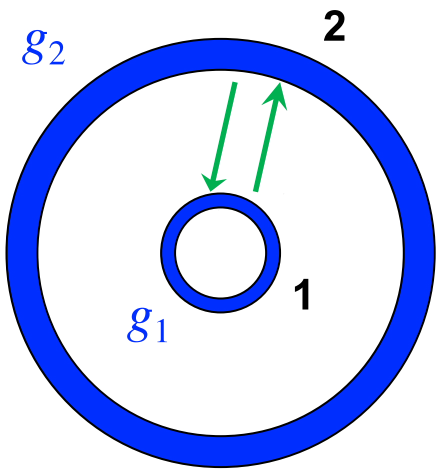
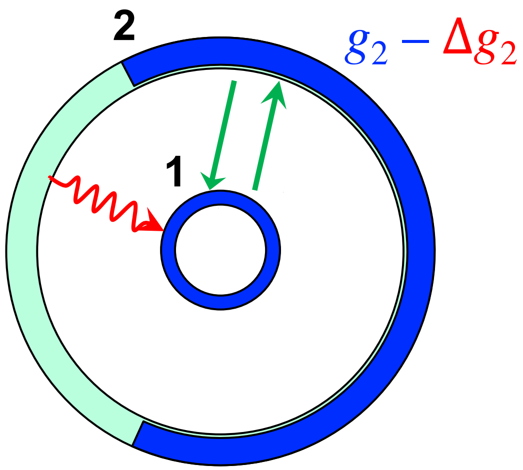
Nonequilibrium Thermodynamics Under Collisional-Radiative Equilibrium

Isolated two-level atom



$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\varepsilon_{21}/kT}$$

Reduce occupation probability by radiative decay



$$\frac{N_2}{N_1} = \frac{g_2 - \Delta g_2}{g_1} e^{-\varepsilon_{21}/kT}$$

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Summary

We have applied an atomic occupation-probability approach to thermodynamic energy and pressure of a radiating gas under collisional-radiative equilibrium

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- Collisional-radiative equilibrium (CRE) is the very important steady state of continuous, freely, and irreversibly escaping radiation
- Properties of matter under CRE are functions of local thermodynamic variables, so they can be tabulated for use in numerical radiation-hydrodynamic simulations with the tools of classical equilibrium thermodynamics
- The simplest atomic system shows small reductions in pressure and energy that are characteristic of radiation effects under CRE that are absent under local thermodynamic equilibrium (LTE)

Collaborators

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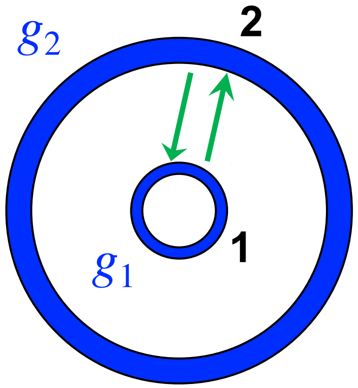
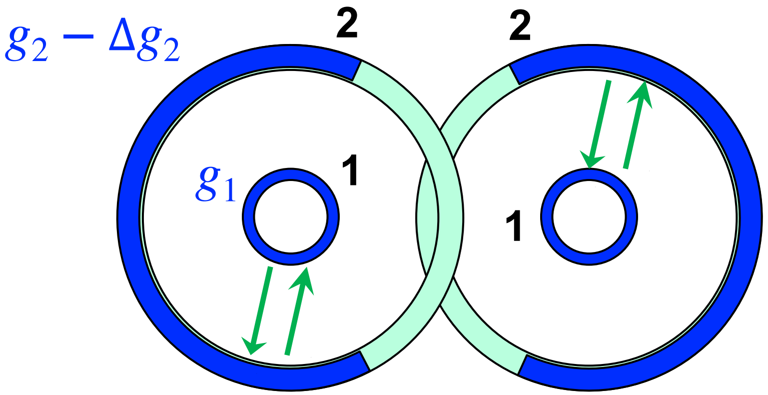
The Hummer–Mihalas* framework introduces nonideal equation-of-state (EOS) effects through modified atomic state occupation probabilities

