IN DUST WE TRUST: AN OVERVIEW OF OBSERVATIONS AND THEORIES OF INTERSTELLAR DUST

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Abstract. The past century of interstellar dust has brought us from first ignoring it to finding that it is an important component of the interstellar medium and plays an important role in the evolution of galaxies, the formation of stars and planetary systems, and possibly, the origins of life. Current observational results in our galaxy provide a complex physical and chemical evolutionary picture of interstellar dust starting with the formation of small refractory particles in stellar atmospheres to their modification in diffuse and molecular clouds and ultimately to their contribution to star forming regions. In this review, a brief history of the studies of interstellar dust is presented. Our current understanding of the physical and chemical properties of interstellar dust are summarized, based on observational evidences from interstellar extinction, absorption, scattering, polarization, emission (luminescence, infrared vibrational emission, and microwave rotational emission), interstellar depletions, and theoretical modelling. Some unsolved outstanding problems are listed.

1. Introduction

It has been over 70 years since the existence of solid dust particles in interstellar space was first convincingly shown by Trumpler (1930) based on the discovery of color excesses. Interstellar dust has now become a subject of extensive study and one of the subjects in the forefront of astrophysics.

``The role of dust is that of observer and of catalyst.''
—— J. Mayo Greenberg [1963]

Historically, interstellar dust was regarded by astronomers as an annoying interstellar "fog" which prevented an accurate measurement of distances to stars. About 40 years ago, one of us (J.M.G.) wrote in the first volume of *Annual Review of Astronomy and Astrophysics* (Greenberg 1963):[1] "... Among the various performers of our Galaxy – the stars, the gas clouds, the cosmic rays – the grains seem to be the least dramatic. Their role is generally that of observer and of catalyst of events rather than prime mover. Why then are we so interested in these small particles whose total mass, by the most generous estimate, is only of the order of 1 per cent of that of the gas clouds? ... [It is because of] the three important activities of the grains: (a) the negative one of extinction [blocking the light from distant stars]; (b) the positive one of tracer of physical conditions [e.g. the Galactic magnetic fields and the gas temperature]; and (c) physical interactions with other components of the interstellar medium [e.g. the formation of molecules and stars]."

``We now recognize, dust plays a role not only as a tracer of what goes on in space, a corrector for making different modifications in our idea of the morphology of galaxies, but also actively contributing to the chemical evolution of molecular clouds.''
—— J. Mayo Greenberg [1996]

It is seen now that the role of interstellar dust was significantly underestimated 40 years ago. The advances of infrared (IR) astronomy, ultraviolet (UV) astronomy, laboratory astrophysics, and theoretical modelling over the past 40 years have had a tremendous impact on our understanding of the physical and chemical nature, origin and evolution of interstellar grains and their significance in the evolution of galaxies, the formation of stars and stellar systems (planets, asteroids, and comets), and the synthesis of complex organic molecules which possibly leads to the origins of life.

``Dust is both a subject and an agent of the Galactic evolution.''
—— J. Dorschner & Th. Henning [1995]

Instead of being a passive "observer", interstellar dust plays a vital role in the evolution of galaxies. Besides providing $\sim 30\%$ of the total Galactic luminosity via their IR emission, dust grains actively participate in the cycle of matter (gas and dust) from the interstellar medium (ISM) to stars and back from stars to the ISM: (1) solid grains condense in the cool at-

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[1] The contents in the square brackets were added by A. Li, for completeness, to summarize the then understanding as discussed in Greenberg (1963).

mospheres of evolved stars, Wolf-Rayet stars, planetary nebulae, and novae and supernovae ejecta, and are then ejected into the diffuse ISM; (2) in the diffuse ISM, interacting with hot (shocked) gas, stellar UV radiation, and cosmic rays, grains undergo destruction (sputtering by impacting gas atoms, vaporization and shattering by grain-grain collisions; see Tielens 1999 for a review); (3) in molecular clouds (formed through shock compression of diffuse gas, agglomeration of small clouds and condensation instabilities), grains are subject to growth through accretion of an ice mantle and coagulation; (4) cycling between the diffuse and molecular clouds, dust grains either form a carbonaceous organic refractory mantle as a result of UV processing of the ice mantle accreted on the silicate core in molecular clouds (Greenberg et al. 1972; Greenberg & Li 1999a), or perhaps grains re-condense in dense regions followed by rapid exchange of matter between diffuse gas and dense gas (Draine 1990); (5) collapse of dense molecular clouds leads to the birth of new stars. At the late stages of stellar evolution, gas and newly formed dust will eventually return to the ISM either through stellar winds or supernova explosions. It is clear that the life cycle of dust is associated with that of stars; stars are both a sink and a major source for the Galactic dust.

In addition to the fact that stars form out of interstellar dust and gas clouds, dust plays an important role in the process of star formation in molecular clouds: (1) IR emission from dust removes the gravitational energy of collapsing clouds, allowing star formation to take place; (2) dust grains provide shielding of molecular regions from starlight and thereby reduce the ionization levels and speed up the formation of protostellar cores (Ciolek 1995);[2] (3) IR emission from dust provides an effective probe for the star-formation processes (Shu, Adams, & Lizano 1989).

> ''The importance of grains in various aspects of astrochemistry is evident: they shield molecular regions from dissociating interstellar radiation, catalyze formation of molecules, and remove molecules from the gas phase.''
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> —— E.F. van Dishoeck, G.A. Blake, B.T. Draine, & J.I. Lunine [1993]

The interstellar chemistry problem concerns the chemical reactions between dust and atoms and molecules in space; dust plays an active role in those reactions (see van Dishoeck et al. 1993, van Dishoeck 1999 for reviews): (1) grain surfaces provide the site for the formation of molecu-

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[2] Molecular clouds are partially supported by magnetic fields; star formation occurs if ambipolar diffusion deprives cloud cores of magnetic support. Charged grains can couple to the magnetic field and increase the collisional drag on the neutrals, and thereby slow the rate of ambipolar diffusion within a cloud and increase the time needed to form a protostellar core (Ciolek 1995).

lar hydrogen (see Pirronello 2002 for a review), and probably other simple molecules through grain surface reactions and complex organic molecules through UV photoprocessing (e.g. see Greenberg et al. 2000; Allamandola 2002); (2) dust reduces the stellar UV radiation and protects molecules from photodissociation; (3) dust provides the major heating source for interstellar gas – photoelectrons ejected from grains; (4) dust grains are also involved in ion-molecule chemistry by affecting the electron/ion densities within the cloud.

Dust is one of the basic ingredients in comets. There is growing evidence from cometary observations that comets are a storage place for products of the chemical evolution which takes place in interstellar space. The complex chemistry and molecular evolution leading to what is now seen in comets may be the necessary precursor to life on the Earth and there is reason to believe from the evidence available that the oceans on the Earth were made of comets bringing interstellar ice to our young planet (Ehrenfreund & Charnley 2000).

In this review, we start in §2 with a historically oriented discussion of the discovery of interstellar extinction and dust, the development of early dust models as well as current modern models. Following up in §3 we present the present state-of-the-art understanding of interstellar dust observations and theories. In §4 we present a personal perspective of future dust studies.

2. History of Dust Studies

2.1. INTERSTELLAR DUST: EARLY OBSERVATIONAL EVIDENCES

> ''Surely, there is a hole in the heavens!''
> —— Sir William Herschel [1785]

The Milky Way looks patchy with stars unevenly distributed: looking at the sky in the direction of Sagittarius it is clear that there are tremendously dark lanes especially in the region toward the Galactic Center. The subject of these dark patches and what makes them dark also have a very patchy history. The existence of dark regions in the Milky Way was first pointed out by Sir William Herschel in the late 18th century. At that time, these dark lanes – the dust clouds which obscure the light from the background stars, were considered as "holes in the heavens" (Herschel 1785).

> ''They are really Obscuring bodies!''
> —— Agnes Clerke [1903]

In August 1889, Edward Barnard started to take pictures and reported vast and wonderful cloud forms with their remarkable structure, lanes, holes and black gaps. At the beginning of the 20th century, astronomers started to realize that they "were really obscuring bodies" rather than holes devoid of stars (Barnard 1919). Agnes Clerke (1903) stated in an astrophysics text that "... The fact is a general one, that in all the forest of the universe there are glades and clearings. How they come to be thus diversified we cannot pretend to say; but we can see that the peculiarity is structural — that it is an outcome of the fundamental laws governing the distribution of cosmic matter. Hence the futility of trying to explain its origin, as a consequence, for instance, of the stoppage of light by the interposition of obscure bodies, or aggregations of bodies, invisibly thronging space."

Heber D. Curtis and Harlow Shapley[3] held a famous debate in 1920 (Shapley & Curtis 1921); among the points of contention was whether what is seen as the dark lanes in the Milky Way is caused by obscuring material. Curtis said the dark lanes observed in our Galaxy were obscuring material, while Shapley said he found no evidence of obscuring material in his observations of globular clusters. Later observers became aware that Shapley's argument was irrelevant because the globular clusters are out of the plane of the Galaxy. The obscuring dust was confined to the so called "plane of avoidance" which is the Galactic plane.

> ''Stars are dimmed!''
> —— Wilhelm Struve [1867]

The presence of interstellar extinction was pointed out as early as in 1847 by F.G. Wilhelm Struve. He found that the number of stars per unit volume seems to diminish in all directions receding from the Sun. This could be explained either if the Sun was at the center of a true stellar condensation, or if the effect was only an apparent one due to absorption (which may have been understood to include light scattering). He argued that there could be an visual extinction of about $1\,\mathrm{mag\,kpc^{-1}}$ in interstellar space.

Jacobus C. Kapteyn (1904) had found a roughly spherical distribution of stars around the Sun. He assumed a constant stellar density and then used the observed density to arrive at a value for the extinction (absorption) of light $\approx 1.6\,\mathrm{mag\,kpc^{-1}}$ (Kapteyn 1909), which differs little from current values ($\approx 1.8\,\mathrm{mag\,kpc^{-1}}$ assuming a hydrogen density of $n_{\mathrm{H}} = 1\,\mathrm{cm^{-3}}$).[4]

In 1929 Schalén examined the question of stellar densities as a function of distance. He did a very detailed study of B and A stars, including those in Cygnus, Cepheus, Cassiopeia, and Auriga. He obtained rather differ-

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[3] Henry Norris Russell (1922), Shapley's advisor at Princeton, believed that the existence of dark clouds accounted for the obscuration and argued that this obscuring matter had to be the form of fine dust. But Shapley did not follow his advice.

[4] But Kapteyn did not take this seriously; for example, he assumed no extinction in his grand 1922 paper on the motion of stars in the Galaxy (Kapteyn 1922).

ent values of the absorption coefficient, particularly in Cygnus and Auriga where there are large dark patches. So obviously the absorption is more in some regions and less in others.

> ``Cosmic dust particles produce the selective absorption.''
> —— Robert J. Trumpler [1930]

It was not until the work of Robert J. Trumpler in 1930 that the first evidence for interstellar reddening was found. Trumpler (1930) based this on his study of open clusters in which he compared the luminosities and distances of open clusters with the distances obtained by assuming that all their diameters were the same. By observing the luminosities and knowing the spectral distribution of stars he was able to find both absorption ($\approx 0.7\,\mathrm{mag\,kpc^{-1}}$) and selective absorption or color excess (between photographic and visual; $\approx 0.3\,\mathrm{mag\,kpc^{-1}}$) with increasing distance, and produce a reddening curve.[5] It was this work which led to the general establishment of the existence of interstellar dust.

