P H Y S I C A L   R E V I E W   L E T T E R S

Approach to Thermal Equilibrium in Atomic Collisions

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The energy relaxation of fast atoms moving in a thermal bath gas is explored experimentally and theoretically. Two time scales characterize the equilibration, one a short time, in which the isotropic energy distribution profile relaxes to a Maxwellian shape at some intermediate effective temperature, and the second, a longer time in which the relaxation preserves a Maxwellian distribution and its effective temperature decreases continuously to the bath gas temperature. The formation and preservation of a Maxwellian distribution does not depend on the projectile to bath gas atom mass ratio. This two-stage behavior arises due to the dominance of small angle scattering and small energy transfer in the collisions of neutral particles. Measurements of the evolving Doppler profiles of emission from excited initially energetic nitrogen atoms traversing bath gases of helium and argon confirm the theoretical predictions.

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The energy distribution function is critical to the determination of the physical and chemical consequences of the presence of hot atoms in a bath gas, as may occur in applications of plasma physics, atmospheric physics, astrophysics, and chemical physics. The approach of the hot atoms to thermal equilibrium depends on the mass ratio of the hot atoms to the bath gas atoms and on the interaction between them [1,2]. In some cases [1–3], the hot atoms relax to a final equilibrium state by a sequence of Maxwellian distributions characterized by a continuously decreasing effective temperature. In other cases [1–3], the distributions do not follow the Maxwellian form. The analyses made use of the hard-sphere approximation or they were based on an interaction potential varying as an inverse power of internuclear distance R.

We have carried out a theoretical and experimental investigation of the evolution of energetic atoms in atomic bath gases to explore the sensitivity to the mass ratio. We have studied the accuracy of the representation of the nonequilibrium energy distribution by an evolving Maxwellian form.

The translational energy relaxation of a dilute nonequilibrium system of particles as it traverses a uniform bath gas of atoms or molecules is described by a distribution function $f(E, t)$ of kinetic energy E and time t given by the solution of the linear Boltzmann equation. Solving the equation presents a severe challenge and approximations have been made. Two limits have been explored. For one, the Lorentz gas, the mass m_b of the bath gas atoms is much larger than the mass m of the particles and for the other, the Rayleigh gas, the opposite is the case. It has been shown for the hard-sphere Rayleigh gas that an initial Maxwellian distribution with an effective temperature T_{eff} larger than

the bath gas temperature T remains Maxwellian during the entire thermalization process [1,2]. The mathematical conditions necessary and sufficient to preserve a Maxwellian shape have been formulated for the asymptotic regime of small energy transfers [1,2] for which the integral Boltzmann equation may be replaced by the differential Fokker-Planck equation [4,5]. The energy relaxation may then be described by a single time-dependent function $T_{eff}(t)$ [2]. The effective temperature relaxes exponentially with time to the bath gas temperature. The approach to equilibrium of an initial anisotropic distribution involves a more complicated interplay of momentum and energy relaxation [6–8]. Shizgal and Blackmore [9] showed that the relaxation of an initially anisotropic hard-sphere Lorentz gas occurs by a two-stage process. A fast relaxation to an isotropic distribution is followed by a slow approach to the equilibrium Maxwellian form. These fundamental studies can be questioned because of the assumption that the collisions of the particles with the bath gas can be described by the hard-sphere approximation. For collisions of neutral atoms or molecules the hard-sphere approximation is a serious misrepresentation of the dependence on velocity and scattering angle, and it does not reproduce the strong forward scattering that arises from the attractive long-range van der Waals interaction. For a Lorentz gas, because of the small mass ratio, translational energy losses occur by a series of small energy transfer collisions, and the Fokker-Planck equation can be used in place of the Boltzmann equation [5,10,11]. The Fokker-Planck equation has been solved for scattering by an interaction potential varying as R^{-s} with $s \geq 4$ but the analysis is based on a classical model of the collisions [10].

It appears that no precise test of the theory of translational equilibration has ever been made. Recent experiments by Nakayama *et al.* [12] in conjunction with theoretical analysis make possible a critical assessment. We present here the results of detailed measurements of the Doppler profiles of initially energetic N(^4S) atoms traversing bath gases of helium and argon as functions of time. The experimental profiles may be compared directly with our predictions. We have determined the N(^4S)-He and N(^4S)-Ar interaction potentials by *ab initio* methods, and we have computed the corresponding quantum-mechanical differential scattering cross sections and constructed the kernel of the Boltzmann equation describing the rate of the energy transfer collisions [13]. We carried out direct numerical integrations of the time-dependent linear Boltzmann equation and compared the theoretical Doppler profiles with the measurements.

