Entropy production and kinetic effects of light

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We study the production of total entropy in the situation where light has kinetic effects on atoms or molecules. The radiation entropy has the standard form of boson entropy, and the matter entropy is the sum of Boltzmann entropies for excited and nonexcited particles. The matter entropy density is separated into three parts, corresponding to the total velocity distribution, the distribution over internal states, and the correlation between the two. Each of these parts can be changed by the interaction with light. We calculate explicitly the production of both matter and photon entropy in several cases where light is known to induce macroscopic flows in gases. The production rate of matter entropy is expressed in macroscopic quantities. Some other examples, such as laser cooling, are considered briefly. In all cases, the increase of photon entropy is found to be several orders of magnitude larger than the decrease of matter entropy.

PACS number(s): 05.70.Ln, 42.50.Vk, 05.20.Dd

I. INTRODUCTION

Light can create order in matter. Since the advent of lasers it has become possible to manipulate atoms, molecules, and ions in an accurately controllable way; see, for instance, [1–3]. One utilizes the laser photon momentum, well defined both in direction and in magnitude, to control the particle velocities. For example, workers have recently succeeded in cooling atoms to very low temperatures in the microkelvin region using so-called polarization gradient cooling [4,5]. Here, the polarization of the photons plays an important role as well. Finally, it has become possible to trap neutral atoms in a light field. Also single ions in an electromagnetic trap can be cooled down to a few millikelvins [6,7]. For a small number of ions crystals can be formed [8]. Hence, with laser light the accessible volume in phase space of matter can be diminished dramatically, both by narrowing the velocity spread of the particles and by confining them to a small spatial volume.

Furthermore, light can induce macroscopic flows of particles, translational energy, or particle momentum in a gas at room temperature or higher and with much higher densities such that particle collisions are important. These effects are not based on the transfer of photon momentum, since the particle momentum is much higher, so that particles exchange much larger amounts of momentum during velocity-changing collisions. Now a difference in collisional properties of excited and nonexcited particles may lead to the net transport of particle momentum and energy. Experiments have been done on several manifestations of these light-induced kinetic effects (LIKE). Macroscopic flows have been demonstrated in gases resulting from collisions of the optically active gas with (i) a foreign buffer gas [9], (ii) the walls of a cell [10], and (iii) the gas itself [11]. In these cases the light keeps the gas out of thermal equilibrium, resulting in light-induced gradients of density, mean velocity, or translational temperature. The velocity distribution

function of the gas is no longer a Maxwellian, even in a stationary state.

Thus light is apparently able to lower the entropy of matter. Furthermore, light can keep matter in a (stationary) state with entropy lower than in thermal equilibrium. Moreover, when matter in a closed volume is kept in a stationary state, but not in thermal equilibrium, there can be a negative production of matter entropy in the bulk. This must be compensated for by a flow of entropy through the wall so that the entropy of the outside world (the wall) decreases. Because of the second law of thermodynamics, the entropy of the photons must increase in all of these cases. In the just-mentioned examples, the unidirectional character of the laser photons is crucial, as is the subsequent spontaneous emission of the photon. Spontaneously emitted photons are spread over all directions, and thus have a larger entropy, because the number of modes occupied by the photons increases. This is the most important reason why the entropy in the radiation field increases. Weinstein [12] compared the increase of photon entropy with the decrease of matter entropy resulting from spontaneous decay of a sample of atoms.

When both matter and photons are near thermal equilibrium, the entropy exchange during their relaxation towards complete equilibrium is more subtle. Changes in radiation entropy are brought about by Doppler shifts in the frequencies of the photons. The presence of a black boundary rather than a perfectly reflecting wall is crucial for the process of reaching a state with a single temperature for matter and photons [13].

Eu and Mao [14] recently developed a kinetic theory for both photons and particles. In this way they obtain an "H theorem." That is, a quantity is found that always increases during the interactions of particles and photons except in complete thermal equilibrium. In thermal equilibrium this quantity corresponds to the sum of the thermodynamical entropies of matter and radiation.

In the present paper we first obtain, following the approach of Eu and Mao with a slight modification, an H

theorem using the standard expression for nonequilibrium entropy for both matter and photons. We also indicate some similarities between the approximations used to derive this H theorem, on the one hand, and the well-known Boltzmann H theorem on the other hand.

Section III deals with general aspects of the local production of matter entropy, such as the sign and interpretation of various terms. Furthermore, a natural separation of the matter entropy itself arises, with each part having a clear interpretation. In Sec. IV we give an expression for the production of photon entropy resulting from the scattering of laser photons by matter.

Subsequently we calculate the rate of matter entropy production under the typical experimental conditions encountered in LIKE. The entropy production takes the standard form of the product of a macroscopic flux and the gradient of a corresponding macroscopic quantity [15].

To our knowledge there is only one paper in which an explicit calculation is given on the entropy production in a particular laser-cooling experiment [16]. In the present paper we will be mainly concerned with LIKE in gases. We give explicit expressions for the change of entropy of the gas as a function of the laser parameters and particle properties, and for the resulting change of the radiation entropy. These two expressions are compared for typical values of the controllable parameters. The gain of order in the gas turns out to be, typically, at least six orders of magnitude smaller than the loss of order in the photon field, which confirms that these processes are highly irreversible. Finally, we also consider briefly other experiments, such as laser cooling, in which laser photons transfer part of their order to matter, and estimate the efficiency of these processes.

II. ENTROPY AND H THEOREMS

The Boltzmann equation for a single-component gas is a rate equation for the distribution function $f(\mathbf{c}, \mathbf{r}, t)$ over velocity $\mathbf{c}$ and position $\mathbf{r}$ at time t. It reads [15,17]

$$\frac{\partial f}{\partial t} = -\mathbf{c} \cdot \nabla f + \left[\frac{\partial f}{\partial t} \right]_{\text{coll}} ,   \tag{1}$$

with

$$\left[\frac{\partial f}{\partial t} \right]_{\text{coll}} = \int d\mathbf{c}_1 \int d\mathbf{c}_2 \int d\mathbf{c}_3 W(\mathbf{c}, \mathbf{c}_1 | \mathbf{c}_2, \mathbf{c}_3)(f_2 f_3 - f f_1)   \tag{2}$$

the rate of change due to collisions. Here $W(\mathbf{c}, \mathbf{c}_1 | \mathbf{c}_2, \mathbf{c}_3)$ is the transition probability density for velocity changes in an elastic collision

$$\mathbf{c}, \mathbf{c}_1 \leftrightarrow \mathbf{c}_2, \mathbf{c}_3 .$$

This transition probability density contains δ functions that take care of conservation of momentum and energy. Because of reversibility of elastic collisions, it satisfies

$$W(\mathbf{c}, \mathbf{c}_1 | \mathbf{c}_2, \mathbf{c}_3) = W(\mathbf{c}_2, \mathbf{c}_3 | \mathbf{c}, \mathbf{c}_1) .   \tag{3}$$

This was, in fact, already used in (2).