The wavelength dependence of extinction in the optical was measured for the first time by Rudnick (1936) using the still-widely-used "pair-match" method. Further observations carried out by Hall (1937) and Stebbins, Huffer & Whitford (1939) pointed to an λ^{-1} reddening "law" (at that time limited to $1-3\,\mu\mathrm{m}^{-1}$): the reddening curve showed a rise inversely proportional to the wavelength λ.

In 1934 Paul W. Merrill reported the discovery of the 5780 Å, 5797 Å, 6284 Å, 6614 Å "unidentified interstellar lines". These widened absorption lines, now known as "Diffuse Interstellar Bands", still remain unidentified (see Krelowski 2002 for a review).

The existence of diffuse interstellar radiation, originally detected by van Rhijn (1921), was verified and attributed to small dust grains by Henyey & Greenstein (1941). Henyey & Greenstein (1941) found that interstellar particles are strongly forward scattering and have a high albedo.

> ``Starlight is polarized!''
> —— John S. Hall [1949]; W.A. Hiltner [1949]

At the end of 1940s, two investigators (Hall 1949; Hiltner 1949), inspired by a prediction of Chandrasekhar on intrinsic stellar polarization, independently discovered instead the general interstellar linear polarization. Magnetic fields were believed to confine cosmic rays and to play a role in the spiral structure of the Galaxy. The implication of the linear polarization was that the extinction was caused by non-spherical particles aligned

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[5] Trumpler's observations indicated reddening even where he saw no clouds. Dufay (1957) questioned whether interstellar space outside dark clouds and nebulae should be considered perfectly transparent.

by magnetic fields (Davis & Greenstein 1951). The wavelength dependent polarization curve was later shown to be well represented by the Serkowski law, an empirical formula (Serkowski 1973). In addition to the extinction curve which was later also extended to a wide wavelength range, the polarization law as well as the polarization to extinction ratio provide further insight into the physical and chemical nature of interstellar dust.

The circular polarization produced by interstellar birefringence (Martin 1972) was originally predicted by van de Hulst (1957). It was first detected along the lines of sight to the Crab Nebula by Martin, Illing, & Angel (1972) and to six early-type stars by Kemp & Wolstencroft (1972).

2.2. INTERSTELLAR MATTER: THEORETICAL EVIDENCES

> `‘‘There must be more matter than stars......’’`
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> —— Jan H. Oort [1932]

In the 1930's Jan H. Oort took another approach to the problem by looking at the statistics of the motions of K giants perpendicular to the plane of the Galaxy, that is, at bulge objects. He used these to estimate the mass of material in the plane. He found that there had to be more material there than could be seen in stars. Oort (1932) estimated that the mass of the non-stellar material (dust and gas) is about $12 \times 10^9\,\mathrm{m}_\odot$. If this mass is distributed uniformly, the density of this non-stellar material is $\rho_{\rm ism} \approx 6 \times 10^{-24}\,\mathrm{g\,cm^{-3}}$ – this is the mass required to explain the observed motions.

The question then becomes what kind of material distributed with this density with what mass absorption coefficient could give rise to an extinction of about $1\,\mathrm{mag\,kpc^{-1}}$, as observed. So what is required is that the scattering/extinction cross section of the material blocking the light per unit length is on the order of $1\,\mathrm{mag\,kpc^{-1}}$.

2.3. INTERSTELLAR DUST: EARLY MODELLING EFFORTS

> `1930s: Metallic grains`
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> —— C. Schalén; J.L. Greenstein

But what caused the interstellar reddening? Since hyperbolic meteors were thought to exist, first attempts were made to tie the interstellar dust to the meteors. Small metallic particles were among the materials initially proposed to be responsible for the interstellar reddening, based on an analogy with small meteors or micrometeorites supposedly fragmented into finer dust (Schalén 1936; Greenstein 1938).[6] Reasonably good fits to the λ^{-1} extinction law were obtained in terms of small metallic grains with sizes of the order of $0.01\,\mu$m.[7] It became evident later that meteors or micrometeorites are not of interstellar origin.

In 1948 Whitford published measurements of star colors versus spectral types over a wavelength range from about 3500Å (UV) to the near IR. The relation was not the expected straight line, but showed curvature at the near UV and IR regions. Things were beginning to make some physical sense from the point of view of small particle scattering.

`1940s: Dirty ice grains`
—— J.H. Oort & H.C. van de Hulst

Based on the correlation between gas concentration and extinction, Lindblad (1935) argued that it seemed reasonable to grow particles in space since, as hypothesized by Sir Arthur Eddington, gaseous atoms and ions which hit a solid particle in space would freeze down upon it. Lindblad (1935) further put forward the hypothesis that interstellar dust could have formed by condensation (or more properly, accretion) of interstellar gas.

In the 1940's van de Hulst (1949) broke with tradition and published the results of making particles out of atoms that were known to exist in space: H, O, C, and N. He assumed these atoms combined on the surface to form frozen saturated molecules. The gas condensation scenario was further investigated by Oort & van de Hulst (1946) and led to what later became known as the "dirty ice" model.[8]

The dirty ice model of dust by van de Hulst was a logical followup of the then existing information about the interstellar medium and contained the major idea of surface chemistry leading to the ices H_2O, CH_4, NH_3. But it was not until the advent of IR astronomical techniques made it possible to observe silicate particles emitting at their characteristic $10\,\mu$m wavelength in the atmospheres of cool stars that we had the cores on which the matter could form. Interestingly, their presence was predicted on theoretical grounds by Kamijo (1963). As van de Hulst said, he chose to ignore the nucleation problem and just go ahead (where no one had gone before) with

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[6] Greenstein (1938) concluded that a dust size distribution of $dn/da \sim a^{-3.6}$ "seems to provide the best agreement of theory and observation (interstellar extinction)." Interesting enough, this power law distribution was very close to the $dn/da \sim a^{-3.5}$ distribution derived about 40 years later for the silicate/graphite dust model (Mathis, Rumpl, & Nordsieck 1977; Draine & Lee 1984).

[7] Another possible influencing factor of proposing the metallic dust model might have been the fact that it was easier to compute the scattering by metallic particles using the Mie theory because to get a λ^{-1} law required smaller particles than if they were dielectric and computations for large particles were too tedious (van de Hulst 1986).

[8] A. Li noted: the term "dirty ice" was invented by J.M. Greenberg as recalled by H.C. van de Hulst (1997).

the assumption that "something" would provide the seeds for the mantle to grow on. By 1945 we had many of the theoretical basics to understand the sources of interstellar dust "ices" but it was not until about 1970 that the silicates were established. Without having a realistic dust model, van de Hulst developed the scattering tools to provide a good idea of dust properties.

`1960s: Graphite grains`
—— F. Hoyle & N.C. Wickramasinghe

A "challenge" to the dirty ice model came out just after the discovery of interstellar polarization (Hall 1949; Hiltner 1949) since it seemed that the dirty ice model could not explain the rather high degree of polarization relative to extinction (see van de Hulst 1957; this was later shown not to be true by Greenberg et al. 1963a, b).

This led to the re-consideration of metallic grains and the consideration of graphite condensed in the atmospheres of carbon stars as a dust component (Cayrel & Schatzman 1954; Hoyle & Wickramasinghe 1962) because of their enormous potential for polarizing stellar radiation (as a result of its anisotropic optical properties of graphite). The graphite proposal seemed to be further supported by the detection of the 2175 Å hump extinction (Stecher & Donn 1965), although we know nowadays that the graphite model is not fully successful in explaining the 2175 Å hump and the ultimate identification is still not made (see §3.1.2).

Kamijo (1963) first proposed that SiO_2, condensed in the atmospheres of cool stars and blown out into the interstellar space, could provide condensation cores for the formation of "dirty ices". It was later shown by Gilman (1969) that grains around oxygen-rich cool giants are mainly silicates such as Al_2SiO_3 and Mg_2SiO_4. Silicates were first detected in emission in M stars (Woolf & Ney 1969; Knacke et al. 1969a), in the Trapezium region of the Orion Nebula (Stein & Gillett 1969), and in comet Bennett 1969i (Maas, Ney, & Woolf 1970); in absorption toward the Galactic Center (Hackwell, Gehrz, & Woolf 1970), and toward the Becklin-Neugebauer object and Kleinmann-Low Nebula (Gillett & Forrest 1973). Silicates are now known to be ubiquitous, seen in interstellar clouds, circumstellar disks around young stellar objects (YSOs), main-sequence stars and evolved stars, in HII regions, and in interplanetary and cometary dust (see Li & Draine 2001a for a review).

2.4. CONTEMPORARY INTERSTELLAR DUST MODELS

`Since 1970s: Modern models`
—— J.M. Greenberg; J.S. Mathis; B.T. Draine; and their co-workers

The first attempt to find the 3.1 μm feature of H_2O was unsuccessful (Danielson, Woolf, & Gaustad 1965; Knacke, Cudaback, Gaustad 1969b). This was, at first, a total surprise to those who had accepted the dirty ice model. However, this gave the incentive to perform the early experiments on the UV photoprocessing of low temperature mixtures of volatile molecules simulating the "original" dirty ice grains (Greenberg et al. 1972; Greenberg 1973) to understand how and why the predicted H_2O was not clearly present. From such experiments was predicted a new component of interstellar dust in the form of complex organic molecules, as mantles on the silicates. This idea was further developed in the framework of the cyclic evolutionary silicate core-organic refractory mantle dust model (Greenberg 1982a; Greenberg & Li 1999a). Similar core-mantle models have also been proposed by others (Désert, Boulanger, & Puget 1990; Duley, Jones, & Williams 1989; Jones, Duley, & Williams 1990).

According to the cyclic evolutionary model, ices evolve chemically and physically in interstellar space, so do the organics. Where and how the interstellar dust is formed appears to involve a complex evolutionary picture. The rates of production of refractory components such as silicates in stars do not seem to be able to provide more than about 10% of what is observed in space because they are competing with destruction which is about 10 times faster by, generally, supernova shocks (Draine & Salpeter 1979a,b; Jones et al. 1994). At present the only way to account for the observed extinction amount is to resupply the dust by processes which occur in the interstellar medium itself. The organic mantles on the silicate particles must be created at a rate sufficient to balance their destruction. Furthermore, they provide a shield against destruction of the silicates. Without them the silicates would indeed be underabundant unless most of the grain mass was condensed in the ISM, as suggested by Draine (1990).

What is currently known about the organic dust component is based very largely on results of laboratory experiments which attempt to simulate interstellar processes. The organic refractories which are derived from the photoprocessing of ices contain a mixture of aliphatic and aromatic carbonaceous molecules (Greenberg et al. 2000). The laboratory analog suggests the presence of abundant prebiotic organic molecules in interstellar dust (Briggs et al. 1992).

The silicate core-organic mantle model is recently revisited by Li & Greenberg (1997) in terms of a trimodal size distribution consisting of (1) large core-mantle grains which account for the interstellar polarization, the visual/near-IR extinction, and the far-IR emission; (2) small carbonaceous grains of graphitic nature to produce the 2175 Å extinction hump; (3) polycyclic aromatic hydrocarbons (PAHs) to account for the far-UV extinction as well as the observed near- and mid-IR emission features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm. This model is able to reproduce both the interstellar extinction and linear and circular polarization.

An alternative model was proposed by Mathis, Rumpl, & Nordsieck (1977) and thoroughly extended by Draine & Lee (1984). It consists of two separate dust components – bare silicate and graphite particles. Modifications to this model was later made by Sorrell (1990), Siebenmorgen & Krügel (1992), and Rowan-Robinson (1992) by adding new dust components (amorphous carbon, PAHs) and changing dust sizes.

