delta S_{\text{photons}}=\left[\frac{N_a\Delta t}{2\tau}\right]\left[\left[\int\int(\Psi_2-\Psi_1)dA\,dt\right]-k_B\vartheta\ln\left[\frac{\vartheta}{2\pi}\right]\right] , \tag{36}$$

where ϑ is the initial phase coherence of the laser beam. For the conditions presented in Table II, the change of entropy for a rotating dipole is approximately 15% smaller than for an isotropic radiator dissipating the same amount of energy (cf. Appendix B). The change of entropy of the atoms is

$$\Delta S_{\text{atoms}}=(kN_a)\left[\tfrac{1}{2}\ln\left[\frac{T_2}{T_1}\right]-\int dv\,w_3(v)\ln\left[\frac{w_3(v)}{w_1(v)}\right]\right]<0 . \tag{37}$$

Comparison of these two quantities for an experiment like the one described in Ref. 1, yields

$$|\Delta S_{\text{photons}}| > |\Delta S_{\text{atoms}}| . \tag{38}$$

Ideally, coherent radiation can produce an infinite temperature in an absorber, thus delivering heat at zero entropy. It can also produce work with no dissipation of energy. Therefore the above process can be modeled as having a reversible component that converts one form of zero-

TABLE II. Typical values of the parameters for representative experimental conditions.

Atomic species		Sodium
Excited transition		${}^2S_{1/2}(F=2,\ m_F=2)\rightarrow{}^2P_{3/2}(F=3,\ m_F=3)$
	ν_0	5.048×10^{14} Hz
	τ	16 ns$=$9.95 MHz
	μ	6.46 D
Field	E	6.88×10^{3} V/m
	$(\Delta\nu)_{\text{laser}}$	10 MHz
Experiment	R	1.6 m
	N_a	1×10^{5}
	$\overline{v}_{\text{initial}}$	1000 m/s
	$\overline{v}_{\text{final}}$	0.665 m/s
	B	3.07×10^{-7}
Control parameters	δ	0 to -5
	G	0–40

entropy energy into another ($\Delta S=0$), plus an irreversible part that takes into account all other entropy changes.[40] The total entropy change is then

$$\Delta S_{\text{total}}=\Delta S_{\text{irrev}}=(\Delta S_{\text{photons}}-|\Delta S_{\text{atoms}}|)>0\ . \tag{39}$$

The result is that the photon beam undergoes an entropy gain orders of magnitude larger than the corresponding entropy loss in the samples of atoms. This is apparent when we consider that for a typical experiment the number of scattered photons required to bring one atom to a stop is of the order of 30 000. The contribution of the loss of coherence to the change in entropy is negligible.

In what follows, we conduct a thermodynamic analysis of the process. The brightness temperatures for the laser beam before and after the absorption (under the conditions of run 1, Table I) are 5.6×10^{9} and 4666 K, respectively. Treating this process as a heat pump operating between these two temperatures yields a Carnot efficiency

$$\eta_C=1-\left[\frac{T_{\text{cold}}}{T_{\text{hot}}}\right]=1-(8.4\times10^{-7})\ . \tag{40}$$

This heat engine converts as much heat as possible into work (i.e., there are no inherent irreversibilities in its operation). The entropy flow generated if this engine were operated infinitely slowly would be negligible because it would entail taking one photon at a time out of the beam and changing its direction. In this case, the phase coherence of one photon is devoid of meaning. However this engine operates at a nonzero rate and must therefore pay a price—entropy must be generated. The irreversibility of the process is then an excess irreversibility.

In Ref. 17, it is shown that the minimum temperature in the slowed-down atomic beam is

$$T_{\min}=\frac{7}{20}\left[\frac{\hbar}{k_B\tau_s}\right]\ , \tag{41}$$

where $\tau_s=\tau/(1+G)^{1/2}$. Since the laser is not perfectly tuned on resonance and the absorption line has a finite natural width, this minimum temperature is not reached. For a beam of atoms stopped to $\bar{v}=0$ with a laser detuned at Υ, the actual temperature reached is

$$T_{\min}(\bar{v}=0)\approx\left[\frac{|\Upsilon|\tau_s}{2}\right]T_{\min}\ , \tag{42}$$

so that, for a chosen spectral line, the minimum temperature attainable depends only on the detuning off-resonance. It is this temperature that is used to obtain the kinetic energy of the final equilibrium distribution to which the nonequilibrium velocity distribution would relax (cf. Fig. 3) if the constraint of the radiation pressure were lifted. As mentioned before, in the analysis of this process we consider the entropy actually produced, by both inherent irreversibilities (equilibrium to nonequilibrium) and excess irreversibilities (finite-time operation), as composed of an equilibrium-to-equilibrium step with no inherent reversibilities plus a step from that second equilibrium state to the final nonequilibrium state in which we take into account all irreversibilities.

