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**Infrared Emission from Interstellar Dust.**

I. Stochastic Heating of Small Grains

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**ABSTRACT**

We present a method for calculating the infrared emission from a population of dust grains heated by starlight, including very small grains for which stochastic heating by starlight photons results in high temperature transients. Because state-to-state transition rates are generally unavailable for complex molecules, we consider model PAH, graphitic, and silicate grains with realistic vibrational mode spectra and realistic radiative properties. The vibrational density of states is used in a statistical-mechanical description of the emission process. Unlike previous treatments, our approach fully incorporates multiphoton heating effects, important for large grains or strong radiation fields.

We discuss how the “temperature” of the grain is related to its vibrational energy. By comparing with an “exact” statistical calculation of the emission process, we determine the conditions under which the “thermal” and the “continuous cooling” approximations can be used to calculate the emission spectrum.

We present results for the infrared emission spectra of PAH grains of various sizes heated by starlight. We show how the relative strengths of the 6.2, 7.7, and 11.3µm features depend on grain size, starlight spectrum and intensity, and grain charging conditions. We show results for grains in the “cold neutral medium”, “warm ionized medium”, and representative conditions in photodissociation regions. Our model results are compared to observed ratios of emission features for the Milky Way and other galaxies, and for the M17 and NGC 7023 photodissociation regions.

**Subject headings:** Galaxies: ISM; Infrared: ISM: Continuum; ISM: Dust

1. **Introduction**

Very small grains – consisting of tens to hundreds of atoms – play a major role in the infrared emission from the interstellar medium. These grains are small enough that the time-averaged vibrational energy ⟨E⟩ is smaller than or comparable to the energy of the starlight photons which heat
the grains. Stochastic heating by absorption of starlight therefore results in transient “temperature spikes”, during which much of the energy deposited by the starlight photon is reradiated in the infrared.

The idea of transient heating of very small grains was first introduced by Greenberg (1968). Its importance was not apparent until the detection of the near infrared emission of reflection nebulae (Sellgren et al. 1983) and detection by the Infrared Astronomical Satellite (IRAS) of 12 and 25µm Galactic emission which was far in excess of the emission expected for interstellar dust at $T \approx 20$ K (Boulanger & Pérault 1988). Subsequent measurements by the Diffuse Infrared Background Experiment (DIRBE) instrument on the Cosmic Background Explorer (COBE) satellite confirmed this and detected additional broadband emission at 3.5 and 4.9µm (Arendt et al. 1998). More recently, spectrometers aboard the Infrared Telescope in Space (IRTS) (Onaka et al. 1996; Tanaka et al. 1996) and the Infrared Space Observatory (ISO) (Mattila et al. 1996) have shown that the diffuse interstellar medium radiates strongly in emission features at 3.3, 6.2, 7.7, 8.6, and 11.3µm. These emission features, previously observed from a small number of bright reflection nebulae, planetary nebulae, and HII regions, have been tentatively identified as emission from polycyclic aromatic hydrocarbons, or PAHs (Léger & Puget 1984; Allamandola, Tielens, & Barker 1985).

To understand these observations we need to be able to calculate the infrared emission expected for a given model of interstellar dust. The question we address here is: what approximations can be used to carry out accurate calculations of thermal emission from a population of very small grains exposed to stochastic heating by starlight?

There have been a number of previous studies of the discrete heating of very small grains (Duley 1973; Greenberg & Hong 1974; Gail & Seldmayr 1975; Greenberg 1976; Purcell 1976; Drapatz & Michel 1977; Andriese 1978; Aannestad & Kenyon 1979; Léger & Puget 1984; Draine & Anderson 1985; Puget et al. 1985; Désert et al. 1986; Dwek 1986; Guhathakurta & Draine 1989; Aannestad 1989; Siebenmorgen et al. 1992; Manske & Henning 1998; Duley & Poole 1998). Most studies have made three approximations: (1) the “thermal” approximation for excitation; (2) use of “bulk” specific heats; and (3) the “continuous cooling” approximation. While accurate for large grains, these approximations could potentially introduce significant inaccuracies for very small grains.

Barker & Cherchneff (1989) and d’Hendecourt et al. (1989) found that the thermal approximation was valid for computing thermal emission spectra. Allamandola, Tielens, & Barker (1989), Schutte, Tielens, & Allamandola (1993), and Cook & Saykally (1998) compared calculations of infrared emission from PAHs using the thermal approximation with the results of a more detailed statistical treatment; they found that the thermal approximation provided a good approximation for the emission from low-frequency modes, although it overestimated the emission from high frequency modes such as the 3.3µm C-H stretching mode. All of these studies used the “continuous cooling” approximation to discuss the overall emission from a PAH following single-photon heating.

The validity of the “continuous cooling” approximation has been questioned by Siebenmorgen
et al. (1992), Manske & Henning (1998), and Duley & Poole (1998). Siebenmorgen et al. (1992) and Manske & Henning (1998) attempted to treat the cooling process as discrete events, but did not correctly evaluate the transition probabilities, as we show below in §6.1.

The present paper addresses the vibrational excitation of interstellar grains, both small and large, and the resulting infrared emission. If energy levels and transition probabilities were known, we could (at least in principle) solve for the statistical steady-state populations of the different energy levels of grains illuminated by a known radiation field. However, this level of detailed information is generally unavailable, for even the smallest and simplest PAH molecules. We therefore construct a “model PAH” grain, $C_nH_m$, with a realistic spectrum of energy levels. Following previous workers (e.g., Schutte et al. 1993, Boulanger et al. 1998) we adopt realistic absorption cross section $C_{abs}(\lambda)$, depending on the number of C atoms, the H/C ratio, and whether the PAH is neutral or ionized. We construct a similar model for silicate grains, with appropriate mode spectrum and absorption cross section. We divide the energy level spectrum into a manageable number of “bins”, estimate the “bin-to-bin” transition probabilities, and can then solve for the steady-state probability $P_j$ of occupying energy bin $j$.

Our analysis allows for discrete quantum states at low vibrational energies, and what is effectively a continuum of vibrational levels at large energies. As we show, the only simplifying assumptions that need to be made are: (1) the absorption cross section $C_{abs}(\lambda)$ is independent of the degree of vibrational excitation, and (2) internal vibrational relaxation rapidly redistributes internal energy among the vibrational degrees of freedom of the grain. While not exact, these are both expected to be good approximations. Once $C_{abs}(\lambda)$ is adopted and the spectrum of vibrational “normal modes” (and from this the vibrational density of states) is specified, the physics of absorption and emission of radiation by the grain is essentially fully determined. With these assumptions, we can solve for the energy distribution function $P(E)$ for a given grain in an arbitrary radiation field, with full inclusion of “multiphoton heating” effects which become important for large grains or intense radiation fields. Because we solve for $P(E)$ including all radiative transitions, we obtain the “exact” solution against which we can then test solutions obtained using the thermal approximation and the continous cooling approximation.

In §2 we estimate the spectrum of vibrational modes for small PAH and silicate grains, and obtain the vibrational density of states for such grains. The transition probabilities depend on the photon absorption cross sections, and in §3 we describe the cross sections adopted for PAH grains.

We formulate the “exact” statistical treatment in §4. In §5 we discuss how the “temperature” of a grain is related to its vibrational energy content, and in §6 we show how the “thermal” approximation is related to the exact treatment. The radiative cooling time for vibrationally-excited grains is estimated as a function of $E$ and grain size in §7.

In §8 we discuss the method used to solve for the steady-state energy distribution. In §9 we show how the infrared emission spectrum can be calculated from the energy distribution, both for the exact statistical treatment and using the thermal approximation. We show some sample
solutions in §10, where we assess the accuracy of the “thermal” approximation. We find the thermal approximation to be quite accurate for calculation of the overall emission spectrum from a population of very small grains. Furthermore, we find that the “continuous cooling” approximation is itself quite accurate, and can therefore be used to greatly reduce the amount of computation required to find the temperature distribution functions.

The above studies therefore provide a methodology for computing the infrared emission from dust grains irradiated by starlight. The method is accurate, and can be used for any specified mixture of grain sizes and compositions; we present results for both carbonaceous and silicate materials. We discuss our results in §11 and summarize the main points in §12.

The paper is largely concerned with the physics of infrared emission from stochastically-heated grains, and practical methods for calculating the emission spectrum. Readers who are interested only in the resulting emission spectrum may wish to proceed directly to §10. In a following paper (Li & Draine 2001a) we apply this methodology to construct models to account for the observed infrared emission from the diffuse interstellar medium.

2. Vibrational Mode Spectrum and Level Degeneracies

A grain containing \( N_a \) atoms will have 3 translational degrees of freedom, 3 rotational degrees of freedom, and \( N_m = 3N_a - 6 \) vibrational modes. Each vibrational mode \( j = 1, \ldots, N_m \) has a fundamental frequency \( \omega_j \). If we approximate the vibrational modes as harmonic oscillators, then the vibrational energy of the grain (not including zero-point energy) is

\[
E = \sum_{j=1}^{N_m} v_j \hbar \omega_j ,
\]

where the integer \( v_j \geq 0 \) is the vibrational quantum number for mode \( j \). If the vibrational system is in thermal equilibrium at temperature \( T \), the expectation value of the energy \( E \) is

\[
\langle E(T) \rangle = \sum_{j=1}^{N_m} \frac{\hbar \omega_j}{\exp(\hbar \omega_j / kT) - 1} .
\]

where \( k \) is Boltzmann's constant. The heat capacity

\[
C(T) \equiv \frac{dE}{dT} = k \sum_{j=1}^{N_m} e^{-\hbar \omega_j / kT} \left[ \frac{\hbar \omega_j / kT}{1 - \exp(-\hbar \omega_j / kT)} \right]^2 .
\]

Ideally, we would have accurate knowledge of the \( N_m \) frequencies \( \omega_j \). Since the complete mode spectrum is known only for a small number of grain candidates such as \( \text{C}_2\text{H}_4\text{H}_{12} \) coronene (see below), we need to estimate the normal mode spectrum for candidate grains of different sizes and materials.
2.1. Normal Modes: Polycyclic Aromatic Hydrocarbons

A polycyclic aromatic hydrocarbon molecule containing \( N_C \) C atoms and \( N_H \) H atoms has \( N_m = 3(N_H + N_C - 2) \) distinct vibrational modes. These can be separated into \( 3(N_C - 2) \) modes of the C-C skeleton, and \( 3N_H \) modes associated with the C-H bonds at the periphery. The frequencies of these normal modes have been computed for a small number of polycyclic aromatic hydrocarbons, with some frequencies determined experimentally, but mode spectra are not yet available for most PAHs of interest. Here we estimate the mode spectrum for “generic” PAHs. We will treat 5 different types of vibration separately: out-of-plane C-C modes, in-plane C-C modes, out-of-plane C-H bending, in-plane C-H bending, and C-H stretching.

Graphite is a useful guide to the C-C modes. Krumhansl & Brooks (1953) found that the lattice vibration specific heat of graphite could be approximated by a model where the out-of-plane and in-plane C-C vibrations each had a mode spectrum given by a two-dimensional Debye model, with Debye temperatures \( \Theta_{op} \approx 950 \text{ K} \) for the out-of-plane modes, and \( \Theta_{ip} \approx 2500 \text{ K} \) for the in-plane modes. This suggests that the C-C vibrational modes for a PAH might be similarly approximated.