Very recently, Draine and his co-workers (Li & Draine 2001b, 2002a; Weingartner & Draine 2001a) have extended the silicate/graphite grain model to explicitly include a PAH component as the small-size end of the carbonaceous grain population. The silicate/graphite-PAHs model provides an excellent quantitative agreement with the observations of IR emission as well as extinction from the diffuse ISM of the Milky Way Galaxy and the Small Magellanic Cloud.

Mathis & Whiffen (1989) have proposed that interstellar grains are composite collections of small silicates, vacuum ($\approx$ 80% in volume), and carbon of various kinds (amorphous carbon, hydrogenated amorphous carbon, organic refractories). However, the composite grains may be too cold and produce too flat a far-IR emissivity to explain the observational data (Draine 1994).[9] This is also true for the fractal grain model (Wright 1987).

In view of the recent thoughts that the reference abundance of the ISM (the abundances of heavy elements in both solid and gas phases) is subsolar (Snow & Witt 1995, 1996), Mathis (1996, 1998) updated the composite grain model envisioned as consisting of three components: (1) small silicate grains to produce the far-UV ($\lambda^{-1} > 6\,\mu\mathrm{m}^{-1}$) extinction rise; (2) small graphitic grains to produce the 2175 Å extinction hump; (3) composite aggregates of small silicates, carbon, and vacuum ($\approx$ 45% in volume) to account for the visual/near-IR extinction. The new composite model is able to reproduce the interstellar extinction curve and the 10 μm silicate absorption feature. But it produces too much far-IR emission in comparison with the observational data (Dwek 1997).

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[9] Let $C_{\rm abs}(\lambda) \propto \lambda^{-\beta}$ be the far-IR absorption cross section; $T_{\rm d}$ be the characteristic dust temperature; $j_\lambda \propto C_{\rm abs}(\lambda) \times 4\pi B_\lambda(T_{\rm d}) \propto \lambda^{-(4+\beta)}$ be the dust far-IR emissivity (where $B_\lambda[T_{\rm d}]$ is the Planck function at wavelength λ and temperature $T_{\rm d}$). While the observed emission spectrum between 100 μm and 3000 μm (Wright et al. 1991; Reach et al. 1995) is well represented by dust with $\beta = 1.7$, $T_{\rm d} \approx 19.5\,$K or $\beta = 2.0$, $T_{\rm d} \approx 18.5\,$K (Draine 1999), fluffy composite grains have $\beta \approx 1.60$ (Mathis & Whiffen 1989). A $\beta = 2.0$ emissivity law is naturally expected for solid compact dust: the far-IR absorption formula for spherical submicron-sized grains is $C_{\rm abs}(\lambda)/V = 18\pi/\lambda \times \left\{\epsilon_{\rm im}/\left[(\epsilon_{\rm re}+2)^2+\epsilon_{\rm im}^2\right]\right\}$ where V is the grain volume; $\epsilon_{\rm re}$ and $\epsilon_{\rm im}$ are respectively the real and imaginary part of the dielectric function. For dielectrics $\epsilon_{\rm im} \propto \lambda^{-1}$ and $\epsilon_{\rm re} \propto$ const ($\epsilon_{\rm im} \ll \epsilon_{\rm re}$) while for metals $\epsilon_{\rm im} \propto \lambda$, $\epsilon_{\rm re} \propto$ const ($\epsilon_{\rm im} \gg \epsilon_{\rm re}$) so that one gets the same asymptotic relation for both dielectrics and metals $C_{\rm abs}(\lambda) \propto \lambda^{-2}$.

2.5. SCATTERING OF LIGHT BY SMALL PARTICLES: AN ESSENTIAL TOOL FOR DUST STUDIES

Our knowledge about dust grains is mainly inferred from their interaction with starlight: a grain in the line of sight between a distant star and the observer reduces the starlight by a combination of scattering and absorption; the absorbed energy is then re-radiated in the IR. For a non-spherical grain, the light of distant stars is polarized as a result of differential extinction for different alignments of the electric vector of the radiation. Therefore, to model the observed interstellar extinction, scattering, absorption, polarization and IR emission properties, knowledge of the optical properties (extinction, absorption and scattering cross sections) of interstellar dust is essential. This requires knowledge of the optical constants of the interstellar dust materials [i.e., the complex index of refraction $m(\lambda) = m'(\lambda) - i\, m''(\lambda)$], and the dust sizes and shapes. Phrasing this differently, to infer the size, morphology, and chemical composition of interstellar dust, an important aspect of the modelling of interstellar grains involves the computation of extinction, absorption and scattering cross sections of particles comprised of candidate materials and in comparison with astronomical data.

During the recent years, dramatic progress has been made in measuring the complex refractive indices of cosmic dust analogues, e.g. by the Jena Group (Henning & Mutschke 2000) and the Naples Group (Colangeli et al. 1999). Interstellar particles would in general be expected to have non-spherical, irregular shapes. However, our ability to compute scattering and absorption cross sections for nonspherical particles is extremely limited. So far, exact solutions of scattering problems exist only for bare or layered spherical grains ("Mie theory"; Mie 1908; Debye 1909), infinite cylinders (Lind & Greenberg 1966), and spheroids (Asano & Yamamoto 1975; Asano & Sato 1980; Voshchinnikov & Farafonov 1993). For grains with sizes much smaller than the wavelength of the incident radiation, the dipole approximation can be used to evaluate cross sections for bare or coated spheroidal grains (van de Hulst 1957; Gilra 1972; Draine & Lee 1984; Bohren & Huffman 1983). The "T-matrix" (transition matrix) method, originally developed by Barber & Yeh (1975) and recently substantially extended by Mishchenko, Travis, & Mackowski (1996), is able to treat axisymmetric (spheroidal or finite cylindrical) grains with sizes comparable to the wavelength. The discrete dipole approximation (DDA), originally developed by Purcell & Pennypacker (1973) and recently greatly improved by Draine (1988), is a powerful technique for irregular heterogeneous grains with sizes as large as several times the wavelength. The VIEF (volume integration of electric fields) method developed by Hage & Greenberg (1990), based on an integral representation of Maxwell's equations, is physically similar to the DDA method. The microwave analog methods originally developed by Greenberg, Pedersen & Pedersen (1960) provide an effective experimental approach to complex particles. This method is still proving to be powerful (Gustafson 1999; Gustafson et al. 1999) as the needs still outstrip the capacities of computers.

Although interstellar particles are obviously non-spherical as evidenced by the observed polarization of starlight, the assumption of spherical shapes (together with the Bruggeman or the Maxwell-Garnett effective medium theories for inhomogeneous grains; Bohren & Huffman 1983) is usually sufficient in modelling the interstellar absorption, scattering and IR emission. For IR polarization modelling, the dipole approximation for spheroidal grains is proven to be successful in many cases. The DDA method is highly recommended for studies of inhomogeneous (e.g. coated) grains and irregular grains such as cometary, interplanetary, and protoplanetary dust particles.

2.6. COMETS

The origin of comets is closely linked to the solar system and they played an important role in cosmogony. Cometary nuclei have been created far away from the early Sun[10] and have been mostly kept intact since their formation. Although it is generally accepted that comets contain the most pristine material in the solar system, it is still a matter of considerable debate whether they are made of unmodified protosolar nebula interstellar dust or this material has been (completely or partially) evaporated before becoming a part of comets (see Mumma, Stern, & Weissman 1993; Crovisier 1999; Irvine & Bergin 2000 for reviews).

The internal structure and chemical composition of cometary nuclei have been a topic receiving much attention. Before 1950, the prevailing view was that the comet nucleus is composed of a coherent swarm of meteoroidal-type particles which are independent of each other (termed the "flying sandbank" model). It was shown by Russell, Dugan, & Stewart (1926) that the "swarm" concept of the cometary nucleus was inadequate since the solar heating would vaporize icy bodies up to 30 cm in diameter.

Since 1950 a number of models for the comet nucleus have been proposed. For the most part, the icy-conglomerate model (also known as the "dirty snowball" model) of Whipple (1950) has been the standard which others have followed. According to Whipple (1950), the comet nucleus is a

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[10] The current view is that Jupiter family comets (with small inclinations and orbital periods $P < 20$ yrs) formed in the trans-Neptune region now known as the "Kuiper Belt"; Halley-type comets (with relatively longer periods $20 < P < 200$ yrs and larger inclinations) as well as long-period comets (with all possible inclinations and orbital periods $200 < P < 10^7$ yrs) formed somewhere beyond the orbits of Jupiter and Saturn. See Li & Greenberg (1998a) and references therein.

solid body consisting of a conglomerate of refractory dust grains and frozen gases (mostly of H_2O ice). More recently, the computer simulation of dust aggregates formed by random accumulation (Daniels & Hughes 1981) led Donn, Daniels, & Hughes (1985) to postulate the fractal model in which the comet nucleus is considered as a heterogeneous aggregate of ice and dust grains with substantial voids. Weissman (1986) proposed a primordial rubble-pile model as a modification of the basic icy-conglomerate model in which the cometary nucleus is envisaged as a loosely bound agglomeration of smaller fragments, weakly bonded by local melting at contact interfaces. Gombosi & Houpis (1986) suggested an icy-glue model. According to them, the comet nucleus is composed of rather large porous refractory boulders (tens of centimeters to hundreds of meters) “cemented” together with the icy-conglomerate type ice-dust grain mix (“Whipple glue”).

Alternatively, Greenberg (1982b) proposed the interstellar dust model of comets in which the basic idea is that comets have formed directly through coagulation of interstellar dust (Greenberg 1982b; Greenberg 1998; Greenberg & Li 1999b). The morphological structure of comet nuclei is thus modelled as an aggregate of presolar interstellar dust grains whose mean size is of the order of one tenth micron. The representative individual presolar grain consists of a core of silicates mantled first by an organic refractory material and then by a mixture of water dominated ices in which are embedded thousands of very small carbonaceous particles/large molecules (Greenberg 1998; Greenberg & Li 1999b). Greenberg and his co-workers have further shown how the IR emission for several distinctly different types of comets bear a general resemblance to each other by reproducing the IR emission of various comets (Halley – a periodic comet [Greenberg & Hage 1990; Greenberg et al. 1996]; Borrelly – a Jupiter family short period comet [Li & Greenberg 1998a]; Hale-Bopp – a long period comet [Li & Greenberg 1998b]; and extra-solar comets in the β Pictoris disk [Li & Greenberg 1998c]) within the framework that all comets are made of aggregated interstellar dust.

3. The Current State of the Art

The last 40 years have seen a revolution in the study of interstellar dust. This has been a four-fold process. First of all, the observational access to the UV and the IR brought into focus the fact that there had to be a very wide range of particle sizes and types to account for the blocking of the starlight. Secondly, the IR provided a probe of some of the chemical constituents of the dust. Thirdly, laboratory techniques were applied to the properties and evolution of possible grain materials. Fourthly, advances in numerical techniques and the speed and memory of computers have greatly enhanced our modelling capabilities.

Thanks to the successful performances of IUE (*International Ultraviolet Explorer*), IRAS (*Infrared Astronomical Satellite*), COBE (*Cosmic Background Explorer*), HST (*Hubble Space Telescope*), ISO (*Infrared Space Observatory*) as well as various ground-based UV, optical and IR instruments, we have witnessed an explosive accumulation of new observational information on interstellar extinction, polarization, scattering, IR continuum emission and spectral features, as well as elemental depletion. Rapid progress on laboratory experiments has also been made. Below we present an overview of our current knowledge of the dust which brings many related astrophysical problems to the fore.