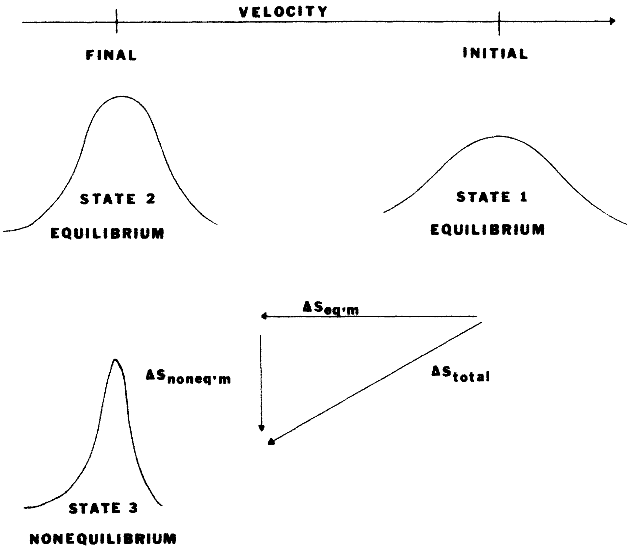

FIG. 3. Schematic changes in the velocity distribution function.

The formalism of finite-time thermodynamics[41] may be brought to bear on this problem in the determination of the optimal path for the process with $G(t)$ and $\Upsilon(t)$ as control variables and the total time of the process fixed. We take objective function (to be minimized, in this case) as the entropy produced

$$\Delta S=\int_0^{\Delta t}dt\,\dot{S}(G(t),\Upsilon(t))\ . \tag{43}$$

Equation (32) could then be solved to give the time evolution of the narrowing distribution under the conditions of power and detuning that vary with time to produce the minimum entropy.

Without solving the optimal control problem, we can treat the process as refrigeration without a thermostat; that is, the temperature decreases with time down to some specified value in time Δt. Initially the temperature of the atoms is 1095 K and any heat removed at this temperature can be assumed to be dumped through the radiation field to a sink at 4666 K; subsequently the atomic temperature decreases to a temperature on the order of 1 K. Calculating the efficiency for a refrigerator[42]

$$\eta_{\text{refrig}}=\left[\frac{T_{\text{cold}}}{T_{\text{hot}}-T_{\text{cold}}}\right]\ , \tag{44}$$

gives an initial efficiency decreasing from 0.31 down to 2×10^{-4} and lower. In a model for which the temperature depends on the square of the velocity which in turn decreases linearly with time, the rate of change of the efficiency is

$$\dot{\eta}_{\text{refrig}}(t)=\left[\frac{T_{\text{hot}}}{[T_{\text{hot}}-T(t)]^2}\right]\dot{T}(t)\ . \tag{45}$$

Hence, even though the laser provides a constant stopping power to the atoms it does not narrow the velocity distribution at a constant rate. The work that the laser transfers to the atoms appears as work in the slowing down of the atoms. The heat that is removed from the atoms in narrowing their velocity distribution appears as entropy in the reradiated photons' more nearly isotropic propagation and incoherence. The former process involves the transformation of one zero-entropy form of energy into another while the latter process does not.

There are other parts of this experimental procedure that can be studied to find their sources of irreversibilities such as the traps[5] that have been designed to contain the atoms once they have been slowed down to velocities of the order of 1 m/s. In one such optical trap,[6] for example, the atoms again lose momentum by scattering photons. Apart from carrying on an analysis as the above, it is now possible to perform a classical hydrodynamical treatment[8] of the problem because in this three-dimensional problem the fluctuations discussed before should average out to zero. The trap can be modeled as a region of high viscosity and the way the velocity distribution functions inside and outside the high viscosity region change with time would yield information on the transfer of energy from the field to the atoms.

ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy. The authors wish to thank Dr. Harold Metcalf for pointing this problem out to us.