A \( n \)-dimensional Debye spectrum has modes uniformly distributed in \( E^n \) up to a maximum energy \( k\Theta \). Consider a mode spectrum of the form

\[
h\omega_j = k\Theta_D \left[ \frac{(1 - \beta_n)}{N_m} (j - \delta_j) + \beta_n \right]^{1/n} \quad j = 1, ..., N_m.
\]

For the PAH C-C modes we set the dimensionality \( n = 2 \), with \( N_m = N_C - 2 \) for the out-of-plane modes, and \( N_m = 2(N_C - 2) \) for the in-plane modes.

If \( \delta_j \) is independent of \( j \), the modes are uniformly distributed in \( E^2 \). We will in fact take

\[
\delta_j = \begin{cases} 
1/2 & \text{for } j \neq 2 \text{ or } 3 \\
1 & \text{for } j = 2 \text{ or } 3
\end{cases}
\]

because this shift of modes 2 and 3 to lower frequency improves the match to the actual mode spectrum of coronene.

As discussed in Appendix A we assume PAHs to be planar for \( N_C \leq 54 \), approximately spherical for \( N_C > 102 \), with intermediate shape for \( 54 < N_C < 102 \). Thus for \( N_C \leq 54 \) we expect the lowest frequency mode \( \omega_1 \propto N_C^{-1/2} \), approximately constant \( \omega_1 \) for \( 54 < N_C < 102 \), and \( \omega_1 \propto N_C^{-1/3} \) for \( N_C > 102 \). We achieve this by taking

\[
\beta_2 = \begin{cases} 
0 & \text{for } N_C \leq 54 \\
\frac{1}{(2N_m - 1)} \left( \frac{N_C - 54}{52} \right) & \text{for } 54 < N_C \leq 102 \\
\frac{1}{(2N_m - 1)} \left[ \frac{(N_C - 2)}{52} \left( \frac{102}{N_C} \right)^{2/3} - 1 \right] & \text{for } N_C > 102
\end{cases}
\]

(7)
We use equations (4-7) with \( N_m = N_C - 2 \) and \( k\Theta_{op}/hc = 600 \text{ cm}^{-1} \) for \( \Theta_{op} = 863 \text{ K} \) for the out-of-plane C-C modes, and \( N_m = 2(N_C - 2) \) and \( k\Theta_{ip}/hc = 1740 \text{ cm}^{-1} \) for \( \Theta_{ip} = 2504 \text{ K} \) for the in-plane C-C modes.

We can adequately approximate the C-H stretching and bending modes by \( N_H \) out-of-plane bending modes at \( \lambda^{-1}_{\text{CH,op}} = (11.3 \mu\text{m})^{-1} = 886 \text{ cm}^{-1} \), \( N_H \) in-plane bending modes at \( \lambda^{-1}_{\text{CH,ip}} = (8.6 \mu\text{m})^{-1} = 1161 \text{ cm}^{-1} \), and \( N_H \) C-H stretching modes at \( \lambda^{-1}_{\text{CH,str}} = (3.3 \mu\text{m})^{-1} = 3030 \text{ cm}^{-1} \).

For our model “astronomical PAH” sequence, we will assume

\[
N_H = \text{int}(0.5N_C + 0.5) \quad N_C \leq 25 \\
= \text{int}(2.5\sqrt{N_C} + 0.5) \quad 25 \leq N_C \leq 100 \\
= \text{int}(0.25N_C + 0.5) \quad N_C \geq 100
\]

(8)

where \( \text{int}(x) \) is the integer part of \( x \). The pericondensed species coronene \( \text{C}_{24}\text{H}_{12} \), circumcoronene \( \text{C}_{54}\text{H}_{18} \), and dicircumcoronene \( \text{C}_{96}\text{H}_{24} \) are members of the sequence prescribed by eq. (8). Beyond \( N_C = 100 \) we assume \( \text{H}/\text{C} \approx 0.25 \). For a carbonaceous grain containing \( N_C \) carbon atoms, we associate a representative “radius” \( a = 10 \AA (N_C/468)^{1/3} \), corresponding to the carbon density \( \rho = 2.24 \text{ g cm}^{-3} \) of graphite.

We use \( \text{C}_{24}\text{H}_{12} \) coronene, for which the mode spectrum is known (Cyvin 1982; Cyvin et al. 1984), to test the above model. As shown in Figure 1, our “synthetic” mode spectrum is in excellent agreement with the actual mode spectrum of coronene.

Applying our synthetic mode spectrum for PAHs in the limit \( N_C \to \infty \) and \( N_H = 0 \), the mode spectrum of the C-C modes reduces to the 2-dimensional Debye model. The heat capacity becomes

\[
C_{\text{graph}} = (N_C - 2)k \left[ f'_2(T/863 \text{ K}) + 2f'_2(T/2504 \text{ K}) \right]
\]

(9)

\[
f_n(x) \equiv \frac{1}{n} \int_0^1 \frac{y^n dy}{\exp(y/x) - 1} , \quad f'_n(x) \equiv \frac{d}{dx} f_n(x) \quad .
\]

(10)

In Figure 2 we compare eq. (9) with experimental data for (bulk) graphite. The excellent agreement confirms that our model spectrum for the C-C vibrational modes applies from small PAH molecules up through macroscopic samples of graphite.

### 2.2. Normal Modes: Silicate Grains

In the case of silicate grains, we use experimental specific heats as a guide to the vibrational mode spectrum. The specifics heat of \( \text{SiO}_2 \) glass, obsidian glass (75% \( \text{SiO}_2 \) and 25% metal oxides by mass), and basalt glass (50% \( \text{SiO}_2 \), 50% metal oxides by mass) reported by Léger, Jura, & Omont (1985) are plotted Figure 2. As seen in Figure 2, the experimental results for bulk silicates (basalt and obsidian) can be satisfactorily reproduced if 2/3 of the vibrational modes are distributed
Fig. 1.— $N_{\text{modes}}(E)$, the number of vibrational modes with energy $< E$, for coronene $C_{24}H_{12}$ (solid lines) compared to the model spectrum (broken lines) given by eq.(4-7) with $N_m = 22$ modes with $k\Theta_{op}/hc = 600 \text{ cm}^{-1}$, $N_m = 44$ modes with $k\Theta_{ip}/hc = 1740 \text{ cm}^{-1}$, $N_m = 12$ modes with $\lambda^{-1} = 886, 1161, \text{ and } 3030 \text{ cm}^{-1}$ (see text).

according to a Debye model with $n = 2$ and Debye temperature $\Theta = 500 \text{ K}$, and $1/3$ of the modes are described by a Debye model with $n = 3$ and $\Theta = 1500 \text{ K}$:

$$C_{\text{sil}} = (N_a - 2)k \left[ 2f'_2(T/500 \text{ K}) + f'_3(T/1500 \text{ K}) \right]$$

where $N_a$ is the number of atoms in the cluster, and $f_n$ is given by eq. (10). Eq. (11) agrees quite well with the measured specific heats for obsidian and basalt, so we use this model to estimate the mode spectrum for silicate grains.

We expect the lowest frequency mode $\omega_1 \propto N_a^{-1/3}$. To achieve this scaling for modes distributed according to an $n-$dimensional Debye model [eq. (4)], we set

$$\beta_n = \frac{N_m^{1-n/3} - 1}{2N_m - 1} ;$$

note that for $n = 3$ this gives $\beta_3 = 0.$
For small silicate grains, two-thirds of the vibrational modes are then approximated by eqs. (4-6) with \( n = 2, \Theta_D = 500 \text{ K}, \) and \( N_m = 2(N_a - 2), \) and the remaining third by eqs. (4-6) with \( n = 3, \Theta_D = 1500 \text{ K}, \) and \( N_m = N_a - 2. \) The resulting normal mode spectrum is shown in Figure 3.

### 2.3. Density of States

Let there be a total of \( N_m = 3(N_a - 2) \) distinct normal modes. The general vibrational state can then be specified by the \( N_m \)-tuple \( (v_1, v_2, ..., v_{N_m}) \) giving the vibrational quantum numbers for each of these modes. If each mode is approximated by a harmonic oscillator, then \( N(E) \), the number of distinct vibrational states with total vibrational energy less than or equal to \( E \), can be calculated using the Beyer-Swinehart algorithm (Beyer & Swinehart 1973; Stein & Rabinovitch 1973). In Figure 4 we show \( N(E) \) computed for \( \text{C}_{24}\text{H}_{12} \), using both the actual normal mode spectrum for
coronene and our model normal mode spectrum for C_{24}H_{12} (see Figure 1). The resulting $N(E)$ are essentially identical for $E/hc \gtrsim 300$ cm$^{-1}$.

The Beyer-Swinehart algorithm is remarkably efficient, and with IEEE standard 64-bit arithmetic can be applied to calculate $N(E)$ up to $E/hc = 10^5$ cm$^{-1}$ for clusters with up to $\sim$600 atoms. For a given cluster, we employ the Beyer-Swinehart algorithm for energies up to an energy $E_t$ where $N(E_t) \approx 10^{300}$, beyond which we are limited by inability to calculate floating point numbers exceeding $2^{1024} \approx 10^{308}$. For $E > E_t$ we calculate the density of states by integrating $dS = dQ/T$:

$$\ln N(E) = \ln N(E_t) + \int_{E_t}^{E} \frac{dE'}{kT(E')} ,$$

(13)

where $T(E)$ is the temperature at which the grain has energy $E$ (see §5). Figures 4 and 5 show $N(E)$ evaluated for C_{24}H_{12}, C_{400}H_{100}, C_{800}H_{200}, and C_{4000}H_{1000} using our model density of states.
3. Absorption Cross Sections

Following previous workers (e.g., Schutte et al. 1993), we estimate the absorption cross sections for both neutral and ionized PAHs from far ultraviolet to far infrared (see Li & Draine 2001a for details) based on available experimental data (Allamandola et al. 1999; Hudgins & Allamandola 1999; and references therein) and guided by astronomical observations (e.g., Boulanger et al. 1998). In the ultraviolet and infrared the resulting cross sections are mainly a collection of Drude profiles: the $\sigma - \sigma^*$ transition mode ($\lambda^{-1} \simeq 14 \mu m^{-1}$); the $\pi - \pi^*$ transition ($\lambda^{-1} \simeq 4.6 \mu m^{-1}$); the C-H stretching mode ($\lambda = 3.3 \mu m$); the C-C stretching modes ($\lambda = 6.2, 7.7 \mu m$); the C-H in-plane bending mode ($\lambda = 8.6 \mu m$); the C-H out-of-plane bending modes ($\lambda = 11.3, 11.9, 12.7 \mu m$); and a few weak features attributed to the C-C bending modes ($\lambda = 16.4, 18.3, 21.2, 23.1 \mu m$). In addition to these features, we have included continuous absorption in the far-UV, near-UV/visible, as well as a small amount of continuous absorption in the infrared. [For further information see Li & Draine (2001)]. In Figure 6 we display the adopted absorption cross sections for neutral and ionized PAHs.
Fig. 5.— Total number of vibrational states $N(E)$ with energy less than $E$ for $\text{C}_{400}\text{H}_{100}$ and $\text{C}_{800}\text{H}_{200}$. Solid line is the direct Beyer-Swinehart calculation for $N < 10^{300}$; broken line is from eq. (13).