The Boltzmann entropy density s_B is defined by

$$s_B = -k \int d\mathbf{c} f \ln(af) ,   \tag{4}$$

with k Boltzmann's constant and a an arbitrary constant such that af is dimensionless. From the quantum-mechanical density of states, one finds that a is equal to [15]

$$a = h^3/m^3 ,   \tag{5}$$

where m is the atomic mass. For this value of a, af is the number of atoms in a unit cell in phase space with dimension $dm\,c\,d\mathbf{r} = h^3$.

With the help of the reversibility property (3) and the obvious symmetry relation

$$W(\mathbf{c}_1, \mathbf{c} | \mathbf{c}_3, \mathbf{c}_2) = W(\mathbf{c}, \mathbf{c}_1 | \mathbf{c}_2, \mathbf{c}_3) ,   \tag{6}$$

one can prove the H theorem [15,17]

$$\left[\frac{\partial s_B}{\partial t} \right]_{\text{coll}} \geq 0 .$$

Thus entropy always increases during collisions. Only in thermal equilibrium does the entropy remain constant. As is well known, the H theorem leads to the velocity distribution function of a gas in thermal equilibrium, the Maxwell distribution. It is given by

$$W_0(\mathbf{c}) = n \left[\frac{m}{2\pi kT} \right]^{3/2} \exp[-m(\mathbf{c} - \mathbf{v})^2/2kT] .   \tag{7}$$

The number density n, the mean velocity $\mathbf{v}$, and the translational temperature T are defined in terms of the distribution function f,

$$n = \int d\mathbf{c} f , \quad n\mathbf{v} = \int d\mathbf{c}\, \mathbf{c} f ,$$
$$\tfrac{3}{2} nkT = \int d\mathbf{c} \tfrac{1}{2} m (\mathbf{c} - \mathbf{v})^2 f .   \tag{8}$$

The Boltzmann equation is an irreversible rate equation for the particle distribution functions. It is based on two assumptions. First, the time between two collisions is assumed to be long compared with the duration of a collision, so that only binary collisions have to be considered. Second, the velocity distributions of the collision partners are assumed to be uncorrelated before the collision. This "Stosszahlansatz" brings in the irreversibility of the Boltzmann equation. These assumptions are justified if the gas is sufficiently dilute. One can then describe the gas by the one-particle distribution function $f(\mathbf{c}, \mathbf{r}, t)$.

The evolution of the internal state of a two-level atom in a radiation field can also be described by rate equations, provided that the bandwidth of the field is broad compared with the homogeneous linewidth of the atom. Then the optical coherences can be adiabatically eliminated and the atoms are described by the velocity distribution functions f_e and f_g for the two internal states, the excited state e and the ground state g. The photon field can be described by a photon distribution function $f_r(\mathbf{k}, \mathbf{r}, t)$, defined as the number of photons per mode, ir-

respective of polarization. Since $2(2\pi)^{-3}d\mathbf{k}$ is the density of modes with wave vector in $d\mathbf{k}$, the normalization of f_r is given by

$$2(2\pi)^{-3} \int d\mathbf{k}\, f_r(\mathbf{k}) = n_r \,, \tag{9}$$

with n_r the number of photons per unit volume. The factor of 2 is due to the two different modes corresponding to the two independent possible polarization directions for each photon.

Next, we introduce a transition probability density $W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k})$ for the spontaneous emission process

$$\mathbf{c}_e \rightarrow \mathbf{c}_g, \mathbf{k}$$

in which an excited particle with velocity $\mathbf{c}_e$ decays to the ground state with velocity $\mathbf{c}_g$ emitting a photon with momentum $\mathbf{k}$ and arbitrary polarization. It is normalized so as to give the Einstein coefficient for spontaneous emission A,

$$A = 2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_g\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k}) \,, \tag{10}$$

independent of $\mathbf{c}_e$. The transition probability density contains a δ function because of conservation of momentum and a Lorentzian around the Doppler-shifted resonance frequency with a width proportional to A. Since the ratio between the rates of stimulated and spontaneous emission into a given mode is given by the number of photons in that mode [18], the rate of stimulated emission is given by

$$B(\mathbf{c}_e) = 2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_g\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k}) f_r(\mathbf{k}) \,, \tag{11}$$

which now does depend on $\mathbf{c}_e$ owing to the Doppler effect. We only have to account for single-photon transitions. This is analogous to the neglect of n-particle collisions with $n > 2$ in the Boltzmann equation.

The equations describing radiative transitions for the velocity distribution functions f_e and f_g of excited- and

ground-state atoms and for the photon distribution function f_r can now be given in a form similar to the Boltzmann equation. When we use the reversibility of stimulated transitions, we find

$$\left[\frac{\partial f_e}{\partial t} \right]_{\mathrm{rad}} = 2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_g\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k})$$
$$\times [f_g f_r - f_e(1+f_r)] \,,$$

$$\left[\frac{\partial f_g}{\partial t} \right]_{\mathrm{rad}} = 2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_e\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k})$$
$$\times [-f_g f_r + f_e(1+f_r)] \,, \tag{12}$$

$$\left[\frac{\partial f_r}{\partial t} \right]_{\mathrm{rad}} = \int d\mathbf{c}_e \int d\mathbf{c}_g\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k})$$
$$\times [-f_g f_r + f_e(1+f_r)] \,.$$

We now introduce the total entropy density s as the sum

$$s = s_m + s_r \,, \tag{13}$$

with

$$s_m = -k \sum_{i=e,g} \int d\mathbf{c}_i f_i \ln(a f_i) \,, \tag{14}$$

the matter entropy density, where a is defined in (5), and with

$$s_r = -k 2(2\pi)^{-3} \int d\mathbf{k}[f_r \ln f_r - (1+f_r)\ln(1+f_r)] \,, \tag{15}$$

the photon entropy density, in the standard form of entropy for a boson system [15]. For the local production of total entropy during radiative transitions, we obtain

$$\left[\frac{\partial(s_m + s_r)}{\partial t} \right]_{\mathrm{rad}} = -k2(2\pi)^{-3} \int d\mathbf{k}[\ln f_r - \ln(1+f_r)] \left[\frac{\partial f_r}{\partial t} \right]_{\mathrm{rad}} - k \sum_{i=e,g} \int d\mathbf{c}_i \ln f_i \left[\frac{\partial f_i}{\partial t} \right]_{\mathrm{rad}}$$

$$= k(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_e \int d\mathbf{c}_g\, W(\mathbf{c}_e|\mathbf{c}_g,\mathbf{k})[\ln f_e + \ln(1+f_r) - \ln f_g - \ln f_r][f_e(1+f_r) - f_g f_r] \,,$$

where we used that the total number of atoms is locally conserved. Since the last term is non-negative, the entropy density s obeys the H theorem

$$\left[\frac{\partial s}{\partial t} \right]_{\mathrm{rad}} \geq 0 \,. \tag{16}$$

Eu and Mao [14] demonstrated with the help of this H theorem that the unique state of thermodynamic equilibrium is described by the Maxwell velocity distribution and the Boltzmann population distribution for the parti-

cles, and the Planck distribution for the photons. Note, however, that they treat spontaneous emission as resulting from the absorption of a photon with momentum zero, and thus introduce a discontinuity in $f_r(\mathbf{k})$ for $\mathbf{k}=0$. The form of their evolution equations therefore differs from ours.