3.1. EXTINCTION (SCATTERING, ABSORPTION) AND POLARIZATION

3.1.1. *Interstellar Extinction and Polarization Curves*

> ``The extinction curve is a sharp discriminator of (dominant) size, but a very poor discriminator of composition.''
>
> —— H.C. van de Hulst [1989]

The most extensively studied dust property may be the interstellar extinction. The main characteristics of the wavelength dependence of interstellar extinction – "interstellar extinction curve" – are well established: a slow and then increasingly rapid rise from the IR to the visual, an approach to levelling off in the near UV, a broad absorption feature at about $\lambda^{-1} \approx 4.6\,\mu\mathrm{m}^{-1}$ ($\lambda \approx 2175\,\mathrm{\AA}$) and, after the drop-off, a "final" curving increase to as far as has been observed $\lambda^{-1} \approx 8\,\mu\mathrm{m}^{-1}$. We note here that the access to the UV was only made possible when observations could be made from space, first by rockets and then by satellites (OAO2 and IUE).

The optical/UV extinction curves show considerable variations which are correlated with different regions.[11] Cardelli, Clayton, & Mathis (1989) found that the extinction curves over the wavelength range of $0.125\,\mu\mathrm{m} \leq \lambda \leq 3.5\,\mu\mathrm{m}$ can be fitted remarkably well by an analytical formula involving only one free parameter: $R_V \equiv A_V/E(B-V)$, the total-to-selective extinction ratio. Values of R_V as small as 2.1 (the high latitude translucent molecular cloud HD 210121; Larson, Whittet, & Hough 1996) and as large as 5.6 (the HD 36982 molecular cloud in the Orion nebula) have been observed in the Galactic regions. More extreme extinction curves are reported for gravitational lens galaxies: $R_V = 1.5$ for an elliptical galaxy at a lens redshift $z_l = 0.96$ and $R_V = 7.2$ for a spiral galaxy at $z_l = 0.68$ (Falco et al. 1999). The Galactic mean extinction curve is characterized by $R_V \approx 3.1$.

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[11] Greenberg & Chlewicki (1983) found that the strength of the $2175\,\mathrm{\AA}$ hump and the far-UV extinction can vary both independently and with respect to the visual extinction. This may imply that the $2175\,\mathrm{\AA}$ hump and the far-UV extinction are produced by two different dust components.

The optical/UV extinction curve and the value of R_V depend on the environment: lower-density regions have a smaller R_V, a stronger 2175 Å hump and a steeper far-UV rise ($\lambda^{-1} > 4\,\mu\mathrm{m}^{-1}$); denser regions have a larger R_V, a weaker 2175 Å hump and a flatter far-UV rise.

The near-IR extinction curve ($0.9\,\mu\mathrm{m} \le \lambda \le 3.5\,\mu\mathrm{m}$) can be fitted reasonably well by a power law $A(\lambda) \sim \lambda^{-1.7}$, showing little environmental variations. The extinction longward of $3\,\mu\mathrm{m}$ is not as well determined as that of $\lambda \le 3\,\mu\mathrm{m}$. Lutz et al. (1996) derived the 2.5–9 μm extinction law toward the Galactic Center (GC) based on the ISO observation of the hydrogen recombination lines. They found that the GC extinction law has a higher extinction level in the 3–8 μm range than the standard Draine (1989a) IR extinction curve.[12]

Existing grain models for the diffuse interstellar medium are mainly based on an analysis of extinction (Mathis, Rumpl, & Nordsieck 1977; Greenberg 1978; Hong & Greenberg 1980; Draine & Lee 1984; Duley, Jones, & Williams 1989; Mathis & Whiffen 1989; Kim, Martin, & Hendry 1994; Mathis 1996; Li & Greenberg 1997; Zubko 1999a; Weingartner & Draine 2001a). All models are successful in reproducing the observed extinction curve from the near IR to the far-UV. The silicate core-organic refractory mantle model and the (modified) silicate/graphite model are also able to fit the HD 210121 extinction curve which has the lowest R_V value (Li & Greenberg 1998d; Larson et al. 2000; Clayton et al. 2000; Weingartner & Draine 2001a) and the Magellanic clouds extinction curves (Rodrigues et al. 1997; Zubko 1999b; Clayton et al. 2000; Weingartner & Draine 2001a). The fact that so many different materials with such a wide range of optical properties could be used to explain the observed extinction curve indicates that the interstellar extinction curve is quite insensitive to the exact dust composition. What the extinction curve does tell us is that interstellar grains span a size ranging from ~ 100 angstrom to submicron (Draine 1995).

The general shape of the polarization curve is also well established. It rises from the IR, has a maximum somewhere in the visual (generally) and then decreases toward the UV, implying that the aligned nonspherical grains are typically submicron in size, and the very small grain component responsible for the far-UV extinction rise is either spherical or not aligned.

The optical/UV polarization curve $P(\lambda)$ can also be fitted remarkably well by an empirical function known as the "Serkowski law", involving the very same free parameter R_V as the Cardelli et al. (1989) extinction

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[12] The silicate core-organic refractory mantle model (Greenberg 1989; Li & Greenberg 1997) may provide a better fit to the 3–8 μm extinction curve than the silicate-graphite model (Mathis et al. 1977; Draine & Lee 1984) because the carbonaceous organic material is IR active at $\lambda > 5\,\mu\mathrm{m}$ due to $\mathrm{C=C}$, $\mathrm{C=O}$, $\mathrm{C-OH}$, $\mathrm{C\equiv N}$, $\mathrm{C-NH_2}$ stretches; CH, OH, and $\mathrm{NH_2}$ deformations, and H wagging (Greenberg et al. 1995).

functional form through $\lambda_{\rm max}$,[13] the wavelength where the maximum polarization $P_{\rm max}$ occurs: $P(\lambda)/P_{\rm max} = \exp[-K\ln^2(\lambda/\lambda_{\rm max})]$ (Serkowski 1973; Coyne, Gehrels, & Serkowski 1974; Wilking, Lebofsky, & Rieke 1982). The width parameter K is linearly correlated with $\lambda_{\rm max}$: $K \approx 1.66\,\lambda_{\rm max} + 0.01$ (Whittet et al. 1992 and references therein).[14]

The near IR ($1.64\,\mu{\rm m} < \lambda < 5\,\mu{\rm m}$) polarization has been found to be higher than that extrapolated from the Serkowski law (Martin et al. 1992). Martin & Whittet (1990) and Martin et al. (1992) suggested a power law $P(\lambda) \propto \lambda^{-\beta}$ for the near IR ($\lambda > 1.64\,\mu{\rm m}$) where the power index β is independent of $\lambda_{\rm max}$ and in the range of 1.6 to 2.0, $\beta \simeq 1.8 \pm 0.2$.[15]

The observed interstellar polarization curve has also been extensively modelled in terms of various dust models by various workers. The silicate core-organic mantle model (Chlewicki & Greenberg 1990; Li & Greenberg 1997), the silicate-graphite model (only silicate grains are assumed to be efficiently aligned; Mathis 1986; Wolff, Clayton, & Meade 1993; Kim & Martin 1995, 1996), and the composite model (Mathis & Whiffen 1989) are all successful in reproducing the mean interstellar polarization curve ($\lambda_{\rm max} = 0.55\,\mu{\rm m}$).

However, the processes leading to the observed grain alignment are still not well established. A number of alignment mechanisms have been proposed. The Davis-Greenstein paramagnetic dissipation mechanism (Davis & Greenstein 1951) together with other co-operative effects such as suprathermal rotation (Purcell 1979), superparamagnetic alignment (Jones & Spitzer 1967; Mathis 1986), radiative torques on irregular grains due to anisotropic starlight (Draine & Weingartner 1996, 1997) seems to be a plausible mechanism for dust in the diffuse ISM. In dense molecular clouds, non-magnetic alignment mechanisms such as streaming of grains through gas (Gold 1952; Purcell 1969; Lazarian 1994), through radiation (Harwit 1970), through ambipolar diffusion (Roberge 1996) have been studied.

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[13] $R_V \approx (5.6 \pm 0.3)\lambda_{\rm max}$ ($\lambda_{\rm max}$ is in micron; see Whittet 1992); i.e., the wavelength of maximum polarization $\lambda_{\rm max}$ shifts with R_V in the sense that it moves to longer wavelengths as R_V increases which is the effect of increasing the particle size.

[14] The far-UV polarization observations only became available in recent years as a consequence of the Wisconsin Ultraviolet Photo-Polarimetry Experiment (WUPPE) (Clayton et al. 1992) and the UV polarimetry of the Hubble Space Telescope (Somerville et al. 1993, 1994; Clayton et al. 1995). It is found that (1) lines of sight with $\lambda_{\rm max} \geq 0.54\,\mu{\rm m}$ are consistent with the extrapolated Serkowski law; (2) lines of sight with $\lambda_{\rm max} \leq 0.53\,\mu{\rm m}$ show polarization in excess of the extrapolated Serkowski law; (3) two lines of sights show a polarization feature which seems to be associated with the $4.6\,\mu{\rm m}^{-1}$ extinction hump (Clayton et al. 1992; Anderson et al. 1996; Wolff et al. 1997; Martin, Clayton, & Wolff 1999).

[15] Martin et al. (1999) proposed a more complicated formula – the "modified Serkowski law" – to represent the observed interstellar polarization from the near IR to the far UV.

The wavelength dependent albedo (the ratio of scattering cross section to extinction) measured from the diffuse Galactic light, reflecting the scattering properties of interstellar dust, provides another constraint on dust models. The silicate core-organic mantle model (Li & Greenberg 1997) and the silicate/graphite-PAHs model (Li & Draine 2001b) are shown to be in good agreement with the observationally determined albedos, whereas the albedos of the composite grain model (Mathis 1996) are too low (Dwek 1997).

Scatterings of X-rays by interstellar dust have also been observed as evidenced by "X-ray halos" formed around an X-ray point source by small-angle scattering. The intensity and radial profile of the halo depends on the composition, size and morphology and the spatial distribution of the scattering dust particles (see Smith & Dwek 1998 and references therein). A recent study of the X-ray halo around Nova Cygni 1992 by Witt, Smith, & Dwek (2001) pointed to the requirement of large interstellar grains, consistent with the recent Ulysses and Galileo detections of interstellar dust entering our solar system (Grün et al. 1994; Frisch et al. 1999; Landgraf et al. 2000).

3.1.2. *Spectroscopic Extinction and Polarization Features*

It is the extinction (absorption) and emission spectral lines instead of the overall shape of the extinction curve provides the most diagnostic information on the dust composition.

1. The 2175 Å Extinction Hump

> ``It is frustrating that almost 3 decades after its discovery, the identity of this (2175 Å) feature remains uncertain!''
>
> —— B.T. Draine [1995]

The strongest spectroscopic extinction feature is the 2175 Å hump. Observations show that its strength and width vary with environment while its peak position is quite invariant. Its carrier remains unidentified 37 years after its first detection (Stecher 1965). Many candidate materials, including graphite (Stecher & Donn 1965), amorphous carbon (Bussoletti et al. 1987), graphitized (dehydrogenated) hydrogenated amorphous carbon (Hecht 1986; Goebel 1987; Sorrell 1990; Mennella et al. 1996; Blanco et al. 1999),[16] nano-sized hydro-

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[16] Mennella et al. (1996) reported that a stable peak position can be obtained by subjecting small hydrogenated amorphous carbon grains to UV radiation. However, the laboratory produced humps are too wide and too weak with respect to the interstellar one. In a later paper (Mennella et al. 1998) they proposed that the 2175 Å carrier can be modelled as a linear combination of such materials exposed to different degrees of UV processing.

genated amorphous carbon (Schnaiter et al. 1998), quenched carbonaceous composite (QCC; Sakata et al. 1995), coals (Papoular et al. 1995), PAHs (Joblin et al. 1992; Duley & Seahra 1998; Li & Draine 2001b), and OH^- ion in low-coordination sites on or within silicate grains (Duley, Jones & Williams 1989) have been proposed, while no single one is generally accepted (see Draine 1989b for a review).