Following Li & Draine (2001), we make a smooth transition from PAH optical properties for $N_C \lesssim 6 \times 10^4$ ($a < 50 \, \text{Å}$) to graphite properties for $N_C \gtrsim 5 \times 10^5$ ($a > 100 \, \text{Å}$), calculated using Mie theory with the 1/3-2/3 approximation (Draine & Malhotra 1993) and dielectric functions from Draine & Lee (1984).

For silicates, we use Mie theory with dielectric constants for astronomical silicate (Draine & Lee 1984).\footnote{We use the “smoothed UV” silicate dielectric function discussed by Weingartner & Draine 2001a, with modifications to the far-infrared emissivity proposed by Li & Draine 2001a, available at http://www.astro.princeton.edu/~draine .}
4. Excitation of Very Small Grains: Exact Statistical Treatment

4.1. Assumptions

We characterize the state of the grain by its vibrational energy $E$. There are too many energy levels to consider individually, so we group them into $M + 1$ “bins” $j = 0, ..., M$, where the $j$-th bin is $[E_{j,\text{min}}, E_{j,\text{max}})$, with representative energy $E_j \equiv (E_{j,\text{min}} + E_{j,\text{max}})/2$, and width $\Delta E_j \equiv E_{j,\text{max}} - E_{j,\text{min}}$. The “degeneracy” $g_j$ is the number of distinct quantum states included in bin $j$. The procedure used for specifying the bins is described in Appendix B.

Let $P_j$ be the probability of finding the grain in bin $j$. The probability vector $P_j$ evolves
according to
\[
\frac{d}{dt}P_i = \sum_{j \neq i} T_{ij}P_j - \sum_{j \neq i} T_{ji}P_i \quad i = 0, 1, ..., M,
\] (14)

where the transition matrix element $T_{fi}$ is the probability per unit time for a grain in bin $i$ to make a transition to one of the levels in bin $f$. All of the physics is embodied in the transition matrix $T$.

A truly exact treatment of the grain excitation would require knowledge of all the state-to-state transition probabilities between energy levels. Given the large number of energy levels to be considered, this is utterly infeasible at this epoch. In order to estimate the required state-to-state rates, we make only the following three assumptions:

- The grain absorption cross section $C_{\text{abs}}(h\nu)$ depends on the photon energy $h\nu$, but does not depend on the vibrational energy of the grain prior to the absorption.
- The vibrational modes of the grain can be approximated by harmonic oscillators.
- The energy of absorbed photons is distributed ergodically among the $3N_a - 6$ vibrational degrees of freedom before any infrared emission takes place.\(^2\)

We now show that with only these three assumptions, together with knowledge of

- the spectrum of fundamental vibrational modes,
- the grain absorption section $C_{\text{abs}}(h\nu)$, and
- the starlight energy density $u_E$,

we can fully determine the emission from interstellar dust grains. Note that the notion of “grain temperature” does not appear in what we will refer to as the “exact-statistical treatment”.

### 4.2. Upward Transitions

In Appendix C we show that the rate for upward transitions $l \rightarrow u$ is

\[
T_{ul} = \frac{c\Delta E_u}{E_u - E_l} \int_{W_1}^{W_4} G_{ul}(E)C_{\text{abs}}(E)u_E dE \quad \text{for } u < M
\] (15)

\[
T_{Ml} = \frac{c}{E_M - E_l} \left[ \int_{W_1}^{W_c} \left( \frac{E - W_1}{W_c - W_1} \right) C_{\text{abs}}(E)u_E dE + \int_{W_c}^{\infty} C_{\text{abs}}(E)u_E dE \right]
\] (16)

\(^2\)Since the grain will in general have angular momentum, and the principal values of the moment of inertia tensor will generally be nondegenerate, in principle some of the heat can appear in rotational excitation (Lazarian & Draine 1999a,b). However, since there are only three rotational degrees of freedom, this is at most a small effect, and will be neglected.
\[ G_{ul}(E) = \begin{cases} \frac{(E - W_1)}{\Delta E_u \Delta E_l} & \text{for } W_1 < E < W_2 \\ \min \left[ \frac{\Delta E_l}{\Delta E_u \Delta E_l}, \frac{\Delta E_u}{\Delta E_u \Delta E_l} \right] & \text{for } W_2 < E < W_3 \\ \frac{(W_4 - E)}{\Delta E_u \Delta E_l} & \text{for } W_3 < E < W_4 \\ 0 & \text{for } E < W_1 \text{ or } E > W_4 \end{cases} \]

and \( u_E dE \) is the energy density due to photons with energies in \([E, E + dE]\). Note that eq. (16) takes energy absorbed in transitions to levels beyond the highest bin and allocates it to the highest bin \((M)\). In practice, we ensure that the highest bin is set high enough that the rate of such transitions is negligible, and the population \( P_M \) is negligibly small.

The factor \( G_{ul}(E) \) represents the correction for finite bin width; if \( \max(\Delta E_l, \Delta E_u) \ll (E_u - E_l) \), then eq. (15) becomes

\[ T_{ul} \approx c \frac{u_E \Delta E_u}{E_u - E_l} \] for \( u < M \)  
\[ T_{MI} \approx c \frac{u_E \Delta E_M}{E_M - E_l} + \frac{c}{E_M - E_l} \int_{E_M - E_l}^{\infty} C_{\text{abs}}(E) u_E dE \] .

Most previous studies (e.g., Guhathakurta & Draine 1989) have used this approximate form, but eq. (15-24) make proper allowance for finite bin width and are to be preferred. Correction for finite bin width is important when the treatment is applied to grains with radii \( a \gtrsim 50 \text{ Å} \), since for tractable numbers of bins \( M \lesssim 10^3 \), many bins will necessarily be broad, with \( \Delta E_u \gtrsim kT_u \).

For the special case of transitions \( u - 1 \rightarrow u \) we include “intrabin” absorptions:

\[ T_{u,u-1} = \frac{c}{E_u - E_{u-1}} \left[ \int_0^{W_4} \Delta E_u G_{u,u-1}(E) C_{\text{abs}}(E) u_E dE + \int_0^{\Delta E_{u-1}} \left( 1 - \frac{E}{\Delta E_{u-1}} \right) C_{\text{abs}}(E) u_E dE \right] \]

but the “intrabin” contribution (second integral in eq. 28) is negligible in all cases of interest.

### 4.3. Downward Transitions

The radiative coupling between levels is determined by the absorption cross section \( C_{\text{abs}}(h\nu) \). The Einstein \( A \) coefficient for radiative decay \( u \rightarrow l \), averaged over the sublevels in bin \( u \), is (see
Appendix C)

\[ T_{lu} = \frac{8\pi}{\hbar^3 c^2} \frac{g_l}{g_u} \frac{\Delta E_u}{E_u - E_l} \int_{W_1}^{W_4} G_{ul}(E) E^3 C_{abs}(E) \left[ 1 + \frac{\hbar^3 c^3}{8\pi E^3} u_E \right] dE \quad \text{for } l < u - 1. \]  

(29)

The degeneracies \(g_u\) and \(g_l\) are the numbers of energy states in bins \(u\) and \(l\), respectively (see §2.3):

\[ g_j \equiv N(E_{j,\text{max}}) - N(E_{j,\text{min}}) \approx \left( \frac{dN}{dE} \right)_{E_j} \Delta E_j. \]  

(30)

The term proportional to \(u_E\) in eq. (29) is the contribution of stimulated emission. For transitions \(u \to u - 1\) to the adjacent bin we have \(W_1 = 0\); even very long wavelength emission can contribute if \(C_{abs} > 0\). For this case we must also include the power radiated in “intrabin” transitions within bin \(u\):

\[ T_{u-1,u} = \frac{8\pi}{\hbar^3 c^2} \frac{g_{u-1}}{g_u} \frac{\Delta E_u}{E_u - E_{u-1}} \int_{0}^{W_4} G_{u,u-1}(E) E^3 C_{abs}(E) \left[ 1 + \frac{\hbar^3 c^3}{8\pi E^3} u_E \right] dE + \]

\[ \frac{8\pi}{\hbar^3 c^2} \frac{1}{E_u - E_{u-1}} \int_{0}^{\Delta E_u} \left( 1 - \frac{E}{\Delta E_u} \right) E^3 C_{abs}(E) \left[ 1 + \frac{\hbar^3 c^3}{8\pi E^3} u_E \right] dE \]  

(31)

Thus we see that we require only \(C_{abs}(E)\), the degeneracies \(g_j\), and the starlight spectrum \(u_E\) to completely determine the transition matrix \(T_{fi}\). We stress that “grain temperature” does not enter the exact-statistical treatment (e.g., eq. 15,29). In §6 below we will discuss “thermal” approximations to estimate the downward transition rates \(T_{lu}\). We first discuss an estimate \(T(E)\) for the “temperature” of a state of specified vibrational energy \(E\).

5. Energy vs. Temperature

5.1. “Exact” Mode Spectrum

Consider a grain with vibrational energy \(E_u\). If the grain is large, we know that the emission can be estimated from the grain “temperature”. We can use eq. (2) to define a “temperature” \(\bar{T}(E_u)\) such that \(\bar{E}(\bar{T}) = E_u\), where \(\bar{E}(T)\) is the expectation value for the vibrational energy \(E\) when in contact with a heat bath at temperature \(T\).

When there are only a few vibrational quanta in the grain, however, “temperature” is not a well-defined concept. As the most extreme example, consider a grain where only the first vibrational mode is excited, with exactly one quantum: \(E_u = \hbar \omega_1\). If the grain has many vibrational degrees of freedom, then the temperature \(\bar{T}\) may be quite low (since it is defined in terms of the expectation value of the vibrational energy summed over all the modes). However, our grain is vibrating in the fundamental vibrational mode and we want to estimate the emission from this mode. One estimate for the temperature characterizing the excitation of this mode would be the temperature for which the occupation number of this mode is equal to 1. We will see in §6 that when this
“temperature” is used in the “thermal approximation”, one obtains the correct rate of emission in the $1 \rightarrow 0$ transition. In fact, we will use this value of the temperature for all energies up to the energy of the 20th vibrational mode. For large grains and large energies, however, $\tilde{T}$ is appropriate. To encompass these two limits, we take the temperature $T_u$ of vibrational level $u$ to be\footnote{For $T = \hbar \omega / k \ln 2$ a quantized harmonic oscillator has occupation number equal to 1.}

$$T_u = \frac{\hbar \omega_1}{k \ln 2} \quad \text{for } E_u \leq \hbar \omega_20$$
$$= \tilde{T}(E_u) \quad \text{for } E_u > \hbar \omega_20,$$

(32)

While the choice of $\hbar \omega_20$ as the energy separating these two approximations is arbitrary, we remind the reader that the very notion of “temperature” is questionable for such low degrees of excitation. Our use of eq. (32) is in fact guided by the fact that the “thermal approximation” of §6, when used with this prescription for $T_u$, gives emission rates in fair agreement with the “exact-statistical” treatment (29). Figures 7 and 8 show our adopted $T(E)$ for selected PAHs and silicates.$^4$

\section*{5.2. Debye Mode Spectrum}

When the number of modes is large, the summation in equation (2) contains many terms. In this case, for PAHs we replace the sums over the C-C modes by the (continuum) Debye model discussed above:

$$\bar{E}_{\text{PAH}}(T) \approx N_H \sum_{j=1}^{3} \frac{\hbar \omega_j}{\exp(\hbar \omega_j / kT)} - 1 + (N_C - 2) \left[ k \Theta_{op} f_2(T/\Theta_{op}) + 2 k \Theta_{ip} f_2(T/\Theta_{ip}) \right],$$

(33)

where $f_2$ is defined by eq. (10), and the summation index $j = 1 - 3$ runs over the C-H out-of-plane bending, in-plane bending, and stretching modes (see §2.1). Similarly, for silicate grains we take

$$\bar{E}_{\text{sil}}(T) \approx (N_a - 2) \left[ 2 k \Theta_2 f_2(T/\Theta_2) + k \Theta_3 f_3(T/\Theta_3) \right]$$

(34)

where $\Theta_2 = 500$ K and $\Theta_3 = 1500$ K. We use eq. (33) and (34) for $E > N_a E_1$.