Levich [19] discusses the derivation of kinetic equations in general, the validity of the assumptions made, and how irreversibility is introduced. Furthermore, he gives a kinetic equation, similar to our result, for electrons in interaction with photons in the special case of isotropic radiation.

III. MATTER ENTROPY

A. Separation of matter entropy production

In this section we consider the production of matter entropy in the light-absorbing gas and discuss the contributions to this production from the physical processes that change the microscopic state of a gas. The distribution functions f_i for $i = e,g$ evolve through stimulated transitions, spontaneous-emission processes, velocity-changing collisions, and free flow of the gas particles. Thus the evolution equations contain the following terms, respectively:

$$\frac{\partial f_i}{\partial t} = \left[\frac{\partial f_i}{\partial t}\right]_{\text{stim}} + \left[\frac{\partial f_i}{\partial t}\right]_{\text{spon}} + \left[\frac{\partial f_i}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial f_i}{\partial t}\right]_{\text{free}} . \quad (17)$$

The first term is given by the terms in (12) that are proportional to the photon distribution function f_r and the second term is given by the remaining term in (12). The collision terms are Boltzmann operators analogous to the Boltzmann expression (2). Finally free flow is described by

$$\left[\frac{\partial f_i}{\partial t}\right]_{\text{free}} = -\mathbf{c} \cdot \nabla f_i . \quad (18)$$

Correspondingly the production of matter entropy density can be expressed as

$$\frac{\partial s_m}{\partial t} = \left[\frac{\partial s_m}{\partial t}\right]_{\text{stim}} + \left[\frac{\partial s_m}{\partial t}\right]_{\text{spon}} + \left[\frac{\partial s_m}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial s_m}{\partial t}\right]_{\text{free}} . \quad (19)$$

The local production of matter entropy resulting from stimulated transitions is given by

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{stim}} = -k \sum_i \int d\mathbf{c}_i \ln f_i \left[\frac{\partial f_i}{\partial t}\right]_{\text{stim}}$$
$$= k2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_e \int d\mathbf{c}_g W(\mathbf{c}_e | \mathbf{c}_g, \mathbf{k})$$
$$\times f_r(f_e - f_g)$$
$$\times \ln(f_e / f_g) . \quad (20)$$

This expression is non-negative since stimulated transitions tend to equalize the distribution functions, thereby maximizing the mixing. For the production of matter entropy due to spontaneous emissions, one analogously finds

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{spon}} = -k \sum_i \int d\mathbf{c}_i \ln f_i \left[\frac{\partial f_i}{\partial t}\right]_{\text{spon}}$$
$$= k2(2\pi)^{-3} \int d\mathbf{k} \int d\mathbf{c}_e \int d\mathbf{c}_g W(\mathbf{c}_e | \mathbf{c}_g, \mathbf{k})$$
$$\times f_e \ln(f_e / f_g) . \quad (21)$$

When $f_e(\mathbf{c}_e) \leq f_g(\mathbf{c}_g)$ for all velocities $\mathbf{c}_e$ and $\mathbf{c}_g$ that differ by at most the maximum possible value of $\hbar\mathbf{k}/m$, this expression is nonpositive. The reason is that spontaneous emissions will lead to a smaller fraction of excited atoms and thereby will decrease the mixing. The contribution of collisions to the production of entropy has the same form as in a standard two-component gas [15,17] and is non-negative because of Boltzmann's theorem for gas mixtures. Finally, the rate of entropy production resulting from free flow can be written as

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{free}} = -\nabla \cdot \mathbf{J}_s , \quad (22)$$

with the entropy flow $\mathbf{J}_s$ given by

$$\mathbf{J}_s = -k \sum_{i=e,g} \int d\mathbf{c} \, \mathbf{c} \, f_i \ln(a f_i) . \quad (23)$$

The net entropy production due to the free flow of a gas that is contained in a closed volume V is then equal, up to its sign, to the net flow of entropy through the boundary of V. The former can therefore also be interpreted as the entropy production at the boundary. For this reason, we will not include the effect of free flow when considering the total entropy production in the bulk of the gas.

B. Separation of the matter entropy

We have seen that an H theorem can be found for the interaction between light and matter if we choose (14) as the matter entropy density. This matter entropy is the sum of Boltzmann entropies of each internal state separately. The distribution functions f_i for $i = e,g$ can generally be written in the form

$$f_i(\mathbf{c}) = p_i f(\mathbf{c})[1 + \phi_i(\mathbf{c})] . \quad (24)$$

Here $f = f_e + f_g$ is the total velocity distribution function and p_i is the local fraction of particles in the state i, with $p_e + p_g = 1$. The functions ϕ_i are a measure for the correlation between the velocity and the internal state of the particles. The ϕ_i satisfy, by definition,

$$\int d\mathbf{c} \, f \phi_i = 0 , \quad \sum_{i=e,g} p_i \phi_i = 0 . \quad (25)$$

The entropy density s_m can now be split up into three parts,

$$s_m = s_B - kn \sum_{i=e,g} p_i \ln p_i$$
$$- k \sum_{i=e,g} \int d\mathbf{c} \, p_i f(1 + \phi_i) \ln(1 + \phi_i) . \quad (26)$$

The first term on the right-hand side is the Boltzmann entropy density in terms of the total distribution function f. It can be interpreted as a measure of disorder in the gas viewed as a whole, i.e., when one does not distinguish between excited- and ground-state atoms. The second term, which is the entropy of mixing, is non-negative since the population fractions are smaller than 1. The third term is nonpositive, since the function $(1+\phi_i)\ln(1+\phi_i)$ is larger than ϕ_i and the average of $f\phi_i$ vanishes because of (25). On the other hand, the sum of the second and the third term is non-negative, since it is the velocity average of $-k\sum_i f_i \ln(f_i/f)$, and f_i is not larger than f. Hence s_m is equal to the Boltzmann entropy density s_B if and only if all atoms are in the ground state.

