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Interstellar Grains – The 75TH Anniversary

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Abstract. The year of 2005 marks the 75th anniversary since Trumpler (1930) provided the first definitive proof of interstellar grains by demonstrating the existence of general absorption and reddening of starlight in the galactic plane. This article reviews our progressive understanding of the nature of interstellar dust.

1. Introduction: A Brief History for the Studies of Interstellar Dust

In 1930 – exactly 75 years ago, the existence of solid dust particles in interstellar space was by the first time firmly established, based on the discovery of color excesses (Trumpler 1930). But the history of the interstellar dust-related studies is a much longer and complex subject, and can be dated back to the late 18th century when Herschel (1785) described the dark markings and patches in the sky as “holes in the heavens”. Below is a summary of the highlights of this history. For a more detailed record of the historical development of dust astronomy, I refer the interested readers to Aiello & Cecchi-Pestellini (2000), Dorschner (2003), Li & Greenberg (2003), and Verschuur (2003).

Early Chronology: From “Holes in the Heavens” to the Firm Establishment of Interstellar Dust

- As early as 1785, Sir William Herschel noticed that the sky looks patchy with stars unevenly distributed and some regions are particularly “devoid” of stars. He described these dark regions (“star voids”) as “**holes in the heavens**”.
- At the beginning of the 20th century, astronomers started to recognize that the “starless holes” were real physical structures in front of the stars, containing **dark obscuring masses of matter** able to absorb starlight (Clerke 1903; Barnard 1919), largely thanks to the new technology of photography which made the photographic survey of the dark markings possible. Sir Harold Spencer Jones (1914) also attributed the dark lanes seen in photographs of edge-on spiral galaxies to obscuring matter. Whether the dark lanes in the Milky Way is caused by obscuring material was one of the points of contention in the Curtis-Shapley debate (Shapley & Curtis 1921).
- Wilhelm Struve (1847) noticed that the apparent number of stars per unit volume of space declines in all directions receding from the Sun. He attributed this effect to **interstellar absorption**.¹ From his analysis of star counts he deduced an visual extinction of $\sim 1 \text{ mag kpc}^{-1}$. Many years later, Jacobus Kapteyn (1904) estimated the interstellar absorption to be $\sim 1.6 \text{ mag kpc}^{-1}$, in order for the observed distribution of stars in space to

¹ To be precise, this should be called “extinction” which is a combined effect of absorption and scattering: a grain in the line of sight between a distant star and the observer reduces the starlight by a combination of scattering and absorption.

be consistent with his assumption of a constant stellar density. This value was amazingly close to the current estimates of $\sim 1.8 \text{ mag kpc}^{-1}$. Max Wolf (1904) demonstrated the existence of discrete clouds of interstellar matter by comparing the star counts for regions containing obscuring matter with those for neighbouring undimmed regions.

- In 1912, Vesto Slipher discovered **reflection nebulae** from an analysis of the spectrum of the nebulosity in the Pleiades cluster which he found was identical to that of the illuminating stars. It was later recognized that the nebulosity was created by the scattering of light from an intrinsically luminous star by the dust particles in the surrounding interstellar medium (ISM).
- Henry N. Russell (1922) argued that **dark clouds accounted for the obscuration and this obscuring matter had to be in the form of millimeter-sized fine dust**. Anton Pannekoek (1920) recognized that the obscuration can not be caused by the Rayleigh scattering of gas, otherwise one would require unrealistically high masses for the dark nebulae. He also noticed that, as suggested by Willem de Sitter, the cloud mass problem can be vanished if the extinction is due to dust grains with a size comparable to the wavelength of visible light.
- In 1922, Mary L. Heger observed two broad absorption features at 5780 Å and 5797 Å, conspicuously broader than atomic interstellar absorption lines. The interstellar nature of these absorption features was established 12 years later by Paul W. Merrill (1934). These mysterious lines – known as the **diffuse interstellar bands (DIBs)**, still remain unidentified.
- In 1930, a real breakthrough was made by **Robert J. Trumpler who provided the first unambiguous evidence for interstellar absorption and reddening which led to the general establishment of the existence of interstellar dust**. Trumpler (1930) based this on a comparison between the photometric distances and geometrical distances of 100 open clusters.² If there was no interstellar absorption, the two distances should be in agreement. However, Trumpler (1930) found that the photometric distances are systematically larger than the geometrical distances, indicating that the premise of a transparent ISM was incorrect.³ Using this direct and compelling method he was able to find both absorption and selective absorption or color excess with increasing distance.⁴ Trumpler (1930) also concluded that **the observed color excess could only be accounted for by “fine cosmic dust”**.
- In 1932, Jan H. Oort demonstrated that the space between the stars must contain a considerable amount of matter. He derived an **upper limit (“Oort limit”) on the total mass of the matter (including both stars and interstellar matter)** in the solar neighbourhood from an analysis of the motions of K giants perpendicular to the plane of the Galaxy (the z -direction). An upper limit of $\sim 1.0 \times 10^{-23} \text{ g cm}^{-3}$ on the total mass density was obtained from measuring the gravitational acceleration in the z -direction. The Oort limit has important implications: (1) **there has to be more material in the galactic plane than could be seen in stars** since the mass density of known stars is only $\sim 4.0 \times 10^{-24} \text{ g cm}^{-3}$; and (2) **the upper limit of $\sim 6.0 \times 10^{-24} \text{ g cm}^{-3}$ on the**

² The photometric distances were obtained by comparing apparent and absolute magnitudes, with the latter determined from the spectral types of the stars in the clusters. The geometrical distances were determined from the angular diameters of the clusters, assuming that all their diameters were the same.