\section*{6. Thermal Approximations for Spontaneous Emission}

Given the above assumptions about the vibrational mode spectrum (§2), the assumption that the absorption cross section depends only on the photon energy (§3), and the assumption of rapid internal vibrational redistribution, the “statistical” approach described above (§4) is “exact”. It is

\footnote{The discontinuity in $T(E)$ at $E = \hbar \omega_20$ is obviously unphysical, but we note that the discontinuity is only appreciable for large grains at very low energies, and these make a negligible contribution to the overall emission spectrum.}
often desirable, however, to use an alternative “thermal” approximation which is less computationally demanding.

The thermal approach has been frequently used (Greenberg 1976; Purcell 1976; Aannestad & Kenyon 1979; Léger & Puget 1984; Draine & Anderson 1985; Puget et al. 1985; Désert et al. 1986; Dwek 1986; Guhathakurta & Draine 1989; Aannestad 1989; Manske & Henning 1998). The only difference between the thermal approach and the statistical approach concerns the calculation of the downward transition rates $T_{lu}$ which, in contrast to the exact-statistical treatment [eq. (29)], uses the notion of “grain temperature”.

We will consider two different approximations which make use of the thermal approximation, and compare results for energy distributions and infrared emission spectra.
6.1. "Thermal-Discrete" Approximation

In the “thermal-discrete” approximation we use the same energy bins used in the exact statistical treatment discussed in §4, and allow the same upward and downward discrete transitions. However, instead of using eq. (29) to evaluate the downward transition probabilities $T_{lu}$, we replace

$$
\frac{g_l}{g_u} \rightarrow \frac{\Delta E_l}{\Delta E_u} \exp\left(\frac{h\nu}{kT_u}\right) - 1
$$

(35)

where $T_u$ is the “temperature” of the upper level. With this replacement, the downward transition rate becomes, for $l < u - 1$:

$$
T_{lu}^{\text{id}} = \frac{8\pi}{h^3c^2} \frac{\Delta E_l}{E_u - E_l} \int_{W_1}^{W_4} G_{ul}(E) \frac{E^3C_{\text{abs}}(E)}{\exp(E/kT_u) - 1} \left[ 1 + \frac{h^3c^3}{8\pi E^3} u E \right] dE \quad \text{for} \ 0 < l < u - 1.
$$

(36)

Siebenmorgen et al. (1992) discussed both discrete heating and cooling. However, their downward transition elements were evaluated by integrating over the initial, rather than final, enthalpy interval, and hence are in error by a factor $\sim \Delta E_u / \Delta E_l$, which is large when $\Delta E_u \gg \Delta E_l$, as is often the case. Manske & Henning (1998) also
For \( l = u - 1 \) we include the energy-loss in “intrabin” transitions, as in eq. (31):

\[
T_{u-1,u}^{td} = \frac{8\pi}{\hbar^3c^2} \frac{\Delta E_l}{E_u - E_l} \int_0^{E_u} G_{u,u-1}(E) \frac{E^3}{\exp(E/kT_u) - 1} \left[ 1 + \frac{h^3c^3}{8\pi E^3 u_E} \right] dE +
\]

\[
\frac{8\pi}{\hbar^3c^2} \frac{1}{E_u - E_{u-1}} \int_0^{\Delta E_u} \left( 1 - \frac{E}{\Delta E_u} \right) \frac{E^3}{\exp(E/kT_u) - 1} \left[ 1 + \frac{h^3c^3}{8\pi E^3 u_E} \right] dE.
\]

(37)

We refer to eq. (36,37) as the “thermal-discrete” approximation. The advantage of the “thermal-discrete” approximation is that one does not require explicit knowledge of the degeneracies \( g_u \) and \( g_l \) appearing in equation (29,31). We obtain the temperature \( T_u \) from eq. (32).

As discussed in §4.1, the vibrational ground state is in a “bin” with energy \( E_0 = 0 \) and width \( \Delta E_0 = 0 \), for which eq. (36) would give \( T_{0u}^{td} = 0 \). There is really no “correct” way to approximate the energy levels as continuous when dealing with the ground state. We simply replace \( \Delta E_0 \) in eq. (36) by \( \Delta E_1 \).

Thus we do not use eq. (36) for transitions to the ground state, and instead take

\[
T_{0u}^{td} = \frac{8\pi}{\hbar^3c^2} \frac{\Delta E_1}{E_u} \frac{1}{E_u - E_{u-1}} \int_{E_{u,\min}}^{E_{u,max}} \frac{E^3}{\exp(E/kT_u) - 1} \left[ 1 + \frac{h^3c^3}{8\pi E^3 u_E} \right] C_{abs}(E)dE.
\]

(38)

### 6.2. “Thermal-Continuous” Cooling Approximation

In all of the above discussion, the grain is assumed to make discrete transitions to energy levels \( l < u \) by emission of single photons – so-called “discrete cooling”. With discrete cooling included, discussed discrete cooling. In the present notation their equation (4) becomes

\[
T_{iu} = \frac{8\pi}{\hbar^3c^2} \int_{E_{i,u-1,\min}}^{E_{i,u-1,\max}} \frac{E^3/\Delta E_u}{\exp(E/kT_u) - 1} C_{abs}(E)dE.
\]

Comparison with eq. (36) reveals that Manske & Henning’s integrand is off by a factor \( \sim (E_u - E_l)/[\Delta E_u \Delta E_l G_{ul}(E)] \approx (E_u - E_l)/\min(\Delta E_1, \Delta E_u) \). This is a large error for the common case where the photon energy is large compared to the energy bin width, \( E \gg \min(\Delta E_1, \Delta E_u) \).

Note that the thermal approximation (36) reduces to the statistical treatment (29) if the temperature is taken to be

\[
T_u = \frac{h\nu/k}{\ln[1 + (dN/dE)|_{E_u}/(dN/dE)|_{E_u-h\nu}]}
\]

but this definition of \( T_u \) depends on both \( u \) and the emitted photon energy \( h\nu \) – only in the limit of infinite degrees of freedom does \( T_u \) no longer depend on the value of \( h\nu \).

If this seems rather arbitrary, we remind the reader that the “correct” approach to the problem is the statistical treatment given in §4. The “thermal approximation” considered here is inappropriate when discussing low degrees of excitation.

It can be verified that if we use \( \Delta E_1 \) for the width of bins 0 and 1, and \( g_0 = g_1 = 1 \), then \( T_1 = E_1/k\ln2 \) from eq. (32) gives the same transition rate \( T_{01} \) as the exact-statistical treatment.
the transition matrix $T_{fi}$ is generally nonzero through the upper triangular portion $i > f$.

There are substantial computational advantages (see §8 below) if the cooling of the grains is approximated as continuous rather than discrete, so that the only downward transition from a level $u$ is to the adjacent level $u - 1$. We refer to this as the “thermal continuous” cooling approximation. We take

$$T_{iu}^{tc} = 0 \text{ if } l < u - 1$$

$$T_{u-1,u}^{tc} = \frac{1}{(E_u - E_{u-1})} \sum_{l=0}^{u-1} (E_u - E_l) T_{lu}^{td}$$

Using (36), eq.(E1), and eq. (E2), the transition rate (40) from levels $u > 2$ can be approximated

$$T_{u-1,u}^{tc} \approx \frac{1}{(E_u - E_{u-1})} \frac{8\pi}{\hbar^2 c^2} \int_0^{E_u} \frac{E^3 C_{abs}(E)}{\exp(E/kT_u) - 1} dE$$

for $u > 1$.

Because of the computational advantages (see §8.2), the continuous cooling approximation has been often used in previous studies (e.g., Guhathakurta & Draine 1989). While clearly appropriate for large systems with many degrees of freedom (for which $kT \ll E$ and emission of one photon does not result in a large reduction in temperature), validity of the continuous cooling approximation for grains with $\lesssim 10^2$ atoms is certainly not obvious a priori. Manske & Henning (1998) in fact argued that the continuous cooling approximation could lead to significant error. We will examine the accuracy of the continuous-cooling approximation in §10 below, where we will show that it is in fact surprisingly accurate even for grains with as few as $\sim 30$ atoms.

### 7. Cooling Time

The absorption cross section $C_{abs}(E)$ determines both the rate of heating by starlight and the rate of cooling by infrared emission. It is useful to define a “radiative cooling time”

$$\tau_{rad}(E_u) \equiv \frac{E_u}{\sum_{l<u} T_{lu}(E_u - E_l)}$$

$$\approx \left[ \frac{8\pi}{\hbar^2 c^2} \frac{1}{E_u (dN/dE)_u} \int_0^{E_u} x^3 C_{abs}(x) \left[ 1 + \frac{\hbar^2 c^3}{8\pi x^3 u_x} \right] \left( \frac{dN}{dE} \right)_{E_u-x} dx \right]^{-1}$$

where eq. (E2) has been used to obtain eq. (43). In the thermal-discrete approximation, we see from eq. (41) that

$$\tau_{rad}^{td}(E_u) \approx \left[ \frac{1}{E_u \hbar^2 c^2} \int_0^{E_u} \frac{E^3 C_{abs}(E)}{\exp(E/kT_u) - 1} dE \right]^{-1}$$

for $u > 1$.

Cooling times for PAH and silicate grains are plotted in Figs. 9 and 10. The interstellar starlight radiation field (ISRF) of Mathis, Mezger & Panagia (1983, hereafter MMP) has been assumed for
Fig. 9.— The radiative cooling time $\tau_{\text{rad}}$ as a function of vibrational energy $E$ for PAH grains, calculated with the exact-statistical and thermal-discrete cooling models. The lowest energy $E$ shown for each grain corresponds to the lowest vibrationally-excited state $\hbar \omega_1$. The discontinuity in $\tau_{\text{rad}}$ for the thermal-discrete model is due to the different definition of the grain “vibrational temperature” for the lowest 20 excited levels (see §5 and Fig. 7). Note that $\tau_{\text{rad}}$ for the thermal-continuous model is identical to that for the thermal-discrete model [eq. (15) and eq. (36)].