IV. PRODUCTION OF PHOTON ENTROPY

In this section we wish to find an expression for the production of photon entropy in the case that a laser irradiates a gas of two-level atoms. Since photons from the laser beam are redistributed over a much larger number of modes in the fluorescence light, the contribution of laser photons to the total production of photon entropy is negligible. Thus we have to deal only with spontaneously emitted photons.

We assume that the radiating atoms are confined to a closed spatial volume V. The local photon entropy production in this volume is determined by the local photon number density, which *cannot* be expressed in the local density of excited atoms alone but by some average over all excited atoms. Therefore we will not consider the local entropy production within the volume V, but calculate the entropy of the photons after they have left the volume V. More precisely, we will calculate the entropy of photons emitted from V that cross a sphere around V with a radius R that is much larger than the maximum linear dimensions d_m of V. This entropy will turn out to be independent of R. A similar approach was adopted by Weinstein [12]. Consider the photons emitted during a time interval dt at some instant of time. A time T later, these photons are located in a spherical shell of radius $R=cT$. The production of photon entropy is equal to the entropy of the photons in this shell. The physical picture is that the photons travel freely (without having interaction) after being spontaneously emitted so that their entropy remains constant. Here we use that reabsorption of fluorescence photons can be neglected under typical experimental conditions.

We define

$$I(\omega,\Omega,\mathbf{r},t)\,d\omega\,d\Omega\,d\mathbf{r}\,dt$$

to be the number of photons spontaneously emitted in a time interval dt, in a volume $d\mathbf{r}$, into a spectral region $d\omega$, and into a solid angle $d\Omega$. It is nonvanishing only in V. The local production rate of photons is determined by the local excited state density n_e, so that I is normalized according to

$$\int d\omega \int d\Omega\, I(\omega,\Omega,\mathbf{r},t) = An_e(\mathbf{r},t) \ , \tag{27}$$

with A the spontaneous decay rate. Photons emitted in a

time interval dt into the direction $d\Omega$ occupy after a time R/c a volume $dV=R^2 d\Omega c dt$. For the entropy of these photons we need the number of occupied modes in this volume dV. This number is proportional to the solid angle $S(\Omega)/R^2$ subtended by the radiating volume V in the direction of Ω as viewed from dV, where $S(\Omega)$ is defined as the area of the projection of the volume V onto a plane perpendicular to Ω. (Note that by assumption $S\ll R^2$.) The number of occupied modes in dV is then given by

$$\frac{2}{(2\pi)^3}\frac{\omega^2 d\omega}{c^3}\frac{S}{R^2}dV = \frac{\omega^2 d\omega}{4\pi^3 c^2}Sd\Omega dt \ , \tag{28}$$

which is independent of R. Thus the number of modes occupied by photons during their free expansion remains constant and the same holds for their entropy. The number of photons spontaneously emitted at time t in V per mode will be denoted by $f_r(\omega,\Omega,t)$, and can now be calculated. When we assume that the intensity is uniform over a solid angle $d\Omega$, f_r can be found form the normalization (9),

$$f_r(\omega,\Omega,t) = \frac{4\pi^3 c^2}{\omega^2 S(\Omega)}\int_V d\mathbf{r}\, I(\omega,\Omega,\mathbf{r},t) \ . \tag{29}$$

This photon density indeed does not have a local form, since it involves integration of I over the volume V. The corresponding photon entropy production rate is found from (15)

$$\frac{dS_r}{dt} = -k\int d\omega \int d\Omega\frac{\omega^2 S(\Omega)}{4\pi^3 c^2}[f_r\ln f_r$$
$$-(1+f_r)\ln(1+f_r)] \ . \tag{30}$$

We have already assumed that reabsorption of spontaneously emitted photons can be neglected. This implies $f_r\ll1$. Then we can simplify (30) to the form

$$\frac{dS_r}{dt} = k\int d\omega \int d\Omega \int_V d\mathbf{r}\, I(\omega,\Omega,\mathbf{r},t)[1-\ln f_r(\omega,\Omega,t)] \ . \tag{31}$$

The entropy per photon is therefore equal to $k[1-\ln f_r]$, which is larger than k.

V. PRODUCTION OF MATTER ENTROPY IN LIKE

We now wish to focus our attention on the entropy production in LIKE, where light induces macroscopic flows of particles, momentum, or energy in a gas. Therefore we introduce three assumptions which are justified in most experiments on the various manifestations of LIKE. First we assume that the gas is at room temperature, so that photon momentum is small compared to atomic momentum, at least for visible and infrared photons. Second we assume that the total gas density is sufficiently high, so that collisions take place at a time scale comparable to that of radiative transitions. Then the effects of resonance radiation pressure can be neglected. Third we assume that the mean free path $\bar{l}$ is small compared with a typical macroscopic distance L over which the gas is

uniform.

The third assumption implies that the evolution of the gas due to collisions and radiative transitions is much faster than the evolution due to free flow of the gas particles. This can be formally indicated by introducing a parameter ϵ in the microscopic evolution equations in front of terms that contain a scale factor $\bar{l}/L \ll 1$. The role of ϵ is to distinguish the rapid local processes (collisions and radiative transitions) from the slow processes (free flow or transport), and hence it indicates the existence of two time scales. This enables one to define macroscopic quantities by the requirement that they are conserved on the rapid time scale [22]. They are thus locally conserved and can change only due to transport. They consequently vary only on the slow, macroscopic time scale. The idea is that the rapid processes drive the system to a local steady state. Such quasistationary states evolve then only slowly. The macroscopic state of the gas is determined completely by these locally conserved quantities.

The evolution equations for the distribution functions of excited- and ground-state atom are given by

$$\epsilon \frac{\partial f_e}{\partial t} = -Af_e + B(f_g - f_e) + J_e - \epsilon \mathbf{c} \cdot \nabla f_e ,$$

$$\epsilon \frac{\partial f_g}{\partial t} = Af_e - B(f_g - f_e) + J_g - \epsilon \mathbf{c} \cdot \nabla f_g . \tag{32}$$

The rate of stimulated emission $B(\mathbf{c})$ was defined in (11) and is here equal to the rate of stimulated absorption because the transfer of photon momentum has been neglected. For the same reason the evolution terms corresponding to radiative transitions have a simplified form as compared to (12); when photon momentum is neglected, W in (20) and (21) contains a δ function $\delta(\mathbf{c}_e - \mathbf{c}_g)$, which can be integrated out using (10) and (11). The operators J_i give the rate of change of f_i resulting from velocity-changing collisions with gas particles and correspond to Boltzmann operators. The effect of free flow is determined by the spatial gradients of the distribution functions and its order of magnitude is therefore smaller than the preceding terms by $\bar{l}/L$. The factor ϵ on the left-hand side indicate that the distribution functions vary slowly, which is true after a transient time of a few collisions and a few photon emissions and absorptions.