Isolated two-level atom
Collisional LTE ⇄



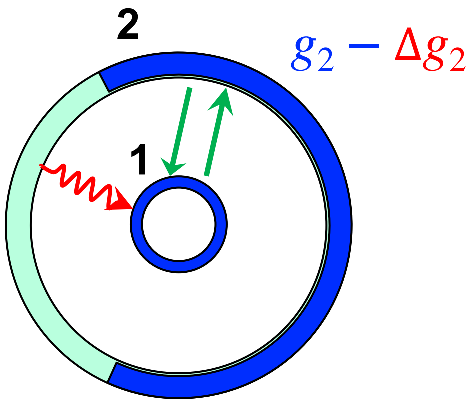
$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\varepsilon_{21}/kT}$$

Reduce occupation probability by pressure ionization



$$\frac{N_2}{N_1} = \frac{g_2 - \Delta g_2}{g_1} e^{-\varepsilon_{21}/kT}$$

Reduce occupation probability by radiative decay



$$\frac{N_2}{N_1} = \frac{g_2 - \Delta g_2}{g_1} e^{-\varepsilon_{21}/kT}$$

Add radiative decay to collisional equilibrium:

$$n_e C_{12} N_1 = \left(n_e C_{21} + A_{21}\right) N_2$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \frac{e^{-\varepsilon_{21}/kT}}{1 + A_{21}/n_e C_{21}}$$

* D. G. Hummer and D. Mihalas, Astrophys. J. 331, 794 (1988).

The need for non-LTE models of radiating matter in rad-hydro numerical simulations has motivated many simplifying approximations

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- **Busquet (RADIOM, 1993):* Obtain non-LTE ionization and opacity from LTE tables using an "ionization temperature"**

$$Z_{\text{non-LTE}} = Z_{\text{LTE}}\left(T_{\text{non-LTE}}, V\right)$$

→ **Epstein (1998):** Calculate and tabulate correct ionization and opacity tables in CRE as an important option to LTE tables**

- **Busquet (1982):† Modify LTE excitation and ionization ratios for radiative decay using phenomenological factors**

→ **This simple CRE correction factor form is familiar and nearly 40 years old**

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\varepsilon_{21}/kT} \Big/ \left(1 + A_{21}/n_e C_{21}\right) \approx \frac{g_2}{g_1} e^{-\varepsilon_{21}/kT} \Big/ \left(1 + \alpha \varepsilon_{21}{}^3 T^{1/2} V / N_e\right)$$

- **Zimmerman & More (1980),‡ Hummer & Mihalas (1988):‡‡ Formulate nonideal effects (e.g., pressure ionization) in the free energy by modifying the occupation probabilities of atomic states**

→ **A CRE free energy based on the same CRE atomic model used for opacity and emissivity will assure overall self-consistency and a thermodynamic consistent EOS.**

$$\frac{N_i}{N} = g_i e^{-\left[\varepsilon_i - \left(\partial f/\partial N_i\right)\right]/kT} \Big/ \tilde{Z}^I$$

* M. Busquet, Phys. Fluids B 5, 4191 (1993).
** R. Epstein *et al.*, Bull. Am. Phys. Soc. 43, 1666 (1998).
† M. Busquet, Phys. Rev. A 25, 2302 (1982).
‡ G. B. Zimmerman and R. M. More, J. Quant. Spectrosc. Radiat. Transf. 23, 517 (1980).
‡‡ D. G. Hummer and D. Mihalas, Astrophys. J. 331, 794 (1988).