$u_E$; for this very dilute radiation field the correction for stimulated emission is entirely negligible ($\hbar^3 c^3 u_E / 8\pi E^3 \ll 1$ for $E / hc \gtrsim 10 \text{ cm}^{-1}$).

We show $\tau_{\text{rad}}$ evaluated using the “exact-statistical” method, as well as using the “thermal-discrete” approximation ($\tau_{\text{rad}}$ for the continuous cooling approximation is, by construction, identical to that for the “thermal-discrete” approximation).

As illustrated in Figs. 9-10, $\tau_{\text{rad}}(E)$ increases with grain size; for a given grain size, $\tau_{\text{rad}}$ decreases rapidly with increasing vibrational energy $E$. The importance of single photon heating is apparent: very small grains emit most of their energy very rapidly (within seconds) following absorption of an energetic photon and spend most of their time in or close to the ground vibrational state.
The substantial difference between the results of the statistical model and the thermal models at low $E$ is mainly due to the treatment of transitions to the ground state, which are problematic in the thermal approximation (see §6.1). The jagged behavior of $\tau_{\text{rad}}$ in the exact-statistical model result from the discreteness of the lowest energy states (see eq. 4) which affects the degeneracies (see eq. 29). The discontinuity in $\tau_{\text{rad}}$ computed in the thermal approximation (Figures 9,10) is due to the discontinuity in the prescription (32) for the grain “vibrational temperature” at $E = \hbar \omega_{20}$ (see Figs. 7,8). Note that with the present prescription for the temperature, our estimates for $\tau_{\text{rad}}$ in the thermal approximation are in reasonable agreement with $\tau_{\text{rad}}$ calculated in the “exact-statistical” method at the lowest energies. For $C_{4000}H_{1000}$ in Figure 9, and $a = 20$ Å in Figure 10, the discontinuity in $\tau_{\text{rad}}$ at $\sim 3 \times 10^4$ cm$^{-1}$ is due to a transition from direct computation of the density of states to use of a continuous Debye model.

The mean time $\tau_{\text{abs}}$ between photon absorptions for a grain is given by

$$\tau_{\text{abs}}^{-1} \equiv \int_0^\infty C_{\text{abs}}(h\nu) \frac{cu_\nu}{h\nu} d\nu ,$$

(45)
In Figure 11 we show \( \tau_{\text{abs}} \) for grains in the MMP ISRF. The mean absorbed photon energy \( \langle h\nu \rangle_{\text{abs}} \) is

\[
\langle h\nu \rangle_{\text{abs}} \equiv \tau_{\text{abs}} \int_0^\infty C_{\text{abs}}(h\nu) c u_\nu \, d\nu.
\]

(46)

Ionized PAHs with \( N_C < 10^4 \) in the MMP radiation field have \( \langle h\nu \rangle_{\text{abs}} \approx 5.2 \text{ eV} \); neutral PAHs have a somewhat higher value of \( \langle h\nu \rangle_{\text{abs}} \) due to their different absorption cross section (see Figure 6).

![Fig. 11. — Radiative cooling time \( \tau_{\text{rad}} \) for a grain containing \( E = 5.2 \text{ eV} \) of vibrational energy, and mean time \( \tau_{\text{abs}} \) between photon absorptions for the MMP ISRF, as a function of grain size, for carbonaceous and silicate grains. The decrease in \( \tau_{\text{rad}} \) as \( N_C \) increases above \( \sim 5 \times 10^4 \) is due to the assumed transition from PAH-like to graphitic optical properties at \( a \approx 50 \text{ Å} \).](image)

Also plotted in Figure 11 is the cooling time \( \tau_{\text{rad}} \) for grains containing 5.2 eV of thermal energy. The critical size \( N_{\text{sph}} \) (and radius \( a_{\text{sph}} \)) for single-photon heating is determined by the condition \( \tau_{\text{rad}}(N_{\text{sph}}) = \tau_{\text{abs}}(N_{\text{sph}}) \). For carbonaceous grains, we find

\[
N_{C,\text{sph}} \approx 5 \times 10^5 \left( \frac{u}{u_{\text{MMP}}} \right)^{-0.00} \quad a_{\text{sph}} \approx 100 \text{ Å} \left( \frac{u}{u_{\text{MMP}}} \right)^{-0.20}
\]

(47)
For grains with \( N < N_{sph} \) atoms, single-photon heating effects are very important: the radiative cooling time is short compared to the interval between photon absorptions, and the grains spend most of the time between photon absorptions at energies \( E \ll \langle h\nu \rangle_{abs} \). Grains with \( N \gg N_{sph} \) heat up until their energy content is large compared to the energies of starlight photons, and individual photon absorptions produce small fractional changes in the thermal energy content. For such large grains, one may therefore estimate the average energy content \( \bar{E} \) by requiring a steady balance between cooling and heating:

\[
\frac{\bar{E}}{\tau_{rad}(E)} = \int d\nu \, c \nu C_{abs}(h\nu) .
\]

(48)

8. Solution Method

8.1. Discrete Cooling

If we define the diagonal elements of \( T \) to be

\[
T_{ii} = -\sum_{j \neq i} T_{ji}
\]

(49)

then equation (14) becomes

\[
\sum_{j=0}^{M} T_{ij} P_j = 0 \text{ for } i = 0, \ldots, M .
\]

(50)

Combining this with the normalization condition \( \sum_{j=0}^{M} P_j = 1 \), we obtain a set of \( M \) linear equations for the first \( M \) elements of \( P_j \):

\[
\sum_{j=0}^{M-1} (T_{ij} - T_{iM}) P_j = -T_{iM} \text{ for } i = 0, \ldots, M - 1 .
\]

(51)

The remaining undetermined element \( P_M \) is obtained by

\[
P_M = - (T_{MM})^{-1} \sum_{j=0}^{M-1} T_{Mj} P_j .
\]

(52)

For small \( M \) we can directly solve eq. (51) for \( P_j \) using Gaussian elimination. When \( M \gtrsim 10^2 \), however, direct solution, requiring \( O(M^3) \) operations, is both slow and numerically ill-behaved. We therefore resort to iterative techniques, and have tried both the bi-conjugate gradient (BiCG) method (Press et al. 1992), and the stabilized bi-conjugate gradient (BiCGstab) method (see Sleijpen & Fokkema 1993 and references therein). We found the BiCG method to be quite efficient even without preconditioning, whereas the convergence rate of the BiCGstab method is dependent on the choice of preconditioner.
Ideally, the adopted highest energy bin $E_M$ for a given grain would be as large as possible, but large values of $M$ entail heavy memory and cpu requirements. In our calculations, we first set $E_M = 13.6$ eV and solve eq. (51) for $P_j$. If $P_M < 10^{-14}$ then we use this $E_M$ and solution $P_j$; otherwise we increase $E_M$ by a factor 1.5 and solve again, repeating until we obtain a solution with $P_M < 10^{-14}$.

Small ($a \lesssim 20\text{Å}$) grains exposed to the interstellar starlight background are able to cool completely between photon absorptions, and $E_M = 13.6$ eV is sufficient. For larger grains, the interval between photon absorptions is shorter and the cooling time at given $E$ is longer (see Figs. 9 and 10), so that the grain generally does not cool off to the ground state between photon absorptions, and $E_M$ must be higher than 13.6 eV. For a grain with $a \gtrsim 100\text{Å}$ only modest cooling takes place between photon absorptions and $P_j$ becomes strongly peaked around a steady state “equilibrium temperature”.

8.2. Continuous Cooling

For the continuous cooling approximation it is straightforward to solve for the steady-state solution vector $P_j$. As shown by Guhathakurta & Draine (1989), if we define $X_j = P_j/P_0$, then $X_0 = 1$ and the remaining $X_j$ may be obtained recursively:

$$X_j = \frac{1}{T_{tc}} \sum_{i=0}^{j-1} B_{j,i} X_i, \quad B_{j,i} \equiv \sum_{u=j}^{M} T_{u,i}^{tc}$$

(53)

The recursion relation $B_{j,i} = T_{j,i} + B_{j+1,i}$ can be used to generate the $B_{j,i}$ in $O(M^2)$ operations, and the $X_j$ can then be computed in $O(M^2)$ operations. Once the $X_j$ are determined for $j = 0, ..., M$, one need only renormalize:

$$P_j = \frac{X_j}{\sum_{j=0}^{M} X_j}.$$  

(54)

Since $M \gtrsim 100$ is required to have suitably narrow energy bins (we often use $M \approx 500$), this $O(M)$ procedure is much faster than the BiCG iterative method required if discrete cooling is included.

9. Infrared Emission Spectrum

Having obtained the steady-state energy distribution $P_j$, we wish to calculate the resulting infrared emission spectrum. Let $F_\nu d\nu$ be the time-averaged power per steradian per grain radiated into frequency interval $[\nu, \nu + d\nu]$. Then the “exact statistical” treatment gives

$$\nu F_\nu = \frac{2h\nu^3}{c^2} C_{abs}(\nu) \left[ \sum_u \left( P_u \sum_{l=0}^{u-1} \frac{q_l}{k} \Delta E_u G_{ul}(h\nu) + \sum'' P_u \left( 1 - \frac{h\nu}{\Delta E_u} \right) \right) \right] \left[ 1 + \frac{\lambda^3}{8\pi} u_E \right]$$

(55)
The single-primed summation – the contribution of “interbin” transitions to the emission – is limited to levels \( u \) with \( E_{u,\text{max}} > h\nu \). The double-primed summation – the contribution of “intrabin” transitions – is limited to levels with \( \Delta E_u > h\nu \).

In the thermal approximation, equation (55) becomes (see Appendix D)

\[
\nu F_\nu \approx \frac{2h\nu^4}{c^2}C_{\text{abs}}(\nu) \left[ \sum_{u} P_u \exp(h\nu/kT_u) - 1 \right] \left[ 1 + \frac{\lambda^3 h\nu}{8\pi uE} \right],
\]

where the single-primed summation is now limited to levels \( u \) with \( E_u > h\nu \).

10. Results

We have calculated the (vibrational) energy probability distribution \( P_j \) for PAHs excited by the MMP ISRF using the above-described methods: the exact-statistical model (§4); the thermal-discrete model (§6.1); and the thermal-continuous model (§6.2).

In Figure 12 we present the cumulative energy probability distributions for selected PAHs obtained from the exact-statistical model, the thermal-discrete model, and the thermal-continuous model. Figure 13 shows the differential probability distributions as a function of grain energy \( E \) for these same grain sizes.

The inset in Figure 13 shows the probability of being in the vibrational ground state as a function of grain size, calculated for the exact-statistical model and the thermal-discrete model. As already illustrated in Figure 12 and Figure 13, the probability of being in the ground state is very large for small grains: for example, for the MMP radiation field, grains with \( N \lesssim 4000 \) spend most of their time at \( E = 0 \) [the exact-statistical model gives \( P_0 = 0.975 \) for \( N = 400 \), and \( P_0 = 0.316 \) for \( N = 4000 \)]. The sharp drop at 13.6 eV (\( E/hc = 1.1 \times 10^5 \text{ cm}^{-1} \)) is due to the radiation field cutoff at 912 Å and to the fact that multiphoton events are rare. The jagged structure at low energies in Figure 13 is due to the quantization of the lowest energy states. These structures are less prominent in the thermal models because the statistical model involves the degeneracies of each “bin” (see eq. 30) which depend on the detailed distribution of energy states (see, e.g., Figure 4).