A full account of the experimental procedures is given in Ref. [12]. Energetic N(^4S) atoms with kinetic energies of about 0.93 eV are produced by the photodissociation of NO_2 by 193 nm pulsed ArF laser photolysis. The Doppler profiles of the nitrogen atoms are obtained by scanning a probe laser of frequency ν across the resonance frequency ν_0 of the transition N($^4S_{3/2}$-$^4P_{1/2}$) to the excited state corresponding to a wavelength of 120.07 nm. The frequency shift $\Delta\nu = \nu - \nu_0$ of the laser-induced fluorescence (LIF) of the fast atoms is related to the projection of the velocity v along the direction of observation of the LIF by the expression $v = c\Delta\nu/\nu_0$, where c is the speed of light. Profiles were obtained for a sequence of delay times from 30 ns to 600 ns for N atoms in helium and argon bath gases at a temperature of 295 K. The direction of observation of the LIF was perpendicular to the probe and photolysis laser beams. Figures 1 and 2 present two sets of the measured profiles as functions of the frequency shift for helium and argon for two experimental runs. The initial energy is 0.93 ± 0.1 eV. The profiles are symmetric about $\nu = \nu_0$. They narrow in time as the nitrogen atoms are slowed by collisions. The profiles gradually assume a Gaussian shape and eventually come into thermal equilibrium at the bath gas temperature, except for anomalous features in the wings that we discuss later.

The time-dependent linear Boltzmann equation for the isotropic distribution function $f(E, t)$ where E is the kinetic energy may be written

$$\frac{\partial}{\partial t} f(E, t) = \int B(E|E')f(E', t)dE' - f(E, t)$$
$$\times \int B(E'|E)dE' - \zeta(E)f(E, t) + S(E, t),$$

(1)

where $S(E, t)$ is the rate production of the fast atoms with energy E and $\zeta(E)$ is the rate of the sink reactions that remove them. The kernel $B(E|E')$ is the rate of energy transfer from an energy E' to an energy E in the laboratory
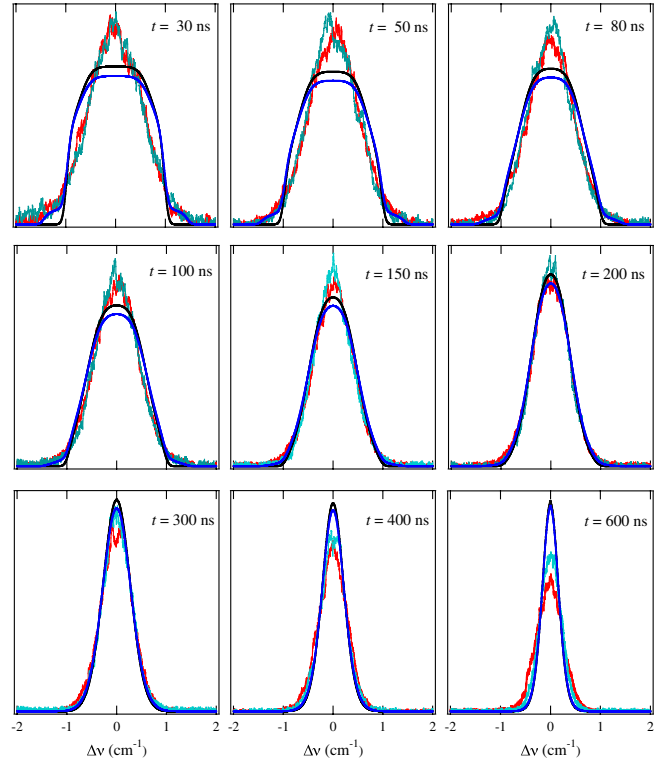

FIG. 1 (color online). Experimental and theoretical Doppler profiles for He bath gas at selected delay times. There are two sets of experimental data (red and teal) that are indistinguishable except near $\Delta\nu = 0$. The smooth curves are theoretical Doppler profiles. The curves (black) without extended wings correspond to an initial energy of 0.93 eV. The curves (blue) with extended wings correspond to a combination of initial energies, 80% with 0.93 eV and 20% with 2.0 eV. The center wavelength is 120.07 nm and $\Delta\nu$ is the Doppler shift.

frame [14]. We have computed $B(E|E')$ values with the quantum mechanically calculated differential cross sections. These kernels are dramatically different from results obtained with the hard-sphere approximation with rates of small energy transfer $|E - E'| \ll E'$ larger by orders of magnitude [13].

