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

- 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

\[
\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{\varepsilon_{21}}{kT}}
\]

Reduce occupation probability by pressure ionization

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

Reduce occupation probability by radiative decay

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

Add radiative decay to collisional equilibrium:

\[
n_e C_{12} N_1 = (n_e C_{21} + A_{21}) N_2
\]

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

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

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

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

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

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

- **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

  \[ \frac{N_1}{N} = g_1 e^{[\varepsilon_1 - (\partial f / \partial N_1)]/kT} / \bar{Z}_f \]

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

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

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.

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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.

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

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

- 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.

- Boltzmann two-level atom:
  \[
  \frac{N_2}{N_1} = \frac{g_2}{g_1} \frac{e^{-\frac{\epsilon_{21}}{kT}}}{1 + A_{21}/n_e C_{21}} = \frac{g_2}{g_1} e^{-\left(\frac{\epsilon_{21} - \delta \mu_{CRE}}{kT}\right)}
  \]

- Saha ionization:
  \[
  \frac{N_{j+1} n_e}{N_j} = \frac{2 g_{j+1} \left( \frac{2 \pi m_e k T}{h^2} \right) e^{-\frac{x_j}{kT}}}{1 + R_{j+1,j}/n_e C_{j+1,j}}
  \]

\( P = -\left( \frac{\partial F}{\partial V} \right)_{T_i[N_i]} \quad E = -T^2 \left( \frac{\partial (F/T)}{\partial T} \right)_{V_i[N_i]} \)
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

\[
F_{\text{CRE}} = F_{\text{LTE}} + f(T,V,\{N_i\}) \quad \frac{N_i}{N} = g_i e^{-\left[\epsilon_i - (\partial f/\partial N_i)\right]/kT} / \tilde{Z}^i
\]

subject to the constraint \( \sum_i (\partial F_{\text{CRE}}/\partial N_i) dN_i = 0 \), where \( \tilde{Z}^i = \sum_i g_i e^{-[\epsilon_i - (\partial f/\partial N_i)]/kT} \)

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

\[
\frac{\partial f}{\partial N_i} = -\delta \mu_i \approx kT N_i \ln \left( 1 + \beta_i T' V'' \right)
\]

- Simultaneous LTE and CRE calculations give \( N_i^{\text{CRE}} / N_i^{\text{LTE}} \) ratios as occupation probability modification values

- A complete set of partial derivatives \( \left\{ \partial \mu_i / \partial T, \partial \mu_i / \partial V \right\} \) at each tabulation point is needed

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

In the non-radiative limit, this CRE nonideal behavior resembles the effect of the volume-dependent interaction energy in a Van der Waals gas.

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

We have applied an atomic occupation-probability approach to thermodynamic energy and pressure of a radiating gas under 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 LTE.