The parameter ϵ serves as an expansion parameter for the distribution functions and can be set equal to 1 in the end. Expansion in ϵ effectively means expansion n $\bar{l}/L$. For instance, the zeroth-order distribution functions are the solutions of the $O(\epsilon^0)$ part of the evolution equations (32),

$$-Af_e^0 + B(f_g^0 - f_e^0) + J_e^0 = 0 ,$$

$$Af_e^0 - B(f_g^0 - f_e^0) + J_g^0 = 0 . \tag{33}$$

These equations determine f_i^0 uniquely for given local values of the macroscopic quantities.

The macroscopic evolution equations are obtained by multiplying (32) with the conserved quantities and integrating over $\mathbf{c}$. These equations contain macroscopic fluxes that drive the evolution of the macroscopic quantities and they are defined in terms of the distribution func-

tions. These fluxes are also expanded in ϵ, i.e., in the ratio $\bar{l}/L$. Macroscopic fluxes resulting from zeroth-order distribution functions are, by definition, zeroth-order fluxes and fluxes proportional to gradients of the macroscopic quantities are first-order fluxes.

A. Broadband light

We now wish to express the local production rates of matter entropy, such as (20) and (21), in terms of gradients of macroscopic quantities and in macroscopic fluxes. This is possible when both functions f_e and f_g are close to a Maxwellian. This is the case when $B(\mathbf{c})$ varies only slightly over the Maxwellian distribution. Then we can write for the stimulated transition rate [21]

$$B(\mathbf{c}) = B_0 + \epsilon B_1(\mathbf{c}) . \tag{34}$$

Here B_0 is independent of the particle velocity $\mathbf{c}$ and corresponds to the flat part of the laser spectrum. For simplicity we have chosen the same parameter ϵ to indicate that the velocity-dependent part of the excitation rate B_1 is much smaller than B_0, namely by approximately a factor $\bar{l}/L$. Since the excitation is not velocity selective to zeroth order, the zeroth-order solutions f_i^0 of (33) are Maxwellians

$$f_i^0(\mathbf{c}) = p_i^0 W_0(\mathbf{c}) , \tag{35}$$

where the fractions of excited and ground-state atoms are given to zeroth order by

$$p_e^0 = 1 - p_g^0 = \frac{B_0}{A + 2B_0} . \tag{36}$$

Under normal experimental conditions reabsorption of spontaneously emitted photons can be neglected, so that the excitation rate is determined directly by the laser intensity.

1. Single-component gas

First we consider the production of matter entropy due to spontaneous emissions in a single-component gas. This entropy is produced on the rapid time scale and the spontaneous entropy production is of zeroth order in ϵ. We find

$$\left[\frac{\partial s_m}{\partial t} \right]_{\text{spon}} = kA \int d\mathbf{c}\, f_e \ln \frac{f_e}{f_g} . \tag{37}$$

This is just the simplified version of (21). Now we apply the separation (24) and expand up to first order in ϵ. Obviously ϕ_i vanishes to zeroth order, so that $W_0 \phi$ integrates to zero up to first order. This leads to the equation

$$\left[\frac{\partial s_m}{\partial t} \right]_{\text{spon}} = kAn_e \ln \frac{p_e}{p_g} , \tag{38}$$

which is correct up to first order, provided that the population fractions p_i are calculated up to first order.

The entropy production due to stimulated transitions is also rapid and of zeroth order in ϵ, and is given by

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{stim}} = k\int d\mathbf{c}\, B\,(f_e - f_g)\ln\frac{f_e}{f_g}\ ,\qquad(39)$$

which is just the simplified version of (20). Now we substitute one of the Eqs. (32) to rewrite $B\,(f_g - f_e)$ and expand up to first order, while using that the zeroth-order terms $J_e^{(0)}$ or $J_g^{(0)}$ vanish because the zeroth-order distributions are Maxwellian. Using that p_e and p_g add up to one, we derive

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{stim}} = -k\,An_e\ln\frac{p_e}{p_g} - kn\left[\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right]\sum_{i=e,g} p_i\ln p_i\ .$$

$$(40)$$

The variations of p_i with time and position are determined by the temporal and spatial variations of the light intensity which are assumed to be slow.

The production rates of entropy (38) due to spontaneous emission and (40) due to stimulated transitions cancel on the rapid time scale. This is due to the fact that the internal state of the atom reaches a local steady state on the rapid time scale. The production of entropy due to

radiative transitions occurs therefore only on the slow time scale and we find from the sum of (38) and (40)

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{rad}} = -kn\left[\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right]\sum_{i=e,g,} p_i\ln p_i\ .\qquad(41)$$

The entropy production due to the combined effect of all rapid processes, radiative transitions, and collisions can be given up to *second* order in ϵ as a product of first-order fluxes and (first-order) gradients of the corresponding macroscopic quantities. We use a standard technique from gas kinetics to obtain this expression [17]. One replaces the time derivative of the distribution functions due to the rapid processes by its first-order expression, as obtained from the $O(\epsilon)$ part of (32),

$$\left[\frac{\partial f_i}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial f_i}{\partial t}\right]_{\text{rad}} = \epsilon\left[\frac{\partial}{\partial t} + \mathbf{c}\cdot\nabla\right](p_i W_0)\ ,\qquad(42)$$

since the zeroth-order part (33) vanishes. When one uses the macroscopic evolution equations for n, $\mathbf{v}$, and T [17,20] to eliminate the time derivative of the Maxwellian W_0, one finds after some algebra

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial s_m}{\partial t}\right]_{\text{rad}} = -\left[\frac{\mathbf{q}}{T^2}\cdot\nabla T + \frac{\overleftrightarrow{\Pi}}{T}:\nabla\mathbf{v}\right] - kn\left[\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right]\sum_{i=e,g} p_i\ln p_i - kn\sum_{i=e,g}\frac{n_i\mathbf{V}_i}{p_i}\cdot\nabla p_i\ ,\qquad(43)$$

up to and including second order in ϵ. The first term here corresponds to the first term in (26). Thus it gives the production of the Boltzmann entropy density s_B and it has the standard form of entropy production in a pure gas without a radiation field present [15]. The heat flux $\mathbf{q}$ and the pressure anisotropy $\overleftrightarrow{\Pi}$ in (43) are defined in terms of the total distribution function $f = f_e + f_g$ by

$$\mathbf{q} = \int d\mathbf{c}\,\tfrac{1}{2}m\,(\mathbf{c}-\mathbf{v})^2(\mathbf{c}-\mathbf{v})f\ ,$$

