Comment on "Approach to Thermal Equilibrium in Atomic Collisions"

Zhang *et al* [1] presented theoretical results for the relaxation of energetic N atoms in a background of He assumed to be at equilibrium at $T_b = 295$ K and density $N = 3.27 \times 10^{16}$ cm^{-3}. They concluded that the approach to equilibrium proceeds with two very different time scales, τ_g and τ, where $\tau/\tau_g = 12.6$–18.5; see Table 1 of [1]. They contend without quantitative evidence that the distribution function (DF), $f(v, t)$, is a Maxwellian by time τ_g and that the DF remains Maxwellian with a time dependent temperature over the time interval τ until equilibrium is attained. The authors state that this two time scale relaxation results from the strongly forward peaked quantum differential cross section, $\sigma(\epsilon, \theta)$, and does not occur for a hard sphere cross section. I contend that the experimental and theoretical results strongly suggest a single relaxation time, τ_E, largely determined by the momentum transfer cross section. The times τ_g and τ can be calculated from the exponential relaxation and are trivially related to τ_E. Moreover, the value for τ of the order of 3000 ns reported in [1] is too long.

The linear Boltzmann equation for the isotropic DF is of the form $\partial f/\partial t = Lf$ where L is the collision operator defined by $\sigma(\epsilon, \theta)$ and m_N/m_{He}. The discrete eigenvalues defined by $L\phi_n = -\lambda_n \phi_n$ are ordered such that $\lambda_0 = 0 < \lambda_1 < \lambda_2 \ldots$. The time dependence of the DF is given by $f(v, t) = \sum_{n=0} a_n e^{-\lambda_n t}\phi_n(v)$ and the average energy is given by $E(t)/E_{\rm th} = 1 + \sum_{n=1} a_n b_n e^{-\lambda_n t}$ where $E_{\rm th} = 3kT_b/2$. The a_n coefficients are determined by the initial DF and the b_n coefficients are the projection of v^2 onto the eigenfunctions, $\phi_n(v)$. Close to thermal equilibrium, $f(v, t) \approx f_m(v, T_b) + a_1 e^{-\lambda_1 t}\phi_1(v)$ where $f_m(v, T_b)$ is the Maxwellian. The time scales are given by the reciprocal of the eigenvalues and the longest is $1/\lambda_1$ [2].

Preservation of a Maxwellian for $t > \tau_g$ in [1] requires that $\lambda_n \propto n$ which does not occur in general [3]. For the potential $V(r) \sim r^{-4}$, the differential cross section is strongly forward peaked and $E(t)$ decays exactly as $\exp(-\lambda_1 t)$ [4], a result that contradicts [1].

I have recalculated the quantum cross sections for N-He collisions in agreement with Zhang *et al* [1,5]. Approximate λ_n can be calculated from the diagonalization of the matrix representative of L, L_{nm}, in the Sonine polynomial basis expressed in terms of $\Omega^{(\ell)}(r) = \int_0^\infty \int_{-1}^1 e^{-y^2} y^{2r+3}\sigma(\epsilon, \theta)(1 - \mu^\ell)d\mu dy$, where $\mu = \cos(\theta)$ and $\epsilon = y^2 k_B T_b$ [6]. The longest relaxation time $\lambda_1^{-1} \approx \frac{3}{2}L_{11}^{-1}(T_b)$ depends primarily on $\Omega^{(1)}(1)$ [7,8].

The energy exchange rate coefficient, $k_E[T(t)]$, in the time rate of change of the average energy $dE^{(0)}/dt = -k_E[E^{(0)} - E_{\rm th}]$ (assuming that the DF is Maxwellian) can be expressed in terms of $\Omega^{(1)}(1)$ [7]. $E^{(0)}(t)$ is shown in Fig. 1 in comparison with the data from Fig. 7 of [5]. Also shown (dashed curve) is the analytic result [9] for $E^{(0)}(t)$ for a hard sphere cross section equal to 18 Å^2. The relaxation time, $k_E^{-1}(t)$, varies from 124 to 231 ns, the latter for $T = T_b = 295$ K which coincides with $\frac{3}{2}L_{11}^{-1}(T_b) \approx \lambda_1^{-1}$. If I assume exponential relaxation, $E(t) - E_{\rm th} = [E(0) - E_{\rm th}]\exp(-t/\tau_E)$, the appropriate semilogarithmic analyses of the theoretical and experimental results in [5] give $\tau_E = 187$ ns (for $E(0) = 0.93$ eV) and 164 ns, respectively, consistent with $k_E^{-1}(T_b)$. The sharply peaked cross section at zero scattering angle does not introduce two distinct time scales as suggested in [1]. The single relaxation time, τ_E, determined largely by the thermal average of the momentum transfer cross section and related to some averaged eigenvalue provides an accurate description of the approach to equilibrium. For exponential relaxation with $E(0) = 0.93$ eV, $E(\tau_g) = 0.29$ eV (Table 1 of [1]) and $\tau_E = 235$ ns, the values of τ_g and τ as defined in [1] are 284 and 1445 ns, respectively. There is no evidence for the relaxation time τ of the order of 3000 ns.

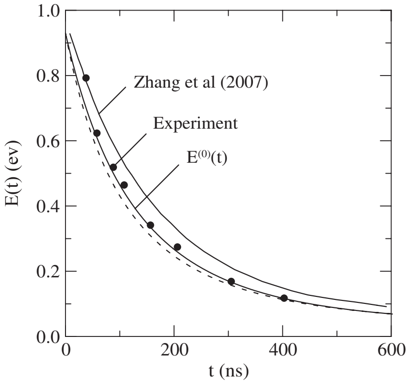

FIG. 1. Comparison of energy relaxation.

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[1] P. Zhang *et al.*, Phys. Rev. Lett. **100**, 103001 (2008).
[2] A. S. Clarke and B. Shizgal, Phys. Rev. E **49**, 347 (1994).
[3] H. C. Andersen *et al.*, J. Math. Phys. (N.Y.) **5**, 522 (1964).
[4] Y. Chang and B. D. Shizgal, AIP CP **1084**, 421 (2008).
[5] P. Zhang *et al.*, Mol. Phys. **105**, 1487 (2007).
[6] B. Shizgal and M. Karplus, J. Chem. Phys. **54**, 4345 (1971).
[7] B. Shizgal, J. Chem. Phys. **72**, 3156 (1980).
[8] S. Kryszewski and J. Gondek, Phys. Rev. A **56**, 3923 (1997).
[9] B. Shizgal and J. M. Fitzpatrick, J. Chem. Phys. **63**, 138 (1975).