Graphite was the earliest suggested and the widely adopted candidate in various dust models (Gilra 1972; Mathis et al. 1977; Hong & Greenberg 1980; Draine & Lee 1984; Dwek et al. 1997; Will & Aannestad 1999). However the hump peak position predicted from graphite particles is quite sensitive to the grain size, shape, and coatings (Gilra 1972; Greenberg & Chlewicki 1983; Draine 1988; Draine & Malhotra 1993) which is inconsistent with the observations. It was suggested that very small coated graphite particles ($a \leq 0.006\,\mu$m) could broaden the hump while keeping the hump peak constant (Mathis 1994).[17] However, this seems unlikely because the proposed particles are so small that temperature fluctuations will prevent them from acquiring a coating (Greenberg & Hong 1974a; Aannestad & Kenyon 1979). Furthermore, it was noted by Greenberg & Hong (1974b) that if the very small particles as well as the large particles accrete mantles the R_V value would *decrease* in molecular clouds, in contradiction with astronomical observations. Rouleau, Henning, & Stognienko (1997) proposed that the combined effects of shape, clustering, and fine-tuning of the optical properties of graphite could account for the hump width variability.

Another negative for graphite, is that the dust grains in circumstellar envelopes around carbon stars which are the major sources of the carbon component of interstellar dust are in amorphous form rather than graphitic (Jura 1986). It is difficult to understand how the original amorphous carbonaceous grains blown out from the star envelopes are processed to be highly anisotropic and evolve to the layer-lattice graphitic structures in interstellar space. Instead, it is more likely that the interstellar physical and chemical processes should make the carbonaceous grains even more highly disordered.

Recently, the PAH proposal is receiving increasing attention. Although a single PAH species often has some strong and narrow UV bands which are not observed (UV Atlas 1966), a cosmic mixture of many individual molecules, radicals, and ions, with a concentration of strong absorption features in the 2000–2400 Å region, may effectively

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[17] Hecht (1981) investigated the effect of coatings on graphite particles and concluded that small coatings could be present on spherical $a \approx 200$ Å particles and still cause the 2175 Å feature.

produce the 2175 Å extinction feature (Li & Draine 2001b). This is supported by the correlation between the 2175 Å hump and the IRAS 12 μm emission (dominated by PAHs) found by Boulanger, Prévot, & Gry (1994) in the Chamaeleon cloud which suggests a common carrier. Arguments against the PAHs proposal also exist (see Li & Draine 2001b for references).

So far only two lines of sight toward HD 147933 and HD 197770 have a weak 2175 Å polarization feature detected (Clayton et al. 1992; Anderson et al. 1996; Wolff et al. 1997; Martin, Clayton, & Wolff 1999). Even for these sightlines, the degree of alignment and/or polarizing ability of the carrier should be very small (if both the hump excess polarization and the hump extinction are produced by the same carrier); for example, along the line of sight to HD 197770, the ratio of the excess polarization to the hump extinction is $P_{2175\,\text{Å}}/A_{2175\,\text{Å}} \simeq 0.002$ while the polarization to extinction ratio in the visual is $P_V/A_V \simeq 0.025$, thus $(P_{2175\,\text{Å}}/A_{2175\,\text{Å}})/(P_V/A_V)$ is only ~ 0.09. Therefore, it is reasonable to conclude that the 2175 Å carrier is either mainly spherical or poorly aligned.

The 2175 Å hump polarization was predicted by Draine (1988) for aligned non-spherical graphite grains. Wolff et al. (1993) and Martin et al. (1995) further show that the observed 2175 Å polarization feature toward HD 197770 can be well fitted with small aligned graphite disks.

Except for the detection of scattering in the 2175 Å hump in two reflection nebulae (Witt, Bohlin, & Stecher 1986), the 2175 Å hump is thought to be predominantly due to absorption, suggesting its carrier is sufficiently small to be in the Rayleigh limit.

2. The 9.7 μm and 18 μm (Silicate) Absorption Features

> ``In my opinion, the only secure identification is that of the 9.7 μm and 18 μm IR features.''
>
> —— B.T. Draine [1995]

The strongest IR absorption features are the 9.7 μm and 18 μm bands. They are respectively ascribed to the Si-O stretch and O-Si-O bending modes in some form of silicate material, perhaps olivine $\mathrm{Mg}_{2x}\mathrm{Fe}_{2-2x}\mathrm{SiO}_4$. The shape of the interstellar silicate feature is broad and featureless both of which suggest that the silicate is amorphous.[18] The originating source of the interstellar silicates is in the atmospheres of cool evolved stars of which the emission features often show a 9.7 μm feature consistent with amorphous silicates and sharper features arising

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[18] Very recently, Li & Draine (2001a) estimated that the abundances of $a < 1\,\mu$m crystalline silicate grains in the diffuse ISM is $< 5\%$ of the solar Si abundance.

from crystalline silicates (Waters et al. 1996).[19] How can interstellar crystalline silicate particles become amorphous? This is a puzzle which has not yet been completely solved. A possible solution may be that the energetic processes (e.g. shocks, grain-grain collision) operated on interstellar dust in the diffuse ISM have disordered the periodic lattice structures of crystalline silicates. Another possible solution may lie in the fact that, according to Draine (1990), only a small fraction of interstellar dust is the original stardust, i.e., most of the dust mass in the ISM was condensed in the ISM, rather than in stellar outflows. The recondensation at low temperatures most likely leads to an amorphous rather than crystalline form.

First detected in the Becklin-Neugebauer (BN) object in the OMC-1 Orion dense molecular cloud (Dyck et al. 1973), the silicate polarization absorption feature in the $10\,\mu$m region is found to be very common in heavily obscured sources; some sources also have the $18\,\mu$m O-Si-O polarization feature detected (see Aitken 1996; Smith et al. 2000 for summaries). In most cases the silicate polarization features are featureless, indicating the amorphous nature of interstellar silicate material (see Aitken 1996) except AFGL 2591, a molecular cloud surrounding a young stellar object, has an additional narrow polarization feature at $11.2\,\mu$m, generally attributed to annealed silicates (Aitken et al. 1988; Wright et al. 1999).

Reasonably good fits to the observed $10\,\mu$m Si-O polarization features can be obtained by elongated (bare or ice-coated) "astronomical silicate" grains (Draine & Lee 1984; Lee & Draine 1985; Hildebrand & Dragovan 1995; Smith et al. 2000). High resolution observations of the BN $10\,\mu$m and $18\,\mu$m polarization features provided a challenge to the "astronomical silicate" model since this model failed to reproduce two of the basic aspects of the observations: (1) the $10\,\mu$m feature was not broad enough and (2) the $18\,\mu$m feature was too low by a factor of two relative to the $10\,\mu$m peak (Aitken, Smith, & Roche 1989). Attempts by Henning & Stognienko (1993) in terms of porous grains composed of "astronomical silicates", carbon and vacuum were not successful. In contrast, it is shown by Greenberg & Li (1996) that an excellent match to the BN $10\,\mu$m and $18\,\mu$m polarization features in shape, width, and in relative strength can be obtained by the silicate core-organic mantle model using the experimental optical constants of silicate and organic

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[19] Crystalline silicates have also been seen in six comets (see Hanner 1999 for a summary), in dust disks around main-sequence stars (see Artymowicz 2000 for a summary), young stellar objects (see Waelkens, Malfait, & Waters 2000 for a summary), in interplanetary dust particles (IDPs) (Bradley et al. 1999), and probably also in the Orion Nebula (Cesarsky et al. 2000).

refractory materials. It seems desirable to re-investigate the 18 μm O-Si-O band strength of "astronomical silicates" (Draine & Lee 1984) by a combination of observational, experimental and modelling efforts.

In the mid-IR, interstellar grains of submicron size are in the Rayleigh limit. The scattering efficiency falls rapidly with increasing wavelength. Therefore the effects of scattering are expected to be negligible for the silicate extinction and polarization.

3. The 3.4 μm (Aliphatic Hydrocarbon) Absorption Feature

> ''When the 3.4 μm feature was detected in VI Cyg #12, the problem of why no H_2O was observed would appear to have been resolved.''
>
> —— J. Mayo Greenberg [1999]

Another ubiquitous strong absorption band in the diffuse ISM is the 3.4 μm feature. Since its first detection in the Galactic Center toward Sgr A W by Willner et al. (1979) and IRS 7 by Wickramasinghe & Allen (1980), it has now been widely seen in the Milky Way Galaxy and other galaxies (Butchart et al. 1986; Adamson, Whittet, & Duley 1990; Sandford et al. 1991; Pendleton et al. 1994; Wright et al. 1996; Imanishi & Dudley 2000; Imanishi 2000). Although it is generally accepted that this feature is due to the C-H stretching mode in saturated aliphatic hydrocarbons, the exact nature of this hydrocarbon material remains uncertain. Nearly two dozen different candidates have been proposed over the past 20 years (see Pendleton & Allamandola 2002 for a review). The organic refractory residue, synthesized from UV photoprocessing of interstellar ice mixtures, provides a perfect match, better than any other hydrocarbon analogs, to the observed 3.4 μm band, including the 3.42 μm, 3.48 μm, and 3.51 μm subfeatures (Greenberg et al. 1995).[20] But, at this moment, we are not at a position to rule out other dust sources as the interstellar 3.4 μm feature carrier. This feature has also been detected in a carbon-rich protoplanetary nebula CRL 618 (Lequeux & Jourdain de Muizon 1990; Chiar et al. 1998) with close resemblance to the interstellar feature. However, after ejection into interstellar space, the survival of this dust in the diffuse

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[20] Pendleton & Allamandola (2002) questioned the robustness of the fit by the organic residue since the broad 5.5–10 μm band seen in the organic residue spectrum was not observed in astronomical spectra. We note that this band, largely attributed to the combined features of the C=O, C-OH, C≡N, C-NH_2, OH, and NH_2 stretches, bendings, and deformations, will become weaker if the organics are subject to further UV photoprocessing which will result in photodissociation and depletion of H, O, N elements. The organic residue samples presented in Greenberg et al. (1995) were processed at most to a degree resembling one cycle (from molecular clouds to diffuse clouds). According to the cyclic evolution model, interstellar grains will undergo ∼ 50 cycles before they are consumed by star formation or becomes a part of a comet (Greenberg & Li 1999a).

ISM is questionable (see Draine 1990).

The $3.4\,\mu$m feature consists of three subfeatures at $2955\,\mathrm{cm}^{-1}$ ($3.385\,\mu$m), $2925\,\mathrm{cm}^{-1}$ ($3.420\,\mu$m), and $2870\,\mathrm{cm}^{-1}$ ($3.485\,\mu$m) corresponding to the symmetric and asymmetric C-H stretches in CH_3 and CH_2 groups in aliphatic hydrocarbons which must be interacting with other chemical groups. The amount of carbonaceous material responsible for the $3.4\,\mu$m feature is strongly dependent on the nature of the chemical groups attached to the aliphatic carbons. For example, each carbonyl (C=O) group reduces its corresponding C-H stretch strength by a factor of ~ 10 (Wexler 1967). Furthermore, not every carbon is attached to a hydrogen as in saturated compounds. Aromatic hydrocarbons do not even contribute to the $3.4\,\mu$m feature although they do absorb nearby at $\approx 3.28\,\mu$m. The fact that the $3.4\,\mu$m absorption is not observed in molecular cloud may possibly be attributed to dehydrogenation or oxidation (formation of carbonyl) of the organic refractory mantle by accretion and photoprocessing in the dense molecular cloud medium (see Greenberg & Li 1999a) – the former reducing the absolute number of CH stretches, the latter reducing the CH stretch strength by a factor of 10 (Wexler 1967) – the $3.4\,\mu$m feature would be reduced *per unit mass* in molecular clouds.