The energy distributions \( P(E) \) found using the thermal-discrete model and the thermal-continuous model are both in good overall agreement with the results of the exact-statistical calculation.

It is not surprising that all three models are in good agreement at high energies since the transition rate from a very high energy state to the ground state is negligibly small, and the

\footnote{Note that only a few terms from \( \sum_{l} \) have \( G_{ul} \neq 0 \) – energy levels \( k \leq l \leq m \) where \( E_{u,\text{min}} - h\nu \in [E_{k,\text{min}}, E_{k,\text{max}}] \) and \( E_{u,\text{max}} - h\nu \in [E_{m,\text{min}}, E_{m,\text{max}}] \). Therefore eq. (55) requires only \( O(M) \) [rather than \( O(M^2) \)] operations per frequency \( \nu \).}
Fig. 12.— The cumulative energy probability distributions for PAHs computed using the exact-statistical model, the thermal-discrete model, and the thermal-continuous model. Note that the lowest energy state \((E = 0)\), not shown here, has \(P(E \geq 0) = 1\).

number of excited degrees of freedom is large enough that a thermal treatment is appropriate. The agreement becomes better with increasing grain size because the lowest vibrational states (i.e., the first few excited states) become closer and approach a “continuum”, and the gap between the ground state and the first excited state becomes smaller.

The resulting IR emission spectra are displayed in Figs. 14 and 15. As expected (from the energy distribution functions plotted in Figs. 12 and 13), the IR spectra of the thermal-discrete model are almost identical to those of the exact-statistical model, even for grains as small as \(N_C = 24\). The thermal-continuous cooling model also results in spectra which are very close to those computed using the exact-statistical model. The discrepancies are mainly at long wavelengths; this can be understood from the energy probability functions and would not affect the interstellar IR emission spectrum modeling.

The statistical model spectra are generally very close to those of the thermal models (Figs. 14
Fig. 13.— The vibrational energy distribution for excited vibrational states of ionized PAHs in the MMP ISRF, computed using the exact-statistical model, the thermal-discrete model, and the thermal-continuous model. The inset shows the probability $P_0$ of being in the ground state.

and 15), except for the sawtooth features at long wavelengths. These sawtooth features are due to our treatment of transitions from the lower excited energy bins to the ground state and first few excited states. However, we stress that the overall spectra are quite similar for all three models – the differences involve only a negligible fraction of the total emission for any given grain size, and thus would be unimportant when modeling the overall interstellar IR emission spectrum.

11. Discussion

11.1. Band Ratios

From Figs. 14 and 15 it is evident that the relative strength of the different PAH emission bands (3.3, 6.2, 7.7, 8.6, 11.3µm) is a strong function of the PAH size: small PAHs radiate strongly...
Fig. 14.— IR emissivities (per C atom) for selected ionized PAHs in the MMP ISRF calculated using the exact-statistical and thermal-discrete models.

at 6.2 and 7.7 µm, while larger PAHs emit most of their power at increasingly long wavelengths.

The 6.2, 7.7, and 11.3 µm features are prominent in many astronomical spectra. Let $P(\lambda_0)$ be the power radiated in the feature with central wavelength $\lambda_0$: for a Drude profile, $P(\lambda_0) = \frac{\pi}{2}(\Delta P_\lambda)_0(FWHM)_{\lambda_0}$, where $(\Delta P_\lambda)_0$ is the peak contribution of the feature to the emission, and $(FWHM)_{\lambda_0}$ is the full-width at half-maximum. In Figure 16 we show how the relative strengths of these emission bands vary depending upon the size and charge state of the PAHs, and upon the starlight intensity $u_E$, characterized by $\chi$ or $G_0$.\(^{10}\) Neutral PAHs have large ratios of $P(11.3\mu m)/P(7.7\mu m)$, while PAH ions have much smaller values. For both neutrals and ions, there is a regular progression of $P(6.2\mu m)/P(7.7\mu m)$ to smaller values with increasing $N_C$. For a given PAH neutral or ion, the emission band ratios are essentially independent of $\chi$ for

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\(^{10}\) $\chi$ is the intensity at 1000 Å relative to the estimate of Habing (1968); $G_0$ is the ratio of the 6–13.6 eV energy density to the estimate of Habing (1968). The MMP spectrum has $G_0 = 0.923\chi$; a $3 \times 10^4$ K blackbody has $G_0 = 0.602\chi$. 

$\chi < 3 \times 10^4 (10^3 / N_C)^{5/3}$ [see eq. (47)]; for larger values of $\chi$, multiphoton heating effects begin to be evident. For $\chi = 10^6$, multiphoton effects are evident even for $N_C = 10^2$ [consistent with eq. (47)].

In Figure 16 we plot the observed ratios of $P(11.3\mu m)/P(7.7\mu m)$ and $P(6.2\mu m)/P(7.7\mu m)$ for (1) the diffuse ISM (Onaka et al. 1996); (2) the average spectrum for a sample of 28 spiral galaxies (Helou et al. 2000); (3) the reflection nebula at the surface of the $\rho$ Oph molecular cloud (Boulanger et al. 1996); (4) the reflection nebula vdB 133, illuminated by F5Iab and B7II stars (Uchida et al. 1998); (5) the reflection nebula/photodissociation region (PDR) NGC 7023, illuminated by a B2.5V star (Cesarsky et al. 1996a); (6) the M17 PDR (Cesarsky et al. 1996b); (7) the starburst galaxies M82 and NGC 253 (Stürm et al. 2000); (8) the Seyfert 2 galaxy in Circinus (Stürm et al. 2000); and (9) the quiescent molecular cloud SMC B1#1 in the Small Magellanic Cloud (Reach et al. 2000). With the exception of SMC B1#1 (which we discuss below), the observed band ratios fall between the neutral and ionized PAH tracks in Figure 16, suggesting that the observed spectra
Fig. 16.— Relative strengths of three PAH emission features (6.2 and 7.7\,\mu m C-C stretching modes, and 11.3\,\mu m C-H out-of-plane bending mode) for neutral and ionized PAHs, labelled by the number of carbon atoms. Results are shown for grains illuminated by the MMP spectrum with $\chi = 1.23$ and 123, and for a $3 \times 10^4$\,K blackbody spectrum (cutoff at 912\,\AA) with $\chi = 10^2$, $10^4$, $10^5$, and $10^6$. Also shown (stars) are observed band ratios for the diffuse ISM, the reflection nebulae NGC 7023 and vdB 133, the M17 PDR, the $\rho$ Oph molecular cloud; the starburst galaxies M82 and NGC 253 (St" urm et al. 2000); the Seyfert 2 galaxy in Circinus; the average of 28 normal galaxies; and a quiescent molecular cloud in the SMC. (See text for citations.) The dotted line connecting the neutral and ionized points for $N_C = 16$ (in a PDR) illustrates the variation in the relative strengths of the 6.2, 7.7, and 11.3\,\mu m features in a PDR as the PAH ion fraction varies from 0 to 1.

can be reproduced by an appropriate mixture of PAH sizes, with an appropriate ionized fraction. The observed band ratios for the Milky Way ISM, $\rho$ Oph, 28 normal galaxies, and the reflection nebulae vdB 133 and NGC 7023 could be reproduced with a relatively low ionized fraction, but larger ionized fractions are required for the M17 PDR, M82, NGC 253, and the Circinus galaxy.

### 11.2. SMC B1#1

The quiescent molecular cloud SMC B1#1 observed by Reach et al. (2000) falls outside the region bounded by the neutral and ionized tracks in Figure 16. Reach et al. point out that SMC B1#1 has a 11.3/7.7 band ratio which differs significantly from that for Milky Way objects, includ-
Fig. 17.—Relative strengths of three PAH emission features (6.2 and 7.7 μm C-C stretching modes, and 11.3 μm C-H out-of-plane bending mode); PAHs are labelled by the number of carbon atoms. Results are shown for 3 charging conditions: CNM, WIM, and PDR (see text). Circles: grains in CNM charging conditions, for \( G_0 = 1.14 \) and 114; diamonds: grains in WIM charging conditions, for \( G_0 = 1.14 \) and 114; squares: grains in PDR conditions, for \( \chi = 10^2, 10^4, 10^5, \) and \( 10^6 \). Stars represent observations as in Fig. 16.

The authors suggest that the enhanced emission in the 11.3 μm C-H bending mode might be due to increased hydrogenation of the PAHs in the SMC, where the gas phase H/C ratio is a factor of 10 higher than in the Milky Way. Given that Milky Way PAHs with \( \gtrsim 25 \) C atoms are expected to be essentially fully hydrogenated (Tielens et al. 1987; Allamandola, Tielens, & Barker 1989; Allain, Leach, & Sedlmayr 1996), it is not clear that greater hydrogenation would be expected in the SMC. As discussed in Paper II, our model calculations assume that interstellar neutral and ionized PAHs have the 11.3/7.7 μm band strength ratio reduced by a factor of 2 relative to PAHs which have been studied in the lab – enhancement of the 7.7 μm feature appears to be necessary to reproduce the low 11.3/7.7 μm band ratios observed in objects such as NGC 253 or M82, and (with the possible exception of SMC B1#1) the reduced 11.3/7.7 μm band strength ratio appears to be consistent with astronomical observations.

While SMC B1#1 appears to fall “outside” the “allowed” region in Figures 16–18, we show elsewhere (Li & Draine 2001b) that the present model can reproduce the observed line ratios by
adding emission from a population of larger PAHs – with \( N_C \approx 3000 \) – which radiate strongly in the 11–13\( \mu \)m region, but produce little emission in the 6–8\( \mu \)m region. These larger PAHs would radiate strongly at 15–50\( \mu \)m; SIRTF will be able to test this hypothesis.

11.3. PAH Ionization

The fraction of PAHs which are charged will depend upon the electron density \( n_e \), temperature \( T \), and the starlight intensity. We consider three different charging environments:

- “Cold neutral medium” (CNM; \( n_e = 0.045 \text{ cm}^{-3} \), \( T = 100 \text{ K} \), and the MMP ISRF spectrum with \( \chi = 1.23 \), \( G_0 = 1.14 \)) and with both radiation field and gas density increased by \( 10^2 \);
“Warm ionized medium” (WIM; \(n_e = 0.1 \text{ cm}^{-3}, T = 8000 \text{ K}, \) and the MMP ISRF with \(\chi = 1.23\)), and with both radiation field and gas density increased by \(10^2\);

Photodissociation region conditions (PDR; \(n_e/n_H = 3 \times 10^{-4}, T = 10^3 \text{ K}, \) and a \(3 \times 10^4 \text{ K} \) blackbody cut off at 912 Å with \(\chi/n_H = 0.1 \text{ cm}^3\)) for \(\chi = 10^2, 10^4, 10^5, \) and \(10^6\). While PDRs come in a range of conditions, recent observations and modeling suggest that at least some PDRs include an extended region with \(T \approx 10^3 \text{ K}, \) and with \(\chi/n_H \approx 0.1 \text{ cm}^3, \) as in a recent model for the NGC 2023 PDR (Draine & Bertoldi 2000).