APPENDIX A

A dipole rotating in the x-y plane ($\theta=\pi/2$) is defined at any given time t by the angle $\phi_0(t)$ it makes with the x axis. Since its radiation pattern is a $\sigma=\sin^2\chi$ distribution about its instantaneous axis of oscillation, the distribution at a general point (θ,ϕ) on the unit sphere will be

$$\sigma=1-\cos^2\chi=1-\cos^2\left(\theta-\frac{\pi}{2}\right)\cos^2[\phi-\phi_0(t)] .$$

Averaging over many periods of dipole rotation on the x-y axis we obtain

$$\sigma=1-\sin^2\theta\cos^2\phi .$$

All points with the same ϕ will have the same distribution so that the normalized distribution is

$$\sigma=\frac{3}{8\pi}(1-\tfrac{1}{2}\sin^2\theta)=\frac{3}{16\pi}(1+\cos^2\theta) .$$

APPENDIX B

The rate of entropy change is

$$\begin{aligned}\dot{S}&=\int\Psi\,dA=B\int\int L_\nu d\nu\,dA ,\\ &=B\int\left[2k_B\nu^2c^{-2}\int_0^{2\pi}\int_0^{\pi}d\phi\,d\theta(\sin\theta)\{[1+n_\nu\sigma(\hat{\mathbf{k}})]\ln[1+n_\nu\sigma(\hat{\mathbf{k}})]-n_\nu\sigma(\hat{\mathbf{k}})\ln n_\nu\sigma(\hat{\mathbf{k}})\}\right]d\nu .\end{aligned}$$

For $n_\nu \ll 1$ the following approximation is valid:

$$\begin{aligned}&[1+n_\nu\sigma(\hat{\mathbf{k}})]\ln[1+n_\nu\sigma(\hat{\mathbf{k}})]-n_\nu\sigma(\hat{\mathbf{k}})\ln n_\nu\sigma(\hat{\mathbf{k}})\\ &\qquad\approx n_\nu\sigma(\hat{\mathbf{k}})-n_\nu\sigma(\hat{\mathbf{k}})\ln n_\nu\sigma(\hat{\mathbf{k}}) .\end{aligned}$$

Substituting this expression in the above integral we obtain

$$\begin{aligned}\dot{S}=B\int&\Bigg[2k_B\nu^2c^{-2}(2\pi)\\ &\times\int_0^{\pi}d\phi\,d\theta(\sin\theta)\\ &\times[n_\nu\sigma(\hat{\mathbf{k}})-n_\nu\sigma(\hat{\mathbf{k}})\ln n_\nu\sigma(\hat{\mathbf{k}})]\Bigg]d\nu .\end{aligned}$$

For the isotropic radiator this integration yields

$$\dot{S}=B\int\left[2k_B\nu^2c^{-2}\left(n_\nu-n_\nu\ln\frac{n_\nu}{4\pi}\right)\right]d\nu .$$

For the rotating dipole oscillator, the integration is simplified by letting $\cos\theta=w$ and integrating over w. The result is

$$\dot{S}=B\int\left\{2k_B\nu^2c^{-2}\left[\left(n_\nu-\nu_\nu\ln\frac{n_\nu}{4\pi}\right)-1.333n_\nu\right]\right\}d\nu .$$

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[1] A. L. Migdall, J. V. Prodan, W. D. Phillips, T. H. Bergeman, and H. J. Metcalf, Phys. Rev. Lett. **54**, 2596 (1985).

[2] J. V. Prodan, A. Migdall, W. D. Phillips, I. So, H. J. Metcalf, and J. Dalibard, Phys. Rev. Lett. **54**, 992 (1985).

[3] J. V. Prodan, W. D. Phillips, and H. J. Metcalf, Phys. Rev. Lett. **49**, 1149 (1982).

[4] W. D. Phillips and H. Metcalf, Phys. Rev. Lett. **448**, 1149 (1982).

[5] W. D. Phillips, J. V. Prodan, and H. J. Metcalf, J. Opt. Soc. Am. B **2**, 1751 (1985).

[6] W. Ertmer, R. Blatt, J. L. Hall, and M. Zhu, Phys. Rev. Lett. **54**, 996 (1985).

[7] S. Chu, L. Hollberg, J. E. Bjorkholm, A. Cable, and A. Ashkin, Phys. Rev. Lett. **55**, 48 (1985).