Very recently, Gibb & Whittet (2002) reported the discovery of a $6.0\,\mu$m feature in dense clouds attributed to the organic refractory. They found that its strength is correlated with the $4.62\,\mu$m OCN^- (XCN) feature which is considered to be a diagnostic of energetic processing.

Attempts to measure the polarization of the $3.4\,\mu$m absorption feature ($P_{\mathrm{C-H}}^{\mathrm{IRS7-obs}}$) was recently made by Adamson et al. (1999) toward the Galactic Center source IRS 7. They found that this feature was essentially unpolarized. Since no spectropolarimetric observation of the $10\,\mu$m silicate absorption feature ($P_{\mathrm{sil}}^{\mathrm{IRS7}}$) has yet been carried out for IRS 7, they estimated $P_{\mathrm{sil}}^{\mathrm{IRS7}}$ from the $10\,\mu$m silicate optical depth $\tau_{\mathrm{sil}}^{\mathrm{IRS7}}$, assuming the IRS 7 silicate feature is polarized to the same degree as the IRS 3 silicate feature; i.e., $P_{\mathrm{sil}}^{\mathrm{IRS7}}/\tau_{\mathrm{sil}}^{\mathrm{IRS7}} = P_{\mathrm{sil}}^{\mathrm{IRS3}}/\tau_{\mathrm{sil}}^{\mathrm{IRS3}}$ where $\tau_{\mathrm{sil}}^{\mathrm{IRS7}}$, $\tau_{\mathrm{sil}}^{\mathrm{IRS3}}$ and $P_{\mathrm{sil}}^{\mathrm{IRS3}}$ were known. Assuming the IRS 7 aliphatic carbon (the $3.4\,\mu$m carrier) is aligned to the same degree as the silicate dust, they expected the $3.4\,\mu$m polarization to be $P_{\mathrm{C-H}}^{\mathrm{IRS7-mod}} = P_{\mathrm{sil}}^{\mathrm{IRS7}}/\tau_{\mathrm{sil}}^{\mathrm{IRS7}} \times \tau_{\mathrm{C-H}}^{\mathrm{IRS7}}$. They found $P_{\mathrm{C-H}}^{\mathrm{IRS7-obs}} \ll P_{\mathrm{C-H}}^{\mathrm{IRS7-mod}}$ (Adamson et al. 1999). Therefore, they concluded that the aliphatic carbon dust is not in the form of a mantle on the silicate dust as suggested by the core-mantle models (Li & Greenberg 1997; Jones, Duley, & Williams 1990).[21] We note that the two key assumptions

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[21] We note that the observed correlation between the $10\,\mu$m silicate and the $3.4\,\mu$m C-

on which their conclusion relies are questionable: (1) $P_{\rm sil}^{\rm IRS7}/\tau_{\rm sil}^{\rm IRS7} = P_{\rm sil}^{\rm IRS3}/\tau_{\rm sil}^{\rm IRS3}$; (2) $P_{\rm C-H}^{\rm IRS7}/\tau_{\rm C-H}^{\rm IRS7} = P_{\rm sil}^{\rm IRS7}/\tau_{\rm sil}^{\rm IRS7}$ (see Li & Greenberg 2002 for details). We urgently need spectropolarimetric observations of IRS 7.

Hough et al. (1996) reported the detection of a weak $3.47\,\mu$m polarization feature in BN, attributed to carbonaceous materials with diamond-like structure, originally proposed by Allamandola et al. (1992) based on the $3.47\,\mu$m absorption spectra of protostars.[22]

4. The $3.3\,\mu$m and $6.2\,\mu$m (PAH) Absorption Features

Recently, two weak narrow absorption features at $3.3\,\mu$m and $6.2\,\mu$m were detected. The $3.3\,\mu$m feature has been seen in the Galactic Center source GCS 3 (Chiar et al. 2000) and in some heavily extincted molecular cloud sight lines (Sellgren et al. 1995; Brooke, Sellgren, & Geballe 1999). The $6.2\,\mu$m feature, about 10 times stronger, has been detected in several objects including both local sources and Galactic Center sources (Schutte et al. 1998; Chiar et al. 2000). They were attributed to aromatic hydrocarbons (Schutte et al. 1998; Chiar et al. 2000). The theoretical $3.3\,\mu$m and $6.2\,\mu$m absorption feature strengths (in terms of integrated optical depths) predicted from the astronomical PAH model are consistent with observations (Li & Draine 2001b). Note the 7.7, 8.6, and $11.3\,\mu$m PAH features are hidden by the much stronger $9.7\,\mu$m silicate feature, and therefore will be difficult to observe as absorption features.

The aromatic absorption bands allow one to place constraints on the PAH abundance if the PAH band strengths are known. But one should keep in mind that the strengths of these PAH absorption bands could vary with physical conditions due to changes in the PAH ionization fraction. In regions with increased PAH ionization fraction, the $6.2\,\mu$m absorption feature would be strengthened and the $3.3\,\mu$m feature would be weakened (see Li & Draine 2001b).

Although it was theoretically predicted that the PAH IR emission

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H hydrocarbon optical depths (Sandford, Pendleton, & Allamandola 1995) is consistent with the core-mantle scenario.

[22] Hydrogenated nanodiamonds were identified in the circumstellar dust envelopes surrounding two Herbig Ae/Be stars HD 97048 and Elias 1 revealed by their $3.43\,\mu$m and $3.53\,\mu$m emission features (Guillois, Ledoux, & Reynaud 1999; van Kerckhoven, Tielens, & Waelkens 2002). Interstellar diamonds were first proposed as a dust component by Saslaw & Gaustad (1969) and first discovered in meteorites by Lewis, Anders, & Draine (1989). The fact that the $3.43\,\mu$m and $3.53\,\mu$m features are not observed in the ISM led Tielens et al. (1999) to infer an upper limit of ≤ 0.1 ppm for hydrogenated interstellar nanodiamonds. If interstellar diamonds are not hydrogenated, they could be much more abundant (van Kerckhoven et al. 2002). Analysis of the interstellar extinction observations show that up to 10% of the interstellar carbon can be locked up in diamond and escape detection (Lewis et al. 1989).

features can be linearly polarized (Léger 1988), no polarization has been detected yet (Sellgren, Rouan, & Léger 1988).

5. The Diffuse Interstellar Bands

In 1922, Heger observed two broad absorption features centering at 5780 Å and 5797 Å, conspicuously broader than atomic interstellar absorption lines. This marked the birth of a long standing astrophysical mystery – the diffuse interstellar bands (DIBs). But not until the work of Merrill (1934) were the interstellar nature of these absorption features established. So far, over 300 DIBs have been detected from the near IR to the near UV. Despite $\sim$ 80 years' efforts, no definite identification (including the recent neutral/charged PAHs [Salama & Allamandola 1992], C_{60}^{+} [Foing & Ehrenfreund 1994], and C_7^- [Tulej et al. 1998] proposals) of the carrier(s) of DIBs has been found. We refer the readers to the two extensive reviews of Krelowski (1999, 2002).

No polarization has been detected for the DIBs (Martin & Angel 1974, 1975; Fahlman & Walker 1975; Adamson & Whittet 1992, 1995; see Somerville 1996 for a review).

6. The Ice Absorption Features

The formation of an icy mantle through accretion of molecules on interstellar dust is expected to take place in dense clouds (e.g., the accretion timescale is only $\sim 10^5$ yrs for clouds of densities $n_{\rm H} = 10^3 - 10^5\,{\rm cm}^{-3}$; Schutte 1996). The detection of various ice IR absorption features (e.g., H_2O [3.05, 6.0 μm], CO [4.67 μm], CO_2 [4.27, 15.2 μm], CH_3OH [3.54, 9.75 μm], NH_3 [2.97 μm], CH_4 [7.68 μm], H_2CO [5.81 μm], OCN^- [4.62 μm]; see Ehrenfreund & Schutte 2000 for a review) have demonstrated the presence of icy mantles in dark clouds (usually with an visual extinction $>$ 3 magnitudes; see Whittet et al. 2001 and references therein). In comparison with that for a gas phase sample, the IR spectrum for the same sample in the solid phase is broadened, smoothed, and shifted in wavelength due to the interactions between the vibrating molecule with the surroundings, the suppression of molecular rotation in ices at low temperatures, and the irregular nature of the structure of (amorphous) solids (see Tielens & Allamandola 1987).

Note not only are the relative proportions of ice species variable in different regions but also the presence and absence of some species. In almost all cases, however, water is the dominant component. An important variability is in the layering of the various molecular components. Of particular note is the fact that the CO molecular spectrum is seen to indicate that it occurs sometimes embedded in the H_2O (a polar matrix) and sometimes not. This tells a story about how the mantles form. As was first noted by van de Hulst, the presence of surface reactions leads to the reduced species H_2O, CH_4, NH_3. Since we now know that CO is an abundant species as a gas phase molecule, we expect to find it accreted along with these reduced species — at least initially.

The two approaches to understanding how the grain mantles evolve are: (1) the laboratory studies of icy mixtures, their modification by UV photoprocessing and by heating; (2) theoretical studies combining gas phase chemistry with dust accretion and dust chemistry. In the laboratory one creates a cold surface (10K) on which various simple molecules are slowly deposited in various proportions. The processing of these mixtures by UV photons and by temperature variation is studied by IR spectroscopy. This analog of interstellar dust mantles is used to provide a data base for comparison with the observations (see Schutte 1999 for a review).

The $3.1\,\mu$m ice polarization has been detected in various molecular cloud sources (see Aitken 1996 and references therein). The detection of the $4.67\,\mu$m CO and $4.62\,\mu$m OCN^- polarization was recently reported by Chrysostomou et al. (1996). The BN ice polarization feature was well fitted by ice-coated grains (Lee & Draine 1985), suggesting a core-mantle grain morphology. However, the AFGL 2591 molecular cloud shows no evidence for ice polarization (Dyck & Lonsdale 1980; Kobayashi et al. 1981) while having distinct ice extinction and silicate polarization (Aitken et al. 1988). Perhaps only the hot, partly annealed silicate grains close to the forming-star are aligned (say, by streaming of ambipolar diffusion) while the ice-coated cool grains in the outer envelope of the cloud are poorly aligned.

3.2. DUST EMISSION

3.2.1. *Dust Luminescence: The "Extended Red Emission"*

> ''The ERE has become an important observational aspect of interstellar grains that future models need to reproduce.''
>
> —— A.N. Witt [2000]

First detected in the Red Rectangle (Schmidt, Cohen, & Margon 1980), "extended red emission" (ERE) from interstellar dust consists of a broad, featureless emission band between ~5400 Å and 9000 Å, peaking at $6100 \leq \lambda_{\rm p} \leq 8200$ Å, and with a width 600 Å $\leq$ FWHM ≤ 1000 Å. The ERE has been seen in a wide variety of dusty environments: the diffuse ISM of our Galaxy, reflection nebulae, planetary nebulae, HII regions, and other galaxies (see Witt, Gordon, & Furton 1998 for a summary). The ERE is generally attributed to photoluminescence (PL) by some component of interstellar dust, powered by UV/visible photons. The photon conversion efficiency of the diffuse ISM has been determined to be near $(10 \pm 3)\%$ (Gordon et al. 1998; Szomoru & Guhathakurta 1998) assuming that all UV/visible photons absorbed by interstellar grains are absorbed by the ERE carrier. The actual photoluminescence efficiency of the ERE carrier must exceed $\sim 10\%$, since the ERE carrier cannot be the only UV/visible photon absorber.