We solve the Boltzmann equation with a direct numerical procedure [14–16] with the source function $S(E, t) = \delta(E - E')\delta(t - t')$. The measured Doppler functions $\xi(\Delta\nu)$ of He and Ar, normalized to unity, are shown in Figs. 1 and 2, respectively, for different delay times. They give the relative intensity of emission at the shifted frequency $\nu = \nu_0 + \Delta\nu$. In terms of the isotropic energy distribution function, $\xi(\Delta\nu)$ is given by

$$\xi(\Delta\nu) = \xi(\nu - \nu_0) = \left(\frac{1}{2\nu_0}\right)\left(\frac{mc^2}{2}\right)^{1/2} \int_{E_0}^\infty f(E, t)\frac{dE}{\sqrt{E}}, \quad (2)$$

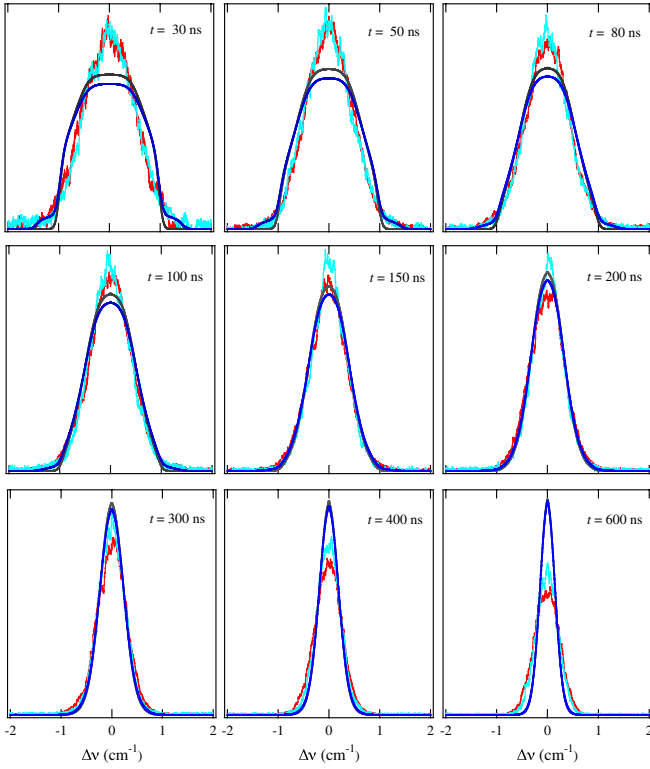where $E_0 = |\frac{\Delta\nu}{\nu_0}|^2 \frac{mc^2}{2}$. The average energy of the atoms is given by

FIG. 2 (color online). As for Fig. 1 with Ar in place of He.

$$\langle E(t) \rangle = \frac{3}{2} mc^2 \int_0^\infty \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \xi(\nu - \nu_0) d\nu. \quad (3)$$

When $\xi(\nu - \nu_0)$ can be represented by a Gaussian function of full width $\Delta\bar{\nu}$ at half maximum [17]

$$\langle E(t) \rangle = \frac{3}{16 \ln 2} \left(\frac{\Delta\bar{\nu}}{\nu_0} \right)^2 mc^2. \quad (4)$$

Figure 3 shows the calculated distribution function $f(E, t)$ at delay times from $t = 0$ to $t = 400$ ns. At $t = 0$, $f(E, t)$ is peaked around the initial energy of 0.93 eV. Collisions then bring about a bimodal structure that arises because for a typical collision $|E - E'| \ll E'$ and the energy relaxation of the initial peak is slow. The structure, prominent in the time derivative of $f(E, t)$, is manifested in the measured profile $\xi(\Delta\nu)$ by its departure from Gaussian. With time the Doppler profile does become Gaussian and remains so until it reaches thermal equilibrium at the bath gas temperature. At least two time scales are needed to characterize thermalization, one the time to relax to a Maxwellian-like distribution and the second to cool continuously to the bath temperature. At higher experimental time resolution, several short relaxation times describing the Boltzmann equation spectrum may be seen [7], and additional time scales may be required to characterize the first stage. The two-stage evolution applies to projectiles both lighter and heavier than the bath gas species. Relaxation proceeds more efficiently in the heavier gas because energy transfer is more rapid in Ar than in He. A detailed comparison of
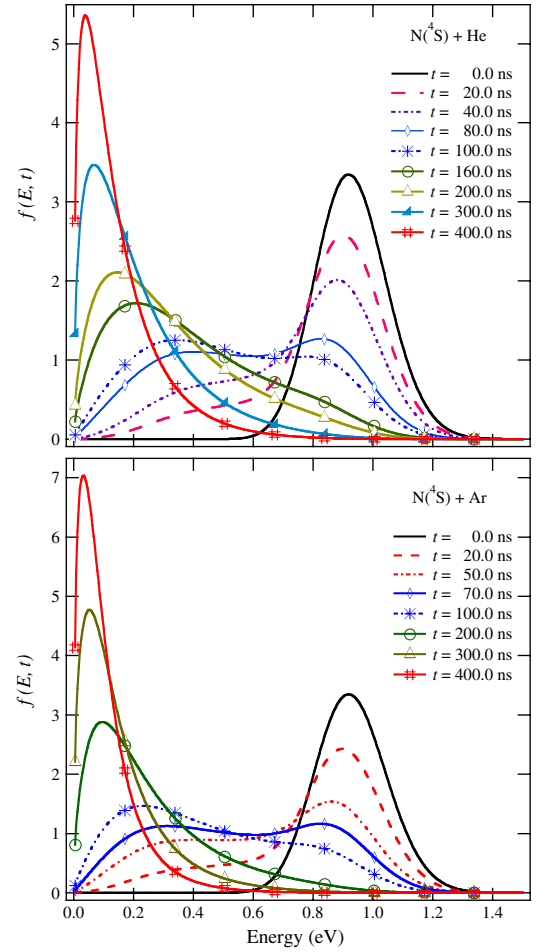