$$\overleftrightarrow{\Pi} = \int d\mathbf{c}[m\,(\mathbf{c}-\mathbf{v})(\mathbf{c}-\mathbf{v}) - \tfrac{1}{3}m(\mathbf{c}-\mathbf{v})^2\overleftrightarrow{\mathbf{I}}]f\ ,\qquad(44)$$

with $\overleftrightarrow{\mathbf{I}}$ the three-dimensional unit tensor. In broadband light these fluxes are of first order in ϵ since the zeroth-order Maxwellian part of the distribution functions gives a vanishing contribution. The first term in (43) is of second order in ϵ. The second term is just the contribution (41) of radiative transitions to the entropy production and corresponds to the second term in (26). It is of first order in ϵ. The third term describes effects of the velocity-selective part of the excitation B_1 and of the gradients of n, $\mathbf{v}$, and T. Only these processes can modify the form of the partial distribution functions relative to the total distribution function, and hence can lead to nonvanishing (first-order) partial relative velocities $\mathbf{V}_i$ for $i = e,g$, defined by

$$n_i\mathbf{V}_i = \int d\mathbf{c}(\mathbf{c}-\mathbf{v})f_i\ .\qquad(45)$$

This the third term in (43) corresponds to the third part of the entropy in (26) and it is of second order in ϵ.

Equation (43) can be compared with the standard expression for the entropy production in a binary gas mixture in the absence of a radiation field [15], in the special case that the two components have identical masses. The expressions have the same form, except for the second line in (43), which is missing in the standard expression. The reason is that in standard gas kinetics the partial densities can vary only slowly through transport, whereas in a light field they are determined by the rapid radiative transitions.

2. Vapor in buffer gas

In a binary gas mixture both components contribute to the production of entropy. We are especially interested in the optical active component (a) of the gas. Therefore we assume the other component, the buffer gas (b), to be in complete thermal equilibrium with a uniform density, a vanishing mean velocity, and a uniform temperature. This is possible when the buffer gas is much more abundant than the active component. It acts as a reservoir of momentum and energy. The entropy production in the bulk is then entirely due to flows and gradients in the active gas (a) and is given by

$$\left[\frac{\partial s_m}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial s_m}{\partial t}\right]_{\text{rad}}$$

$$= -k\mathbf{V}_a \cdot \nabla n_a - kn\left[\frac{\partial}{\partial t} + \mathbf{V}_a \cdot \nabla\right]\sum_{i=e,g} p_i \ln p_i$$

$$- kn_a \sum_{i=e,g} \frac{n_i \mathbf{V}_i}{p_i} \cdot \nabla p_i \ . \tag{46}$$

These expressions are obtained by applying the same techniques as in Sec. V A 1 and are valid up to second order in ϵ. Here n_a is the density of the active gas and $\mathbf{V}_a$ its mean velocity relative to the buffer gas. The partial relative velocities $\mathbf{V}_i$ for $i = e,g$ are defined relative to the velocity of the active gas $\mathbf{V}_a$.

The difference between (43) and (46) is the first term, which now contains the gradient of the density n_a and the velocity $\mathbf{V}_a$, but not the gradients of temperature and velocity. The reason is that now the density n_a of the dilute component is the only macroscopic quantity which uniquely determines the local stationary state and therefore $\mathbf{V}_a$ is the only macroscopic flux [23].

B. Narrowband light

Laser light does not have a flat spectrum, on the contrary, it usually is nearly monochromatic. When the homogeneous linewidth is small compared with the Doppler width, the laser will burn a hole in the velocity distribution function of the ground state and will create a peak in the excited state. The distribution functions will deviate appreciably from a Maxwellian and the results (43) and (46) do not apply. Since narrow-band light will induce larger fluxes than broadband light, we will exclusively consider the production of entropy due to these narrow structures. Furthermore, the interesting feature of kinetic effects of light is not so much hole burning, but rather the possibility of modifying the *total* distribution function (leading to macroscopic fluxes). Therefore we will calculate the local production of Boltzmann entropy s_B when considering explicit examples in Sec. VI. One finds just the standard expressions, valid up to and including second order in ϵ,

$$\left[\frac{\partial s_B}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial s_B}{\partial t}\right]_{\text{rad}} = -\left[\frac{\mathbf{q}}{T^2}\cdot\nabla T + \frac{\overleftrightarrow{\Pi}}{T}:\nabla\mathbf{v}\right] \tag{47}$$

for a single-component gas and

$$\left[\frac{\partial s_B}{\partial t}\right]_{\text{coll}} + \left[\frac{\partial s_B}{\partial t}\right]_{\text{rad}} = -k\mathbf{V}_a\cdot\nabla n_a \tag{48}$$

for a vapor in a buffer gas. They are valid when the total distribution function is close to the Maxwellian W_0. This condition is fulfilled, even in narrow-band light, when the number of excited atoms is relatively small or when the gas-kinetic difference between excited- and ground-state atoms is small, since then light-induced changes in the total distribution function will also remain small. When photon momentum is neglected, the rates of change (47) and (48) of s_B are in fact entirely due to collisions.

C. Illustrations

In a gas in a closed volume without external (radiation) fields present, the entropy productions (43) and (46) reduce to (47) and (48) and must always be positive because of the second law of thermodynamics. In standard gas dynamics, the heat flux and pressure anisotropy in a single-component gas are given by [17]

$$\mathbf{q} = -\lambda\nabla T \ , \quad \overleftrightarrow{\Pi} = -2\eta(\nabla\mathbf{v})_s \ , \tag{49}$$

with $(\ )_s$ denoting the symmetrical traceless part. The heat conductivity λ and the viscosity η are positive constants, so that (47) is indeed never negative. Likewise, in a binary gas mixture consisting of a dilute active gas and a much more abundant buffer gas, the partial relative velocity $\mathbf{V}_a$ of the active component is given by [17]

$$n_a\mathbf{V}_a = -D\nabla n_a \ , \tag{50}$$

with $D > 0$ the diffusion constant. Here the entropy production (48) also is never negative.

In a resonant radiation field, however, fluxes $\mathbf{q}$, $\overleftrightarrow{\Pi}$, and $\mathbf{V}_a$ can be induced independent of the presence of gradients. Therefore the entropy production can be negative. For example, when a temperature gradient exists and the light-induced heat flux is sufficiently large so that the total heat flux is directed along the temperature gradient, the light acts as a heat pump and matter entropy will be destroyed. The latter happens also when light induces a net drift of the optically active atoms directed from lower to higher density.

Negative entropy production is possible even when the gas in a closed volume is in a stationary state, so that the entropy of the gas itself remains constant. Hence the (negative) entropy production in the bulk of the gas must be compensated for by a flow of (negative) entropy through the boundaries to the outside world. In other words, there is a steady flow of entropy from the outside world into the volume. Thus the entropy of the outside world decreases at a constant rate. Note that the radiation field is not in a stationary state, since there is a steady flow of photons into the fluorescence modes.