Various forms of carbonaceous materials – HAC (Duley 1985; Witt & Schild 1988), PAHs (d'Hendecourt et al. 1986), QCC (Sakata et al. 1992), C_{60} (Webster 1993), coal (Papoular et al. 1996), PAH clusters (Allamandola, private communication), carbon nanoparticles (Seahra & Duley 1999), and crystalline silicon nanoparticles (Witt et al. 1998; Ledoux et al. 1998) – have been proposed as carriers of ERE. However, most candidates appear to be unable to simultaneously match the observed ERE spectra and the required PL efficiency (see Witt et al. 1998 for details).

Although high photoluminescence efficiencies can be obtained by PAHs, the lack of spatial correlation between the ERE and the PAH IR emission bands in the compact HII region Sh 152 (Darbon et al. 2000), the Orion Nebula (Perrin & Sivan 1992), and the Red Rectangle (Kerr et al. 1999), and the detection of ERE in the Bubble Nebula where no PAH emission has been detected (Sivan & Perrin 1993) seem against PAHs as ERE carriers.

Seahra & Duley (1999) argued that small carbon clusters were able to meet both the ERE profile and the PL efficiency requirements. However, this hypothesis appears to be ruled out by non-detection in NGC 7023 of the $1\,\mu$m ERE peak (Gordon et al. 2000) predicted by the carbon nanoparticle model.

Witt et al. (1998) and Ledoux et al. (1998) suggested crystalline silicon nanoparticles (SNPs) with 15Å – 50Å diameters as the carrier on the basis of experimental data showing that SNPs could provide a close match to the observed ERE spectra and satisfy the quantum efficiency requirement. Smith & Witt (2001) have further developed the SNP model for the ERE, concluding that the observed ERE in the diffuse ISM can be explained with Si/H = 6 ppm in SiO_2-coated SNPs with Si core radii $a \approx 17.5\,$Å.

Li & Draine (2002b) calculated the thermal emission expected from such particles, both in a reflection nebula such as NGC 2023 and in the diffuse ISM. They found that Si/SiO_2 SNPs (both neutral and charged) would produce a strong emission feature at $20\,\mu$m. The observational upper limit on the $20\,\mu$m feature in NGC 2023 imposes an upper limit of < 0.2ppm Si in Si/SiO_2 SNPs. The ERE emissivity of the diffuse ISM appears to require $> 15\,$ppm ($\geq$42% of solar Si abundance) in Si/SiO_2 SNPs. In comparison with the predicted IR emission spectra, they found that the DIRBE (*Diffuse Infrared Background Experiment*) photometry appears to rule out such high abundances of free-flying SNPs in the diffuse ISM. Therefore they concluded that if the ERE is due to SNPs, they must be either in clusters or attached to larger grains. Future observations by SIRTF will be even more sensitive to the presence of free-flying SNPs.

3.2.2. *Dust Temperatures and IR Emission*

The temperatures of interstellar dust particles depend on their optical properties and sizes (i.e., on the way they absorb and emit radiation) as well as on the interstellar radiation field (ISRF).[23] Most of the visible and UV radiation in galaxies from stars passes through clouds of particles and heats them. This heating leads to reradiation at much longer wavelengths extending to the millimeter. On the average, in spiral galaxies, $\sim 1/4 - 1/3$ of the total stellar radiation is converted into dust emission (Cox & Mezger 1989; Calzetti 2001). The converted radiation is a probe of the particles and the physical environments in which they find themselves.

There is a long history in the study of grain temperature (and emission) since Eddington's demonstration of a 3.2 K black body equilibrium dust temperature assuming a 10^4 K interstellar radiation field diluted by a factor of 10^{-14} (Eddington 1926). Van de Hulst (1949) was the first to provide a realistic dust model temperature, $\sim$ 15 K for dielectric particles. A subsequent extensive investigation was made by Greenberg (1968, 1971) where the temperatures were calculated for various grain types in regions of various radiation fields. The first step to study the shape effects on dust temperatures was taken by Greenberg & Shah (1971). They found that the temperatures of non-spherical dielectric grains are generally lower than those of equivalent spheres, but insensitive to modest shape variations. Later efforts made by Chlewicki (1987) and Voshchinnikov, Semenov, & Henning (1999) essentially confirmed the results of Greenberg & Shah (1971).

The advent of the IRAS, COBE, and ISO space IR measurements provided powerful information regarding the far-IR emission of the large particles (the so-called "cold dust"). The "cold dust" problem has received much attention since it plays an important role in many astrophysical subjects;

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[23] Originally, the ISRF was represented by a 10^4 K black-body radiation diluted by a factor of 10^{-14} (Eddington 1926) which is undoubtedly too crude but serves as a simple and adequate approximation for some purposes. Many attempts have been made to obtain a more reasonable determination of the ISRF either on the basis of direct measurements of the UV radiation from the sky or by calculating the radiation of hot stars using model atmospheres. Van Dishoeck (1994) has summarized the typical ISRF estimates (Habing 1968; Draine 1978; Gondhalekar et al. 1980; Mathis, Mezger, & Panagia 1983). As illustrated in Fig. 2 of van Dishoeck (1994), the various estimates agree within factors of two. The latest work on the local far-UV ISRF by Parravano, Hollenbach, & Mckee (2002) led to a value quite close to Draine (1978).

for example, the presence of "cold dust" would change the current concept on the morphology and physics of galaxies (Block 1996).

The presence of a population of ultrasmall grains was known long before the IR era. Forty-six years ago, Platt (1956) proposed that very small grains or large molecules with radii $\leq 10\text{Å}$ may be present in interstellar space. Donn (1968) further proposed that polycyclic aromatic hydrocarbon-like "Platt particles", may be responsible for the UV interstellar extinction.

These very small grains – consisting of tens to hundreds of atoms – are small enough that the time-averaged vibrational energy $\langle E \rangle$ 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 IR. The idea of transient heating of very small grains was first introduced by Greenberg (1968). Since then, there have been a number of studies on this topic (see Draine & Li 2001 and references therein).

Since the 1980s, an important new window on the "very small grain component" has been opened by IR observations. The near-IR continuum emission of reflection nebulae (Sellgren, Werner, & Dinerstein 1983) and the 12 and $25\,\mu\text{m}$ "cirrus" emission detected by IRAS (Boulanger & Pérault 1988) explicitly indicated the presence of a very small interstellar dust component since large grains (with radii $\sim 0.1\mu\text{m}$) heated by diffuse starlight emit negligibly at such short wavelengths, whereas very small grains (with radii $\leq 0.01\mu\text{m}$) can be transiently heated to very high temperatures (≥ 1000 K depending on grain size, composition, and photon energy). Subsequent measurements by the DIRBE instrument on the COBE satellite confirmed this and detected additional broadband emission at 3.5 and $4.9\,\mu\text{m}$ (Arendt et al. 1998).

More recently, spectrometers aboard the *Infrared Telescope in Space* (IRTS; Onaka et al. 1996; Tanaka et al. 1996) and ISO (Mattila et al. 1996) have shown that the diffuse ISM radiates strongly in emission features at 3.3, 6.2, 7.7, 8.6, and $11.3\,\mu\text{m}$.

> `''PAHs, they are everywhere!''`
> —— L.J. Allamandola [1996]

These emission features, first seen in the spectrum of the planetary nebulae NGC 7027 and BD+30°3639 (Gillett, Forrest, & Merrill 1973), have been observed in a wide range of astronomical environments including planetary nebulae, protoplanetary nebulae, reflection nebulae, HII regions, circumstellar envelopes, and external galaxies (see Tielens et al. 1999 for a review for Galactic sources and Helou 2000 for extragalactic sources). Often referred to as "unidentified infrared" (UIR) bands, these emission features are now usually attributed to PAHs which are vibrationally excited upon absorption of a single UV/visible photon (Léger & Puget 1984; Allamandola, Tielens, & Barker 1985) although other carriers have also been proposed such as HAC (Duley & Williams 1981; Borghesi, Bussoletti, & Colangeli 1987; Jones, Duley, & Williams 1990), QCC (Sakata et al. 1990), coal (Papoular et al. 1993), fullerenes (Webster 1993), and interstellar nanodiamonds with sp^3 surface atoms reconstructed to sp^2 hybridization (Jones & d'Hendecourt 2000).

The emission mechanism proposed for the UIR bands – UV excitation of gas-phase PAHs followed by internal conversion and IR fluorescence[24] – is supported by laboratory measurements of the IR *emission* spectra of gas-phase PAH molecules (Cherchneff & Barker 1989; Brenner & Barker 1989; Kurtz 1992; Cook et al. 1998) and by theoretical investigations of the heating and cooling processes of PAHs in interstellar space (Allamandola, Tielens, & Barker 1989; Barker & Cherchneff 1989; d'Hendecourt et al. 1989; Draine & Li 2001a).

The near-IR (1–5 μm), mid-IR (5–12 μm) emission spectrum along with the far-IR (>12 μm) continuum emission of the diffuse Galactic medium yields further insights into the composition and physical nature of interstellar dust; in particular, the PAH emission features allow us to place constraints on the size distribution of the very small dust component.

Attempts to model the IR emission of interstellar dust have been made by various workers. Following the initial detection of 60 and 100 μm cirrus emission (Low et al. 1984), Draine & Anderson (1985) calculated the IR emission from a graphite/silicate grain model with grains as small as 3Å and argued that the 60 and 100 μm emission could be accounted for. When further processing of the IRAS data revealed stronger-than-expected 12 and 25 μm emission from interstellar clouds (Boulanger, Baud, & van Albada 1985), Weiland et al. (1986) showed that this emission could be explained if very large numbers of 3–10Å grains were present. A step forward was taken by Désert, Boulanger, & Puget (1990), Siebenmorgen & Krügel (1992), Schutte, Tielens, & Allamandola (1993), and Dwek et al. (1997) by including PAHs as an essential grain component. Early studies were limited to the IRAS observation in four broad photometric bands, but Dwek et al. (1997) were able to use DIRBE and FIRAS data.

In recent years, there has been considerable progress in both experimental measurements and quantum chemical calculations of the optical properties of PAHs (Allamandola, Hudgins, & Sandford 1999; Langhoff 1996; and references therein). There is also an improved understanding of the heat capacities of dust candidate materials (Draine & Li 2001) and the stochastic

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[24] PAHs are actually excited by photons of a wide range of wavelengths (Li & Draine 2002c).

heating of very small grains (Barker & Cherchneff 1989; d'Hendecourt et al. 1989; Draine & Li 2001), the interstellar dust size distributions (Weingartner & Draine 2001a), and the grain charging processes (Weingartner & Draine 2001b).

Li & Draine (2001b) have made use of these advances to model the full emission spectrum, from near-IR to submillimeter, of dust in the diffuse ISM. The model consists of a mixture of amorphous silicate grains and carbonaceous grains, each with a wide size distribution ranging from molecules containing tens of atoms to large grains $\geq 1\,\mu$m in diameter. The carbonaceous grains are assumed to have PAH-like properties at very small sizes, and graphitic properties for radii $a \geq 50$Å. On the basis of recent laboratory studies and guided by astronomical observations, they have constructed "astronomical" absorption cross sections for use in modelling neutral and ionized PAHs from the far UV to the far IR. Using realistic heat capacities (for calculating energy distribution functions for small grains undergoing "temperature spikes"), realistic optical properties, and a grain size distribution consistent with the observed interstellar extinction (Weingartner & Draine 2001a), Li & Draine (2001b) were able to reproduce the near-IR to submillimeter emission spectrum of the diffuse ISM, including the PAH emission features at 3.3, 6.2, 7.7, 8.6, and 11.3$\,\mu$m.