[8] V. S. Letokhov, Zh. Eksp. Teor. Fiz. **34**, 506 (1958) [Sov. Phys.—JETP **7**, 348 (1968)].

[9] A. P. Kol'chenko, S. G. Rautian, and R. I. Sokolovskii, Zh. Eksp. Teor. Fiz. **55**, 1864 (1968) [Sov. Phys.—JETP **28**, 986 (1969)].

[10] A. P. Kazantzev, Zh. Eksp. Teor. Fiz. **66**, 1599 (1974) [Sov. Phys.—JETP **39**, 784 (1974)].

[11] V. S. Letokhov, V. G. Minogin, and B. D. Pavlik, Zh. Eksp. Teor. Fiz. **72**, 1328 (1977) [Sov. Phys.—JETP **45**, 698 (1977)].

[12] A. Y. Pusep, Zh. Eksp. Teor. Fiz. **70**, 851 (1976) [Sov. Phys.—JETP **43**, 441 (1976)].

[13] A. Ashkin, Phys. Rev. Lett. **40**, 729 (1978).

[14] I. V. Krasnov and N. Ya. Shaparev, Opt. Commun. **27**, 239 (1978); Zh. Eksp. Teor. Fiz. **77**, 899 (1979) [Sov. Phys.—JETP **50**, 453 (1979)].

[15] J. L. Picqué, Phys. Rev. A **19**, 1622 (1979).

[16] R. J. Cook, Phys. Rev. A **22**, 1078 (1980).

[17] V. G. Minogin, Opt. Commun. **34**, 265 (1980); **37**, 442 (1981).

[18] V. G. Minogin, V. S. Letokhov, and T. V. Zueva, Opt. Commun. **38**, 225 (1981).

[19] V. G. Minogin, Zh. Eksp. Teor. Fiz. **79**, 2044 (1980) [Sov. Phys.—JETP **52**, 1032 (1980)].

[20] V. I. Balykin, V. S. Letokhov, and V. I. Mushin, Zh. Eksp. Teor. Fiz. **29**, 516 (1979) [Sov. Phys.—JETP **29**, 560 (1979)], and all work referenced above.

[21] Atomic beams stopped by laser light, and trapped, Phys. Today **38**(6), 17 (1985).

[22] Sodium atoms stopped and confined, Science **29**, 39 (1985).

[23] A. Ashkin, Phys. Rev. Lett. **24**, 156 (1970).

[24] T. W. Hänsch and A. L. Schawlow, Opt. Commun. **13**, 68 (1975).

[25] M. A. Weinstein, J. Opt. Soc. Am. **50**, 597 (1960), Phys. Rev. **119**, 499 (1960).

[26] P. T. Landsberg and G. Tonge, J. Appl. Phys. **51**, R1 (1980).

[27] M. Planck, *The Theory of Heat* (MacMillan, New York, 1949), p. 147.

[28] P. Rosen, Phys. Rev. **96**, 555 (1954).

[29] A. Ore, Phys. Rev. **98**, 887 (1955).

[30] M. Garbuny, J. Chem. Phys. **67**, 5676 (1977).

[31] S. Kullback, *Information Theory and Statistics* (Wiley, New York, 1958).

[32] C. E. Shannon, Bell Syst. Tech. J. **27**, 379 (1948); **27**, 623 (1948).

[33] E. T. Jaynes, *Papers on Probability, Statistics, and Statistical Physics* (Reidel, Dordrecht, 1983), pp. 60ff.

[34] L. C. Woods, *The Thermodynamics of Fluid Systems* (Clarendon, Oxford, 1975).

[35] H. Risken, *The Fokker-Planck Equation: Methods of Solution and Application* (Springer-Verlag, Berlin, 1984).

[36] M. O. Scully and M. Sargent III, Phys. Today **25**(3), 38 (1972).

[37] M. Sargent, M. O. Scully, and W. E. Lamb, Jr., *Laser Physics* (Addison-Wesley, Reading, Mass., 1974).

[38] M. O. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).

[39] G. F. Carrier and C. E. Pearson, *Partial Differential Equations* (Academic, New York, 1976), Chap. 5.

[40] R. C. Tolman and P. C. Fine, Rev. Mod. Phys. **20**, 51 (1948).

[41] B. Andresen, R. S. Berry, M. J. Ondrechen, and P. Salamon, Accts. Chem. Res. **17**, 226 (1984).

[42] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).