VI. DISCUSSION AND EXAMPLES

We now apply the results obtained so far to some examples in order to find how efficient the decreasing of entropy of matter by photons is in practical cases. As argued in Sec. V B we will consider the production of Boltzmann entropy and use Eqs. (47) and (48) for its production rate. We distinguish two cases and two definitions of the efficiency.

(i) A gas in thermal equilibrium is irradiated by light and reaches a stationary state after some time. The entropy of the gas has changed by a negative amount ΔS_B in this time interval, while the entropy of the photons has increased by ΔS_r. The efficiency of this transient process is defined as

$$\eta_1 = \frac{|\Delta S_B|}{\Delta S_r} \ .$$

Note that photon entropy is still being produced in the stationary state, when the photons are keeping the gas in a state out of thermal equilibrium.

(ii) A gas irradiated by light reaches a stationary state in which there is a constant negative Boltzmann entropy production $\partial S_B / \partial t$. Photon entropy is produced at a rate $\partial S_r / \partial t$. Now the efficiency of maintaining the stationary state is defined as

$$\eta_2 = \left| \frac{\partial S_B}{\partial t} \right| \Big/ \frac{\partial S_r}{\partial t} \ .$$

A. Light-induced drift

One of the most spectacular phenomena in the field of light-induced kinetic effects is light-induced drift (LID). When the optically active component of a gas mixture is velocity-selectively excited, two counterpropagating fluxes of excited and ground-state atoms arise. The friction forces on these two fluxes due to collisions with the buffer gas are different when the velocity damping rates ζ_e of excited atoms and ζ_g of ground-state atoms differ. Then the two fluxes do not cancel and a net flux $n_a \mathbf{V}_a$ of active atoms, pushed by the buffer gas, arises, with n_a the density of active atoms and $\mathbf{V}_a$ the drift velocity. For a general expression for $n_a \mathbf{V}_a$, see [24]. The magnitude of the LID effect is proportional to the relative difference between the damping rates,

$$\alpha = \frac{\zeta_e - \zeta_g}{\zeta_g} \ . \tag{51}$$

In general this is a positive quantity and a typical value for atoms in a noble buffer gas is 10%. The LID velocity can reach values up to about 50 m/s [9]. The deviation from thermal equilibrium can thus be rather large.

We now consider a closed cylindrical cell of length L and radius r. The light is assumed to be uniform over a cross section of the cell so that the problem is in fact one dimensional. Since the particle fluxes must vanish in a stationary state, the entropy production (48) vanishes so that $\eta_2 = 0$ for this process. We therefore calculate the efficiency η_1. The entropy of the optically active gas decreases because the gas is pushed to one end of the cell due to the LID effect. When the velocity distribution function is close to a Maxwellian, the entropy change results only from the change from a uniform density $\bar{n}$ to a nonuniform density $n(z)$ for $0 \leq z \leq L$ and one finds

$$\Delta S_B = -k\pi r^2 \int_0^L dz [n(z)\ln n(z) - \bar{n} \ln \bar{n}]$$
$$= -k\pi r^2 \int_0^L dz \, n(z)\ln(n(z)/\bar{n}) \ , \tag{52}$$

where both the n and $\bar{n}$ are normalized to the total number of active atoms in the cell N_a. The deviation from the Maxwell distribution gives an additional negative contribution.

For explicit results for this case we now make use of the results of Ref. [25]. Only two variables are needed to describe the physical system consisting of gas and laser light: the particle density $n(z)$ and a scaled light intensity $J(z)$ such that J has the same dimension as n. It turns

out that the sum of n and J is constant as a function of z. Therefore the density varies sharply where the absorption of the laser light is large. When saturation can be neglected, n and J can be expressed in the form [25]

$$n(z) = H / \{1 + \exp[-qH(z - z_0)]\} \ ,$$
$$J(z) = H / \{1 + \exp[qH(z - z_0)]\} \ , \tag{53}$$

for $0 \leq z \leq L$. Here z_0 is the position where n and J have the same value $H/2$. The parameter q is the absorption cross section. For $z - z_0 \ll -1/qH$, the density varies exponentially according to $n(z) \approx H \exp[qH(z - z_0)]$. For $z - z_0 \gg 1/qH$, the density approaches the maximal value H. The transition region around $z = z_0$ has a width of the order of $1/qH$. The interesting case arises when the density varies appreciably over the cell. This is true when the transition region lies within the cell and is reasonably well separated from the cell ends. This requires that the vapor is optically thick and that the intensity is sufficiently high. More precisely, when we introduce the optical thickness x by

$$x = q\bar{n}L \tag{54}$$

and the reduced intensity

$$y = H / \bar{n} \ , \tag{55}$$

we require that $x \gg 1$, $y \gg 1$. Then the vapor of active atoms is compressed to the value H at a region of length L/y of the cell. From (52) we find that the Boltzmann entropy change of the vapor amounts to

$$\Delta S_B \approx -k\pi r^2 \left[\frac{L}{y} H \ln H - L\bar{n} \ln \bar{n} \right] = -kN_a \ln y \ . \tag{56}$$

An example of typical values for the various parameters in a LID experiment of the type described here can be found in [9], p. 175. One finds there the values $x = 8.4$ and $y = 12$. The entropy of the gas thus decreases by about 2.5 k per atom. From [9] we also obtain the number of spontaneously emitted photons per atom needed to reach the stationary state, namely more than roughly 10^5. Thus the matter entropy decreases by about 10^{-5} k per spontaneously emitted photon. For the contribution to the radiation entropy of one photon we need the number of photons per mode. An estimate for a typical value of f_r is obtained from (29) when we use that $S(\Omega)$ is larger than the minimum visible area of the cylinder which is given by the minimum of πr^2 and $2rL$, and when we use that the spontaneously emitted photons have a spectral range larger than the homogeneous linewidth determined by A so that $\Delta \omega > 10^{-6} \omega_0$. This leads to the estimate

$$f_r < 10^{-3} \ , \tag{57}$$

much smaller than unity. Hence we can apply (31), which states that the entropy per photon is given by $k(1 - \ln f_r)$. Hence the entropy of one photon increases by at least approximately $10k$. The efficiency of LID is thus $\eta_1 < 10^{-6}$. Note that the entropy per photon does not depend sensitively on f_r, which justifies using rough estimates. It also implies that the efficiency is mainly

determined by the number of photons per atom needed to reach a stationary state since the matter entropy decrease per atom is of the same order of magnitude as the increase in radiation entropy per photon.

B. Light-induced heat flux

In a one-component gas LID is not possible since there is no buffer gas to supply momentum. However, light can induce both a pressure anisotropy $\overset{\leftrightarrow}{\Pi}$ and a heat flux q [26,27]. In this section we consider the effect of a light-induced heat flux and neglect the pressure anisotropy. (By properly choosing the laser detuning from resonance one can make $\overset{\leftrightarrow}{\Pi}$ negligibly small [20].)