For each set of conditions, we consider PAHs with \(N_C \geq 16 \text{ C atoms}, \) and include emission from both neutral and ionized forms, with the neutral fraction calculated assuming a balance between collisional charging by electrons and photodetachment and photoionization (Weingartner & Draine 2001b). The charging of small grains is largely a function of the quantity \(\chi \sqrt{T}/n_e\) (Bakes & Tielens 1994; Weingartner & Draine 2001b). For the CNM, WIM, and PDR conditions considered here, \(\chi \sqrt{T}/n_e = 270, 1100, \) and \(10^4 \text{ cm}^3 \text{K}^{1/2}, \) so we expect grains of a given size to be increasingly positively charged as we move from CNM to WIM to PDR.

The “diffuse ISM” and “28 Galaxies” points fall between the CNM and WIM tracks in Figure 16, implying that one could reproduce the overall emission from normal spiral galaxies by a weighted sum of interstellar conditions ranging from CNM to WIM, with a mixture of grain sizes such that the 6.2 – 11.3µm emission is dominated by grains with \(20 < N_C < 1350\) (from Figure 15 it is apparent that grains with \(N_C > 10^3\) are not likely to contribute significant emission at \(\lambda \leq 11.3\mu\text{m}\)). The observed flux ratios for the diffuse ISM in the Milky Way, and for the average of 28 spiral galaxies, both fall in the shaded region, suggesting that with an appropriate size distribution, one might be able to reproduce the observed emission. The question of size distributions will be addressed in a future paper (Li & Draine 2001a), where it will be shown that the observed infrared emission can be approximately reproduced by grain size distributions similar to those invoked to explain the observed microwave emission.

In Figure 18 we show the emission expected from grains of various sizes, with 43% in the CNM, 14% in the WIM, and 43% in the WNM \((n_e = 0.03 \text{ cm}^{-3}, T = 6000 \text{ K}, \) MMP ISRF, \(\chi \sqrt{T}/n_e = 3200\)). The shaded region shows the flux ratios which could be obtained by grain mixtures containing only grains \(20 < N_C < 1350\) (from Figure 15 it is apparent that grains with \(N_C > 10^3\) are not likely to contribute significant emission at \(\lambda \leq 11.3\mu\text{m}\)). The observed flux ratios for the diffuse ISM in the Milky Way, and for the average of 28 spiral galaxies, both fall in the shaded region, suggesting that with an appropriate size distribution, one might be able to reproduce the observed emission. The question of size distributions will be addressed in a future paper (Li & Draine 2001a), where it will be shown that the observed infrared emission can be approximately reproduced by grain size distributions similar to those invoked to explain the observed microwave emission.
emission from interstellar dust (Draine & Lazarian 1998a,b).

12. Summary

We have presented a method for calculating the infrared emission from dust grains, including very small PAH molecules or silicate clusters. The principal results of this paper are the following:

1. The vibrational mode spectrum and vibrational density of states of very small grains are discussed in §2, where we explicitly consider both polycyclic aromatic hydrocarbons and silicate grains.

2. We use the adopted vibrational mode spectrum to calculate the specific heat of carbonaceous and silicate grains; the results are in agreement with experimental specific heats for graphite and amorphous silicates (Figure 2).

3. Using estimates for the absorption cross sections of carbonaceous and silicate grains, we obtain (in §4) radiative transition rates for emission from vibrationally-excited states of carbonaceous and silicate grains. We refer to this as the “exact-statistical” treatment.

4. We discuss (in §6) how the “thermal approximation” can be used to estimate rates for spontaneous emission. With a judicious estimate for the “temperature”, the thermal approximation provides transition rates which are close to those obtained from the “exact-statistical” treatment. Therefore level populations estimated using the thermal approximation are close to the actual level populations given by the “exact-statistical” treatment.

5. We discuss the “continuous cooling” approximation for modeling the deexcitation of the grain. We show that level populations and emission spectra computed using this approximation are sufficiently accurate for most astrophysical applications, even for grains containing as few as \(\sim 30\) atoms.

6. Methods for numerical solution for the vibrational energy distribution are presented in §8, and the numerical advantages of the continuous cooling approximation are stressed.

7. Relative strengths of the 6.2, 7.7, and 11.3\(\mu\)m features depend on the grain size, on the charging conditions, and on the starlight intensity. Observed 6.2/7.7 and 11.3/7.7 band ratios for the diffuse ISM in the Milky Way, for the \(\rho\) Oph and vdB133 reflection nebulae, and for the 28 “normal” galaxy sample of Helou et al. (2000), appear consistent with grains in the diffuse ISM heated by the average starlight background. The band ratios observed for the starburst galaxies M82 and NGC 253, for the Seyfert 2 “Circinus galaxy”, for the M17 PDR, and for the NGC 7023 PDR appear to require conditions close to our “PDR” conditions, with \(\chi/n_H \approx 0.05 - 0.1\) cm\(^3\).
The unusual band strengths observed for the quiescent molecular cloud SMC B1#1 in the SMC (Reach et al. 2000) cannot be reproduced by a mixture of small $N_C \lesssim 10^3$ PAHs. Either the PAHs in this cloud differ from Milky Way PAHs in their properties, or have a different size distribution.

The present paper has concentrated on the statistical mechanics of the stochastic heating process, and on the resulting emission spectra as a function of grain size. In a separate paper (Li & Draine 2001a) we calculate the emission from grain models with realistic size distributions, and show that the observed infrared emission from interstellar dust can be reproduced by a grain model with $\sim 15\%$ of the interstellar carbon in PAH particles containing less than $10^3$ C atoms.

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A. PAH Geometry

Small PAHs are expected to be planar, with $D \propto N_C^{1/2}$, but large PAHs are expected to be approximately spherical, with $D \propto N_C^{1/3}$. The size at which the transition from planar to spherical geometry occurs is uncertain. We will assume that PAHs have a planar geometry up to $N_C = 54$ (e.g., the pericondensed species circumcoronene $C_{54}H_{18}$). We assume that beyond $N_C = 54$ PAHs consist of multiple sheets. Beyond $N_C = 102$ (e.g., $C_{54}H_{18}$ plus one coronene $C_{24}H_{12}$ on either side) we assume spherical geometry, with $D \propto N_C^{1/3}$.

B. Energy Bins

We specify the energy bins so that the total number $M$ of bins is manageable ($300 \lesssim M \lesssim 1500$), the number of vibrational states per bin is at least 2 for each of bins 3–10, the bin widths vary smoothly for $j > 10$, and the last bin is at a high enough energy that its population $P_M < 10^{-14}$ (see §8.1 below).

Let $\omega_j, j = 1, ..., 3(N_a - 2)$ be the fundamental vibrational modes (see §2), in order of increasing frequency. Bin 0 is the ground state: $E_{0, \text{min}} = E_{0, \text{max}} = E_0 = 0$, to which we assign a "width" $\Delta E_0 = 0$. Bins 1 and 2 contain the first two vibrational modes, and bins 3 through 10 each contain two normal modes:

$$E_{1, \text{min}} = \frac{3}{2} \hbar \omega_1 - \frac{1}{2} \hbar \omega_2$$

$$E_{j, \text{max}} = E_{j+1, \text{min}} = \frac{1}{2} (\hbar \omega_j + \hbar \omega_{j+1}) \quad \text{for } j = 1, 2$$
\[ E_{j,\text{max}} = E_{j+1,\text{min}} = \frac{1}{2} (\hbar \omega_{2j-2} + \hbar \omega_{2j-1}) \quad \text{for} \ 3 \leq j \leq 10 \quad (B3) \]

For \( j = 11, \ldots, K \) we use uniform intervals \( \Delta E \), and for \( j \geq K \) uniform intervals in \( \ln E \):

\[ E_{j,\text{max}} = E_{10,\text{max}} + (j - 10)(E_{10,\text{max}} - E_{9,\text{max}}) \quad \text{for} \ 10 \leq j \leq K \quad (B4) \]

\[ E_{j,\text{max}} = E_{K,\text{max}} \left( \frac{E_{K,\text{max}}}{E_{K-1,\text{max}}} \right)^{j-K} \quad \text{for} \ K \leq j \leq M \quad (B5) \]

\( K \) is chosen so that the total number of bins \( \sim 500 \).

### C. Transition Matrix

Consider energy “bins” \( u \) and \( l \), with \( E_u > E_l \). Suppose bin \( l \) consists of many subbins \( \alpha = 1, \ldots, N_\alpha \), each of width \( \Delta E_\alpha \Delta E_l / N_\alpha \), and bin \( u \) consists of many subbins \( \beta = 1, \ldots, N_\beta \), each with width \( \Delta E_\beta = \Delta E_u / N_\beta \). The upward Einstein \( A \) coefficient from subbin \( \alpha \) to subbin \( \beta \) is

\[ A_{\beta\alpha} = \frac{8\pi \nu_{\alpha\beta}^2}{hc^2} \Delta E_\beta C_{\text{abs}}(\nu_{\alpha\beta}) \quad (C1) \]

and the spontaneous decay rate from subbin \( \beta \) to subbin \( \alpha \) is

\[ A_{\alpha\beta} = \frac{(dN/dE)_\alpha}{(dN/dE)_\beta} \frac{8\pi \nu_{\alpha\beta}^2}{hc^2} \Delta E_\alpha C_{\text{abs}}(\nu_{\alpha\beta}) \quad (C2) \]

where \( \nu_{\alpha\beta} \equiv (E_\beta - E_\alpha)/\hbar \), and \( dN/dE \) is the vibrational density of states. We now assume that \( (dN/dE)_\alpha \approx (dN/dE)_l \), and \( (dN/dE)_\beta \approx (dN/dE)_u \).

To obtain the effective bin-to-bin transition rate \( T_{ul} \), we equate the total rate of energy absorption to \( T_{ul}(E_u - E_l) \). Thus, averaged over subbins \( \alpha \), the transition rate from \( l \to u \) is

\[ T_{ul} = \frac{1}{E_u - E_l} \frac{c}{N_\alpha} \sum_\alpha \sum_\beta \Delta E_\alpha u_E \Delta E_\beta \quad (C3) \]

\[ \rightarrow \frac{c}{\Delta E_l E_u - E_l} \int_{E_{l,\text{min}}}^{E_{l,\text{max}}} dx \int_{E_{u,\text{min}}}^{E_{u,\text{max}}} dy \left[ C_{\text{abs}}(E)u_E \right]_{E=y-x} \quad (C4) \]

The integrand depends only on \( E = y - x \). One can show that

\[ T_{ul} = \frac{c \Delta E_u}{E_u - E_l} \int_{W_1}^{W_4} dE \ G_{ul}(E) C_{\text{abs}}(E) u_E \quad (C5) \]

where \( W_1, W_4 \), and \( G_{ul}(E) \) are defined in equations (19-24).
Similarly, averaged over subbins $\beta$, the energy-weighted transition rate from $u \rightarrow l$ is

\[ T_{lu} = \frac{1}{N_\beta E_u - E_l} \sum_\beta \sum_\alpha A_{\alpha\beta} (E_\beta - E_\alpha) \]  

\[ = \frac{\langle dN/dE \rangle_l}{\langle dN/dE \rangle_u} \frac{8\pi}{h^3 c^2} \frac{\Delta E_\beta}{E_u - E_l} \sum_\beta \sum_\alpha E^3 C_{\text{abs}}(E) \]  

\[ \rightarrow \frac{\langle dN/dE \rangle_l}{\langle dN/dE \rangle_u} \frac{8\pi}{h^3 c^2} \frac{\Delta E_l}{E_u - E_l} \int_{W_4}^{W_4} dE G_{ul}(E) E^3 C_{\text{abs}}(E) \]  

\[ = \frac{g_l}{g_u} \frac{8\pi}{h^3 c^2} \frac{1}{E_u - E_l} \int_{W_4}^{W_4} dE G_{ul}(E) E^3 C_{\text{abs}}(E) \]  

(C6)

(C7)

(C8)

(C9)

In the case of transitions to adjacent bins, we augment $T_{u,u-1}$ by the rate of energy absorption in “intrabin” transitions divided by $E_u - E_{u-1}$, and $T_{u-1,u}$ by the power radiated in intrabin transition, divided by $E_u - E_{u-1}$ (see eq. 28, 31).