FIG. 3 (color online). Translational energy distribution functions at selected delay times during the energy relaxation processes in He and Ar bath gases.

the theoretical and experimental profiles $\xi(\Delta\nu)$ is presented in Figs. 1 and 2 for the two bath gases. The agreement demonstrates that a successful measurement of the time-dependent solution of the Boltzmann equation has been achieved. There remain the differences in the wings of the profiles. They indicate that there is an additional source of N atoms with energies of about 2 eV. The resulting profiles for an admixture of 20% are shown in the figures by the solid blue curves.

Having established that we have a correct solution of the Boltzmann equation, we may calculate time scales and mean energies $E(t)$ for different initial energies E_i. We define the time scales for reaching a Maxwellian shape, τ_g, and for reaching thermal equilibrium at the bath gas temperature, τ, as the times taken to fall within 5% of the intermediate quasithermal energy $\frac{3}{2} kT_{\text{eff}}(\tau_g)$ and the thermal kinetic energy $\frac{3}{2} kT$ of final equilibrium. At τ_g the distribution functions are close to Maxwellian at the intermediate temperature $T_{\text{eff}}(\tau_g)$, which is much higher than the bath gas temperature T. The corresponding times τ_g

TABLE I. Two-stage relaxation times with different initial projectile energies E_i for N atoms traversing He and Ar bath gases. τ_g is the time to reach the Maxwellian distribution.

Initial energy E_i (eV)	Total time τ (ns)	τ_g (ns)	$T_{\text{eff}}(\tau_g)$ (eV)
	He + N		
0.50	3150	250	0.17
0.93	3250	230	0.29
1.50	3320	210	0.44
2.00	3360	205	0.56
2.50	3380	195	0.69
3.00	3400	190	0.82
3.50	3415	185	0.94
	Ar + N		
0.50	2970	210	0.17
0.93	3000	170	0.31
1.50	3040	145	0.49
2.00	3060	135	0.65
2.50	3080	127	0.81
3.00	3100	120	0.99
3.50	3120	115	1.16

and τ for a bath gas density of 3.27×10^{16} cm^{-3} and the mean energies $E(\tau_g)$ expressed as effective temperatures $T_{\text{eff}}(\tau_g)$ are listed in Table I for E_i between 0.5 eV and 3.5 eV. A Maxwellian-like shape of the energy distribution function is attained in a time of 0.1–0.2 μs, whereas 3–4 μs elapses before full thermal equilibrium prevails.

Measurements are reported of the translational relaxation of energetic nitrogen atoms traversing bath gases of helium and argon. The Doppler profiles of the moving atoms are compared to profiles calculated from direct numerical solutions of the linear integral Boltzmann equation for which full account is taken of the energy and angular dependence of the collision cross sections. The scattering is dominated by small angle collisions driven by the long-range van der Waals interaction, and the energy relaxes through a large number of small energy transfer collisions. It is shown that distributions peaked at some initial energy evolve through a bipolar mode into a Maxwellian form at an intermediate effective temperature followed by Maxwellian distributions with effective temperatures, which decrease continuously to the temperature of the bath gas. Thus, the thermalization process has two time scales. Translational equilibration with the formation and preservation of a Maxwellian-like distribution occurs for both Lorentz and Rayleigh gases and may be characterized by a single parameter, the time-dependent effective temperature. These results are very different from the predictions of the hard-sphere model, and they reflect the dominance of small angle scattering and small energy transfer in collisions of neutral particles.

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