When the light propagates along the z direction, the heat flux will also be in this direction. Thus light transports heat from one side of the cell to the other. When these two ends of the cell are kept at different temperatures, there is a nonvanishing entropy production given by (47), even in a stationary state. This entropy production is negative when the total heat flux is directed along the imposed temperature gradient. We estimate the efficiency according to the second definition η_2. There are two contributions to the total heat flux, viz., the standard heat conduction and the light-induced heat flux,

$$q = -\lambda \frac{dT}{dz} + q_0 , \tag{58}$$

with λ the heat conductivity. In a stationary state, this heat flux is uniform. We use the expression from [20] for the light-induced heat flux q_0. It has the order of magnitude

$$q_0 \approx \alpha \frac{A n_e}{A + \kappa_g} kT \left[\frac{kT}{m} \right]^{1/2} , \tag{59}$$

with n_e the density of excited atoms and κ_g the collision rate of ground-state atoms. The local entropy production (47) contains the product of q and dT/dz. For given value of q_0, this entropy production is maximally negative when the temperature difference is chosen such that

$$\frac{dT}{dz} = \frac{q_0}{2\lambda} . \tag{60}$$

The matter entropy production is then quadratic in q_0. When we use the expression [21]

$$\lambda = \frac{5k^2 nT}{2m\kappa_g} \tag{61}$$

for the heat conductivity we can give the total entropy production as

$$\frac{-\partial S_B}{\partial t} \approx \frac{1}{10} \frac{N_e}{N_a} \alpha^2 \frac{A\kappa_g}{(A + \kappa_g)^2} k A N_e . \tag{62}$$

Here N_e is the total number of excited atoms in the stationary state and thus $A N_e$ is the number of photons spontaneously emitted per unit time. The Boltzmann entropy loss is much less than one k per photon since each of the factors in front of $k A N_e$ is (much) smaller than unity. For typical values of the factors one finds this

number to be about 10^{-7} k per photon. Since, typically, the photon entropy is at least one k per photon, $\eta_2 < 10^{-7}$.

C. Other cases

In this section we briefly discuss some other experiments in which lasers are used to manipulate particles and thereby lower the particles' entropy.

1. Laser cooling

We consider the example given by Hänsch and Schawlow [28] in their proposal to cool atoms by what is now known as Doppler cooling. The (one-dimensional) temperature of a gas of magnesium atoms can be reduced by a factor of about 2500 by using laser photons with a frequency somewhat lower than a particular resonance frequency. The entropy of the atoms decreases by $k \ln 2500 \approx 8k$ per atom and each photon gains more than one unit of k (again, this number does not sensitively depend on the number of photons per mode). Here, too, the efficiency of the cooling process is determined by the number of spontaneously emitted photons per atom. The number of photons per atom to reach the quoted reduction of temperature is about 1.3×10^4, which leads to an efficiency $\eta_1 \approx 10^{-5}$. In [16] a much lower estimate for the efficiency was obtained. This discrepancy seems to arise from confusing the entropy per atom with the total entropy.

2. Light-induced viscous flow

Light-induced viscous flow may arise in a pure gas from a pressure anisotropy resulting from a transverse gradient of the intensity [11]. A net particle flow can then be induced from lower to higher pressure. Analogously to the case of a light-induced heat flux negative entropy will be produced in an open cell when a pressure gradient is maintained in a stationary state. This production will be quadratic in the light-induced pressure anisotropy. Since the effect is proportional to the gradient of the intensity, it is of first order in the number $\epsilon \ll 1$, defined in Sec. V. Therefore the efficiency η_2 is smaller by a factor of ϵ^2 compared with the case of a (zeroth-order) heat flux.

3. Light-induced kinetic effects in molecular gas

When experiments are done in molecular gases, it is no longer true that each absorbed laser photon will be reemitted, either spontaneously or by stimulated emission. Instead, molecules deexcite rapidly in inelastic collisions. The photon energy is, in the end, transferred into translational energy. Each absorbed photon will contribute therefore to raising the temperature and hence the entropy of the molecules. On the average, a photon with energy $\hbar\omega$ will raise the temperature of one molecule by $\hbar\omega/k$. The vibrational excitation energy is of the order of 0.15 eV, which corresponds to $5kT$ at room temperature. The entropy of the molecules will then increase by $k \ln \hbar\omega/kT \approx 1.5k$ per absorbed photon. Thus for molec-

ular gases this entropy gain per photon is somewhat smaller than for atomic gases. On the other hand, the parameter determining the strength of LIKE—the relative difference in collisional properties between excited and ground-state particles—is for vibrationally excited molecules also smaller, by at least a factor of 10, than for electronically excited atoms. The efficiency, either η_1 or η_2, is therefore even smaller in molecular gases.

VII. CONCLUSIONS

We considered the entropy balance during the resonant interaction between light and matter. The form of the rate equations describing this interaction leads to a particular definition of matter and photon entropy such that their sum always increases until matter and photons are in thermal equilibrium. The entropy of matter is the sum of the standard Boltzmann entropies for excited and nonexcited atoms, and the entropy of photons has the standard form of boson entropy. We discussed the analogies between Boltzmann's H theorem and the approximations needed to derive it, and the H theorem for the interaction of light and matter.

We divided the matter entropy into three parts: a part related to the translational degrees of freedom of the atoms, a part arising from the internal state of the atoms (the entropy of mixing), and a part describing the correlation between the translational and internal degrees of freedom. For illustrative purposes, we derived expressions for the local production of matter entropy in a gas irradiated by broadband light, which can be separated into three corresponding parts.

We showed that light can lower the entropy of matter and can keep matter in a stationary state out of thermal equilibrium. In both cases the entropy of the photons must increase. In the latter case, there can be a flow of entropy from the outside world into a closed volume containing the matter. The entropy of the volume's boundary then decreases at a constant rate. Of course, the entropy of the radiation field increases also at a constant and larger rate.

We explicitly treated some cases where a gas gains order due to interaction with a laser field. In particular, we discussed light-induced drift, where particles move from lower to higher density. We calculated the entropy loss and compared it with the gain of photon entropy. The latter is found to be larger by, typically at least six orders of magnitude. This small efficiency is mainly due to the large number of photons per atom needed to reach the final state. The same is true for laser cooling, leading to typical efficiencies of about 10^{-5}. As a second example we treated a light-induced heat flow directed from lower to higher temperature. In a stationary state, photon entropy is produced at a rate that is typically seven to eight orders of magnitude larger than the rate at which matter entropy is destroyed.

ACKNOWLEDGMENTS

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