D. Emission Spectrum

$F_\nu$, the power radiated per grain per unit solid angle per unit frequency, can be evaluated by noting from eq. (29) that the contribution from transitions $u \rightarrow l$ is just

\[ \delta F_\nu d\nu = P_u \frac{g_l}{g_u} \frac{2}{h^3 c^2} G_{ul}(E) E^3 C_{\text{abs}}(E) \left[ 1 + \frac{\lambda^3}{8\pi u_E} \right] dE \]  

\[ = \frac{g_l}{g_u} \frac{8\pi}{h^3 c^2} \frac{1}{E_u - E_l} \int_{W_4}^{W_4} dE G_{ul}(E) E^3 C_{\text{abs}}(E) \]  

\[ = P_u \left( 1 - \frac{h\nu}{\Delta E_u} \right) \frac{E}{4\pi} \frac{dA}{dE} \left[ 1 + \frac{\lambda^3}{8\pi u_E} \right] dE \]  

\[ = P_u \left( 1 - \frac{h\nu}{\Delta E_u} \right) \frac{E}{4\pi} \frac{8\pi \nu^2}{hc^2} C_{\text{abs}}(E) \left[ 1 + \frac{\lambda^3}{8\pi u_E} \right] dE \]  

(D1)

(D2)

(D3)

If the width of bin $u$ exceeds $h\nu$, then there is an additional contribution from intrabin transitions originating in the fraction $(1 - h\nu/\Delta E)$ of the subbins which are more than $h\nu$ above $E_{u,\text{min}}$. Using eq. (C2) with $(dN/dE)_\alpha \approx (dN/dE)_\beta$, the intrabin contribution to $F_\nu d\nu$ is

\[ \delta F_\nu d\nu = P_u \left( 1 - \frac{h\nu}{\Delta E_u} \right) \frac{E}{4\pi} \frac{dA}{dE} \left[ 1 + \frac{\lambda^3}{8\pi u_E} \right] dE \]  

where $dA/dE$ is obtained by dividing eq. (C2) by $\Delta E_\alpha$. With $E = h\nu$, it is straightforward to use eq. (D1-D3) to obtain eq. (55).

E. Lemmas

From the definition (19) of $G_{ul}(h\nu)$ one can show that

\[ \sum_{l=0}^{u-1} \Delta E_u \Delta E_l G_{ul}(h\nu) = \min (h\nu, \Delta E_u) \quad \text{for} \quad h\nu < E_{u,\text{min}} - E_{1,\text{min}} \]  

(E1)
\[ \sum_{i=0}^{u-1} \Delta E_i (E_u - E_i) G_{ul}(E) \approx E , \]  
(E2)

which are used to obtain eq. (40) and (43).

REFERENCES

Aannestad, P.A. 1989, in Evolution of Interstellar Dust and Related Topics, ed. A. Bonetti, J.M. Greenberg, & S. Aiello (Amsterdam: North Holland), p. 121

Aannestad, P.M., & Kenyon, S.M. 1979, ApJ, 230, 771

Allain, T., Leach, S., & Sedlmayr, E. 1996, A&A, 305, 602

Allamandola, L.J., Hudgins, D.M., & Sandford S.A. 1999, ApJ, 511, L115

Allamandola, L.J., Tielens, A.G.G.M., & Barker, J.R. 1985, ApJ, 290, L25

Allamandola, L.J., Tielens, A.G.G.M., & Barker, J.R. 1989, ApJS, 71, 733

Andriesse, C.D. 1978, A&A, 66, 169

Arendt, R.G., et al. 1998, ApJ, 508, 74

Bakes, E.L.O., & Tielens, A.G.G.M. 1994, ApJ, 427, 822

Barker, J.R., & Cherchneff, I. 1989, in Interstellar Dust, IAU Symp. 135, ed. L.J. Allamandola & A.G.G.M. Tielens (Dordrecht: Kluwer), p. 197

Beyer, T., & Swinehart, D.F. 1973, Comm. of the ACM, 16, 379

Boulanger, F., Boissel, P., Cesarsky, D., & Ryter, C. 1998, A&A, 339, 194

Boulanger, F., & Pérault, M. 1988, ApJ, 330, 964

Boulanger, F., Reach, W.T., Abergel, A., et al. 1996, A&A, 315, L325

Cesarsky, D., Lequeux, J., Abergel, A., et al. 1996a, A&A, 315, L305

Cesarsky, D., Lequeux, J., Abergel, A., et al. 1996b, A&A, 315, L309

Cook, D.J., & Saykally, R.J., 1998 ApJ, 493, 793

Cyvin, S.J. 1982, J. Molecular Structure, 79, 423

Cyvin, B.N., Brunvoll, J., Cyvin, S.J., & Klaeboe, P. 1984, Spectroscopy Lett., 17, 559

Désert, F.X., Boulanger, F., & Shore, S.N., 1986, A&A, 160, 295
deSorbo, W., & Tyler, W.W. 1953, J. Chem. Phys., 21, 1660

d'Hendecourt, L.B., Léger, A., Boissel, P., & Désert, F.X. 1989, in Interstellar Dust, IAU Symp. 135, ed. L.J. Allamandola & A.G.G.M. Tielens (Dordrecht: Kluwer), p. 207

Draine, B.T., & Anderson, N. 1985, ApJ, 292, 494

Draine, B.T., & Bertoldi, F. 2000, in H$_2$ in Space, ed. F. Combes and G. Pineau des Forets (Cambridge: Cambridge Univ. Press), in press

Draine, B.T., & Lazarian, A. 1998a, ApJ, 494, L19

Draine, B.T., & Lazarian, A. 1998b, ApJ, 508, 157

Draine, B.T., & Lee, H.-M. 1984, ApJ, 285, 89

Drapatz, S., & Michel, K.W. 1977, A&A, 56, 353

Duley, W.W. 1973, Ap&SS, 23, 43

Duley, W.W., & Poole, G. 1998, ApJ, 504, L113

Dwek, E. 1986, ApJ, 302, 363

Furukawa, G.T., & Douglas, T.B. 1972, in American Institute of Physics Handbook, ed. D.E. Gray (New York: McGraw-Hill), p. 4-105

Gail, H.-P., & Seldmayr, E. 1975, A&A, 43, 17

Greenberg, J.M. 1968, in Stars and Stellar Systems, Vol. VII, ed. B.M. Middlehurst & L.H. Aller, (Chicago: Univ. of Chicago Press), p. 221

Greenberg, J.M. 1976, in Far Infrared Astronomy, ed. M. Rowan-Robinson, (New York: Pergamon), p. 299

Greenberg, J.M., & Hong, S.S. 1974, in Galactic Radio Astronomy, IAU Symp. 60, ed. F.J. Kerr & S.C. Simonson (Dordrecht: Reidel), p. 155

Guhathakurta, P., & Draine, B. T. 1989, ApJ, 345, 230

Habing, H. J. 1968, Bull. Astron. Inst. Netherlands, 19, 421

Helou, G., Lu, N.Y., Werner, M.W., Malhotra, S., & Silbermann, N. 2000, ApJ, 532, L21

Hudgins, D.M., & Allamandola, L.J. 1999, ApJ, 513, L69

Krumhansl, J., & Brooks, H. 1953, J. Chem. Phys., 21, 1663

Lazarian, A., & Draine, B.T. 1999a, ApJ, 516, L37
Lazarian, A., & Draine, B.T. 1999b, ApJ, 520, L67
Léger, A., Jura, M., & Omont, A. 1985, A&A, 144, 147
Léger, A., & Puget, J.L. 1984, A&A, 137, L5
Li, A., & Draine, B.T. 2001a, submitted to ApJ (astro-ph/0011319)
Li, A., & Draine, B.T. 2001b, in preparation
Manske, V., & Henning, Th. 1998, A&A, 337, 85
Mathis, J.S., Mezger, P.G., & Panagia, N. 1983, A&A, 128, 212
Mattila, K., Lemke, D., Haikala, L.K., et al. 1996, A&A, 315, L353
Onaka, T., Yamamura, I., Tanabe, T., et al. 1996, PASJ, 48, L59
Press, W.H., Teukolsky, S.A., Vetterling, W.T., & Flannery, B.P. 1992, Numerical Recipes in Fortran, Second Edition (Cambridge: Cambridge University Press), p. 77
Puget, J.L., Léger, A., & Boulanger, F. 1985, A&A, 142, L19
Purcell, E.M. 1976, ApJ, 206, 685
Reach, W.T., Boulanger, F., Contursi, A., & Lequeux, J. 2000, A&A, 361, 895
Robertson, J. 1986, Advances in Physics, 35, 317
Schutte, W.A., Tielens, A.G.G.M., & Allamandola, L.J. 1993, ApJ, 415, 397
Sellgren, K., Werner, M.W., & Dinerstein, H.L. 1983, ApJ, 271, L13
Siebenmorgen, R., Krügel, E., & Mathis, J.S. 1992, A&A, 266, 501
Sleijpen, L.G., & Fokkema, D.R. 1993, Electron. Trans. Numer. Anal., 1, 11
Stein, S.E., & Rabinovitch, B.S. 1973, J. Chem. Phys., 58, 2438
Stürm, E., Lutz, D., Tran, D., et al. 2000, A&A, 358, 481
Tanaka, M., Matsumoto, T., Murakami, H., et al. 1996, PASJ, 48, L53
Tielens, A.G.G.M., Allamandola, L.J., Barker, J.R., & Cohen, M. 1987, in Polycyclic Aromatic Hydrocarbons and Astrophysics, ed. A. Léger, L. d’Hendecourt, & N. Boccara (Dordrecht: Reidel), p. 273
Uchida, K.I., Sellgren, K., & Werner, M.W. 1998, ApJ, 493, L109
Weingartner, J.C., & Draine, B.T. 2001a, ApJ, 548, 000 [astro-ph/0008146]
Weingartner, J.C., & Draine, B.T. 2001b, submitted to ApJ. [astro-ph/9907251]