Local thermodynamic equilibrium thermodynamics must be modified to describe matter in collisional-radiative equilibrium

- **Pressure and internal energy obtained from the free energy $F = E - TS$ are thermodynamically consistent**

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,\{N_\mathrm{i}\}} \qquad E = -T^2\left(\frac{\partial(F/T)}{\partial T}\right)_{V,\{N_\mathrm{i}\}}$$

- **In LTE, constituent populations are constrained by chemical equilibrium**

$$\sum_\mathrm{i} \mu_\mathrm{i} \mathrm{d}N_\mathrm{i} = 0 \qquad N_\mathrm{i}^\mathrm{LTE}(T,V)$$

- **In CRE, constituent populations are not in statistical equilibrium**

$$\sum_\mathrm{i} \mu_\mathrm{i} \mathrm{d}N_\mathrm{i} \neq 0 \qquad N_\mathrm{i}^\mathrm{CRE}(T,V) \neq N_\mathrm{i}^\mathrm{LTE}(T,V)$$

- **A CRE chemical equilibrium with modified chemical potentials is needed to restore thermodynamics, EOS tables, etc., valid for rad-hydro simulations of matter under CRE conditions**

$$\sum_\mathrm{i} \mu_\mathrm{i}^\mathrm{CRE} \mathrm{d}N_\mathrm{i} = 0$$

- **Boltzmann two-level atom:** $\dfrac{N_2}{N_1} = \dfrac{\frac{g_2}{g_1} e^{-\varepsilon_{21}/kT}}{1 + A_{21}/n_\mathrm{e} C_{21}} = \dfrac{g_2}{g_1} e^{-\left(\varepsilon_{21} - \delta\mu_2^\mathrm{CRE}\right)/kT}$

- **Saha ionization:** $\dfrac{N_{j+1} n_\mathrm{e}}{N_j} = \dfrac{\frac{2g_{j+1}}{g_j}\left(\frac{2\pi m_\mathrm{e} kT}{h^2}\right) e^{-\chi_j/kT}}{1 + R_{j+1,j}/n_\mathrm{e} C_{j+1,j}}$

The full Hummer–Mihalas* free energy can be applied to any composition and atomic model that is formulated in terms of state populations

- Correct the free energy for state occupation probability changes caused by radiative decay

$$F_{\mathrm{CRE}} = F_{\mathrm{LTE}} + f\left(T, V, \{N_{\mathrm{i}}\}\right) \qquad \frac{N_{\mathrm{i}}}{N} = g_{\mathrm{i}} e^{-\left[\varepsilon_{\mathrm{i}} - \left(\partial f / \partial N_{\mathrm{i}}\right)\right]/kT} \Big/ \tilde{Z}^{I}$$

subject to the constraint $\sum_{\mathrm{i}} \left(\partial F_{\mathrm{CRE}} / \partial N_{\mathrm{i}}\right) dN_{\mathrm{i}} = 0$, where $\tilde{Z}^{I} = \sum_{\mathrm{i}} g_{\mathrm{i}} e^{-\left[\varepsilon_{i} - \left(\partial f / \partial N_{\mathrm{i}}\right)\right]/kT}$

- Can we find the set of CRE-modified chemical potentials equivalent to a general CRE solution?