The silicate/graphite-PAH model has been shown also applicable to the Small Magellanic Cloud (Li & Draine 2002a; Weingartner & Draine 2001a).

Li & Draine (2002c) have also modelled the excitation of PAH molecules in UV-poor regions. It was shown that the astronomical PAH model provides a satisfactory fit to the UIR spectrum of vdB 133, a reflection nebulae with the lowest ratio of UV to total radiation among reflection nebulae with detected UIR band emission (Uchida, Sellgren, & Werner 1998).

3.2.3. *Microwave Emission: Spinning Dust Grains*

A number of physical processes including collisions with neutral atoms and ions, plasma drag, absorption and emission of photons can drive ultrasmall grains to rapidly rotate (Draine & Lazarian 1998a, 1998b; Draine & Li 2002). The electric dipole emission from these spinning dust grains was shown to be able to account for the 10–100 GHz "anomalous" Galactic background component (See Draine & Lazarian 1998b and references therein).

3.3. INTERSTELLAR DEPLETIONS

> ``Where have all these atoms gone?''
> —— J. Mayo Greenberg [1963]

Derivations of the relative abundances of the elements in our Galaxy are one of the principal needs for understanding the chemical evolution in interstellar space – and ultimately its memory in comets. A major factor in developing consistent dust models was the observation of the "depletion" in low density clouds (atoms locked up in grains are "depleted" from the gas phase) using the UV absorption line spectroscopy as a probe of the gas-phase abundances and assuming a reference abundance (abundances of atoms both in gas and in dust).

The deduced possible dust composition was initially only constrained to the extent that silicates alone could not be responsible for the interstellar extinction (Greenberg 1974). But in recent years, the problem of grain modelling has been exacerbated by the apparent decrease of the available condensible atoms (O, C, N, Si, Mg, Fe) by about 30% (Snow & Witt 1996) since the solar system was born.[25] This implies that the heavy elements are being consumed more than they are being created. However, if one goes back far enough in time, there were no condensible atoms because their initial production must follow the birth of stars. This brings us to the cosmological question of what do high-z galaxies look like and when and how was dust first found in them?

3.4. INTERSTELLAR DUST IN THE SOLAR SYSTEM

Interstellar grains have been found in primitive meteorites and in interplanetary dust particles based on the analysis of isotopic anomalies (see Kerridge 1999 and Bradley 1999 for recent reviews). Most presolar grains identified to date are carbonaceous: diamonds, SiC, and graphite (very small TiC, ZrC, and MoC grains have also been found as inclusions in SiC and graphite grains); also identified are oxides such as corundum (Al_2O_3) and silicon nitride (Si_3N_4). One should keep in mind that much of the less refractory dust incorporated into meteorites is lost during the chemical processing used to extract the refractory grains from meteorites. Therefore, the extracted presolar grains are compositionally not representative of the bulk interstellar dust;[26] for example, the procedures used to isolate interstellar grains in meteorites are designed to deliberately destroy silicate material which constitutes the bulk of the host meteorite (see Draine 1994).

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[25] But see also Sofia & Meyer (2001), who argue that interstellar abundances are approximately solar. It is also possible that the solar system formed out of material with a higher metallicity than the average ISM at that time (there is evidence that stars with planets have higher metallicities than equal age stars without planets). So the metallicity of the ISM may not have declined since the solar system was formed (Draine, private communication).

[26] We have already seen in Footnote-22 that diamond is not a major interstellar dust component. Whittet, Duley, & Martin (1990) found that the abundance of Si in SiC dust in the diffuse ISM is at most 5% of that in silicates.

The solar system is surrounded by the local interstellar cloud with a density $n_{\mathrm{H}} \approx 0.3\,\mathrm{cm}^{-3}$ and moving past the Sun with a velocity $\approx 26\,\mathrm{km\,s}^{-1}$ (Lallement et al. 1994). Interstellar grains embedded in the local cloud with sufficiently low charge-to-mass ratios can penetrate the heliopause and enter the solar system on hyperbolic orbits (small, charged grains are deflected from the heliosphere; Linde & Gombosi 2000). The interplanetary spacecraft Ulysses and Galileo have detected over 600 grains flowing into the solar system and determined their speed, direction, and mass and therefore the mass flux (but not chemical composition since the grains were destroyed by the detection technique; Grün et al. 1993, 1994; Frisch et al. 1999; Landgraf et al. 2000). Including the mass of the large population of interstellar micrometeorites entering the Earth's atmosphere (Taylor et al. 1996; Baggaley 2000), Frisch et al. (1999) found that the total dust-to-gas mass ratio in the local interstellar cloud is about twice the canonical value determined from the interstellar extinction. They also found that there is a substantial amount of mass in large grains of $\sim 1\,\mu\mathrm{m}$ in size which is difficult to reconcile with the interstellar extinction and interstellar elemental abundances.

3.5. FROM INTERSTELLAR DUST TO COMETS

A major advance in our understanding of comets in the 20th century was made by the space probes Vega 1 and 2 and Giotto (see Nature, comet Halley issue, vol. 321, 1986). Until that time no one had ever seen a comet nucleus. The critical new discoveries were: (1) the low albedo (≈ 0.04) of comets; (2) the size distribution of the comet dust extending down to interstellar dust sizes (10^{-15} – $10^{-18}\,\mathrm{g}$), (3) the organic fraction of comet dust (see Greenberg & Li 1999b and references therein). The current ground based observations of the volatile composition of comets implies a close connection with the ices of interstellar dust (see Crovisier 1999 and Irvine & Bergin 2000 for recent reviews).

Most of the current models of comet nuclei presume that to a major extent they are basically aggregates of the interstellar dust in its final evolved state in the collapsing molecular cloud which becomes the protosolar nebula. In addition to the chemical consequences of such a model, there is the prediction of a morphological structure in which the aggregate material consists of tenth micron basic units each of which contains (on average) a silicate core, a layer of complex organic material, and an outer layer of ices in which are embedded all the very small carbonaceous particles characterizing the interstellar UV hump and the far UV extinction. All these components have been observed in the comet comae in one way or another.[27] The implication is that space probes which can examine in detail the composition of comet nuclei will be able to provide us with hands-on data on most of the components of interstellar dust and will tell us what is the end product of chemical evolution in a collapsing protosolar molecular cloud. At this time many laboratories are preparing materials as a data base for comparison with what will be analyzed during the space missions.

4. Future

There are quite a few unsolved or partially solved problems related to interstellar dust which will be demanding close attention in the future (see below for a list). A number of new remote observational facilities which will be available early in the new millennium (Atacama Large Millimeter Array [MMA/LSA], Far Infrared and Submillimeter Telescope [FIRST], Next Generation Space Telescope [NGST], Space Infrared Telescope Facility [SIRTF], Stratospheric Observations for Infrared Astronomy [SOFIA], Submillimeter Wave Astronomy Satellite [SWAS]) will permit further tests of current dust models and promise new observational breakthroughs.

1. What is the source and nature of the Diffuse Interstellar Bands?
2. What is the carrier of the 2175 Å extinction hump?
3. What is the carrier of the "Unidentified Infrared Bands"? if it is PAHs, where are they formed? are they mainly from carbon star outflows or formed in situ by ion-molecule reactions (Herbst 1991) or from the organic refractories derived from photoprocessing of ice mixtures (Greenberg et al. 2000)?
4. What is the carrier of the Extended Red Emission?
5. What are all the sources and sinks (destruction) of interstellar dust? where are interstellar grains made? are they mainly made in the cold ISM (Draine 1990) or are the silicate cores mainly stardust (serving as "condensation seeds") while the organic mantles are formed in the ISM (Greenberg 1982a; Greenberg & Li 1999a)?
6. What are the exact composition and morphology of interstellar dust? are they separate bare silicate and graphite grains or silicate core-carbonaceous mantle grains or composite grains composed of small silicates, carbon and vacuum? if most of interstellar grain mass is con-

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[27] PAH molecules, a significant constituent of interstellar dust (see §3.2.2), would also be present in comets if they indeed contain unprocessed interstellar matter. The presence of PAHs in comets has been suggested by the 3.28 μm emission feature detected in some comets (Bockelée-Morvan, Brooke, & Crovisier 1995). More specifically, a 3-ring PAH molecule – phenanthrene ($C_{14}H_{10}$) – has been proposed as the carrier for the 342–375 nm fluorescence bands seen in comet 1P/Halley (Moreels et al. 1994). Li & Draine (2002d) are currently working on this topic.

densed in the cold ISM, how can pure silicate and graphite grains form (see Draine 1995)?

7. What are the sizes of large dust grains ($> 0.25\,\mu$m)? how much can we learn from X-ray halos and from spacecraft in situ dust detections?
8. Why are crystalline silicates not seen in the ISM while they are present in stardust and cometary dust? how do cometary silicates become crystalized?
9. How do molecular hydrogen and other simple molecules form on grain surfaces? although considerable progress has been made in recently years in studies of the diffusion rates of adsorbed hydrogen atoms on the surfaces of variable dust materials, the recombination reactions, and the restoration of the new molecules to the gas phase (Pirronello et al. 1997; Pirronello et al. 1999; Manicò et al. 2001), the formation of molecular hydrogen is still not well understood (Herbst 2000; Pirronello 2002).
10. How do interstellar grains accrete and deplete mantles in dense molecular clouds? we need high spatial resolution observations of molecule distributions in the gas and in the solid as function of depth in the cloud – interiors of clouds as well as regions of low and high mass star formation.
11. How does dust evolve in protosolar regions? we need higher spatial resolution and sensitivity. Improvements in the theory of dust/grain chemistry, particularly in collapsing clouds leading to star formation as well as in quiescent molecular clouds.
12. Will the chemical and morphological analysis of comet nuclei and dust material reveal the true character of interstellar dust? will they provide further answers to the question of life's origin?
13. How can we resolve the evolution of interstellar matter leading to the material measured and analyzed in meteorites, in interplanetary dust particles?
14. What is the true atomic composition of the interstellar medium? how variable is it in time and space? are there global variation over distances of kiloparsecs?
15. When did dust first form in a galaxy? what are the composition and sizes of dust in extragalactic environments?

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A. Li was deeply saddened by the passing away of Prof. J. Mayo Greenberg on November 29, 2001. As a pioneer in the fields of cosmic dust, comets, astrochemistry, astrobiology and light scattering, Mayo's passing was a great loss for the astro-community. Mayo had been scientifically active till his very last days. Just a few weeks before Mayo passed away, A. Li discussed future collaboration plans with him on dust in high-z galaxies. It was a great experience for A. Li to work with Mayo in Leiden. He will be remembered forever, as a great astrophysicist and as a great mentor. A. Li is also grateful to Profs. Bruce T. Draine and Ewine F. van Dishoeck for their continuous advice, encouragement and support. A. Li thanks Profs. Lou J. Allamandola, Bruce T. Draine, Jonathan Lunine, Valerio Pirronello for valuable discussions, comments and suggestions. Some of the materials of §2 (dust history) were taken from Greenberg & Shen (1999) and the "Introduction" Chapter of A. Li's PhD thesis (Leiden, 1998); of §3.2.1 (dust luminescence) from Li & Draine (2002a); and of §3.2.2 (dust IR emission) from Li & Draine (2001b). This work was supported in part by NASA grant NAG5-7030 and NSF grant AST-9988126 and by a grant from the Netherlands Organization for Space Research (SRON).

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