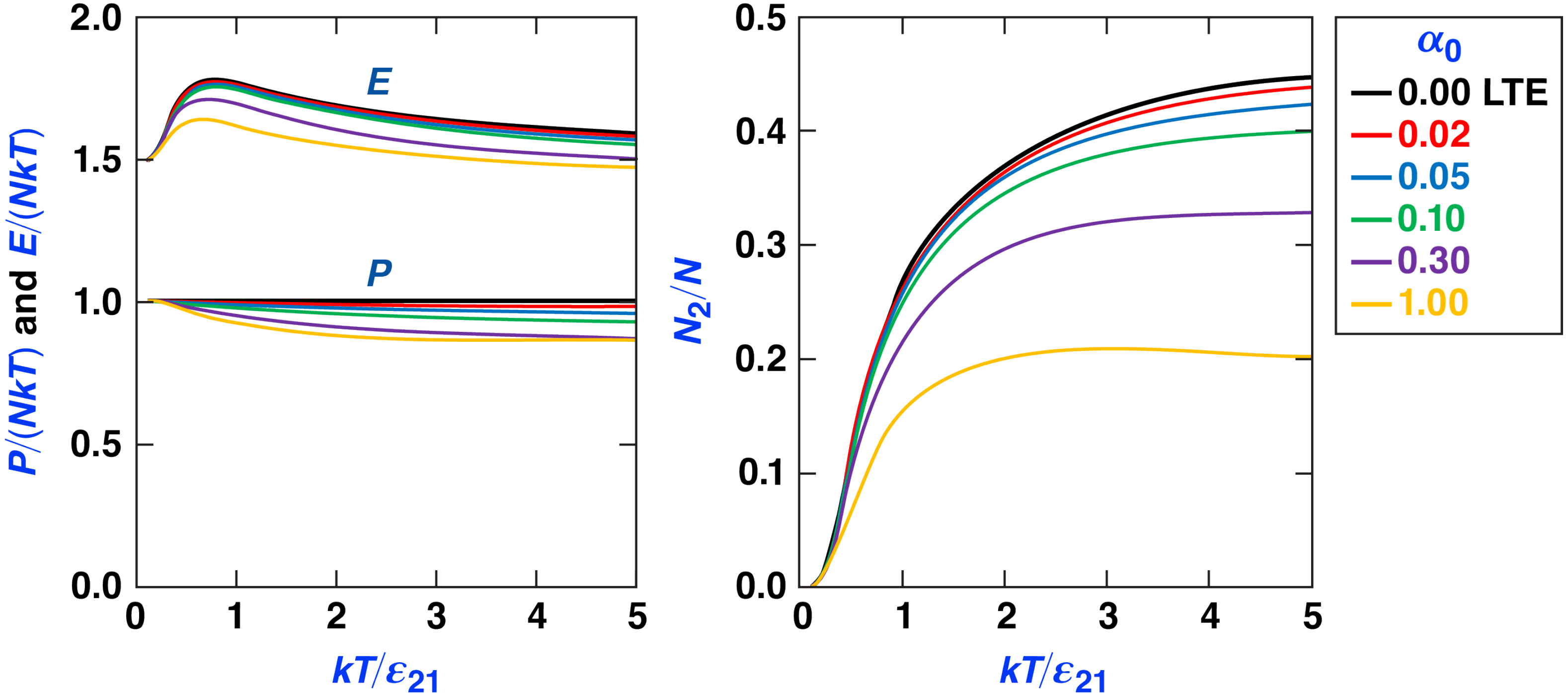
$$\partial f / \partial N_{\mathrm{i}} = -\delta\mu_{\mathrm{i}} \approx kTN_{\mathrm{i}} \ln\left(1 + \beta_{\mathrm{i}} T^{\gamma} V^{\eta}\right)$$

- Simultaneous LTE and CRE calculations give $N_{\mathrm{i}}^{\mathrm{CRE}} / N_{\mathrm{i}}^{\mathrm{LTE}}$ ratios as occupation probability modification values

- A complete set of partial derivatives $\left\{\partial\mu_{\mathrm{i}} / \partial T\big|_{V}, \partial\mu_{\mathrm{i}} / \partial V\big|_{T}\right\}$ at each tabulation point is needed

* D. G. Hummer and D. Mihalas, Astrophys. J. 331, 794 (1988).

In the two-level atomic gas, nonideal CRE EOS effects arise from volume-dependent radiative free-energy terms



$$A_{21}/n_e C_{21} = \alpha_0 \left(\frac{kT}{\varepsilon_{21}}\right)^{1/2} \left(\frac{V}{V_0}\right)$$

- **Ideal gas behavior is recovered in the non-radiative limit**
- **This CRE nonideal behavior resembles the effect of the volume-dependent interaction energy in a Van der Waals gas**

$$P = kT\left\{N - N_2 V \frac{\partial \ln\left[1+\alpha_0\left(kT/\varepsilon_{21}\right)^{1/2}\left(V/V_0\right)\right]}{\partial V}\Bigg|_T\right\}$$

$$E = \frac{3}{2}NkT + N_2\left[\varepsilon_{21} - kT^2 \frac{\partial \ln\left(1+A_{21}/n_e C_{21}\right)}{\partial T}\Bigg|_V\right]$$

$$P = \frac{NkT}{V-Nb} - \frac{N^2 a}{V^2}$$

The rate ratio $A_{21}/n_e C_{21}$ that indicates where CRE affects EOS also indicates generally where CRE is applicable.

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