³ As mentioned earlier in this review, general star counts did suggest the existence of interstellar extinction which increases with distance. However, this evidence is not decisive because interpretation of the star-count data rests on assumptions (generally unproved at the time) as to the true spatial distribution of the stars.

⁴ Trumpler (1930) derived a color-excess of $\sim 0.3 \text{ mag kpc}^{-1}$ between the photographic (with an effective wavelength $\lambda_B \approx 4300 \text{ Å}$) and visual ($\lambda_V \approx 5500 \text{ Å}$) bands, and a general (visual) absorption of $\sim 1.0 \text{ mag kpc}^{-1}$.

mass density of the interstellar matter in the solar neighbourhood places severe restrictions on the source of the obscuration: what kind of material distributed with this density with what mass absorption coefficient could give rise to the observed visual extinction of about 1 mag kpc^{-1} ? apparently, only with small dust grains could so much extinction by so little mass (and the λ^{-1} wavelength dependence; see below) be explained.

Interstellar Absorption and Scattering

- In 1936, Rudnick by the first time measured the wavelength dependence of extinction in the wavelength range 4000–6300 Å based on differential spectrophotometric observations of reddened and unreddened stars of the same spectral type. Rudnick (1936) found that the measured **extinction curve was inconsistent with Rayleigh scattering** (which has a λ^{-4} wavelength dependence). This so-called “**pair-match**” method remains the most common way of deriving an interstellar extinction curve.
- By the end of the 1930s, a λ^{-1} **extinction law in the wavelength range 1–3 μm^{-1}** had been well established (Hall 1937; Greenstein 1938; Stebbins, Huffer, & Whitford 1939), thanks to the advent of the photoelectric photometry, excluding free electrons, atoms, molecules, and solid grains much larger or much smaller than the wavelength of visible light, leaving solids with a size comparable to the wavelength as the sole possibility.
- In 1936, Struve & Elvey demonstrated the scattering of general starlight by interstellar clouds based on a series of observations of the dark cloud Barnard 15, the core of which is appreciably darker than the rim, although the latter is about opaque as the former. They attributed the increased brightness of the outer region to **interstellar scattering**.
- In 1941, Henyey & Greenstein confirmed the existence of **diffuse interstellar radiation** (which was originally detected by van Rhijn [1921]) in the photographic wavelength region. They interpreted the observed intensity of diffuse light as scattered stellar radiation by **interstellar grains which are strongly forward scattering and have a high albedo (higher than ~ 0.3)**.
- In 1943, with the advent of the six-colour photometry (at $3530 \text{ \AA} < \lambda < 10300 \text{ \AA}$) Stebbins & Whitford found that the extinction curve exhibits curvature at the near infrared (IR; $\lambda \approx 1.03 \mu\text{m}$) and ultraviolet (UV; $\lambda \approx 0.35 \mu\text{m}$) regions, **deviating from the simple λ^{-1} law**.
- In 1953, Morgan, Harris, & Johnson estimated the ratio of total visual extinction to color excess to be $A_V/E(B-V) \approx 3.0 \pm 0.2$. This was supported by a more detailed study carried out by Whitford (1958), who argued that there appeared to be a “very close approach to uniformity of the reddening law” in most directions. **A uniform extinction curve with a constant $A_V/E(B-V)$** was welcomed by the astronomical community – at that early stage, interstellar dust was mainly regarded as an annoying mere extinguisher of starlight which prevented an accurate measurement of distances to stars. The proposal of “a uniform extinction curve with a constant $A_V/E(B-V)$ ” made it easier to correct photometric distances for the effects of absorption (also because the determination of the color excess $E(B-V)$ for early-type stars was relatively straightforward).
- In 1955, based on the UBV photometry of early O stars in a region in Cygnus, Johnson & Morgan noted that there may exist **regional variations** in the interstellar extinction curve. The **nonuniformity nature of the interstellar extinction curve** was later confirmed in Cygnus, Orion, Perseus, Cepheus and NGC 2244 by Johnson & Borgman (1963), Nandy (1964), and Johnson (1965). Those authors also found a wide variety of $A_V/E(B-V)$ values (ranging from ~ 3.0 to ~ 7.4) in different regions. Wampler (1961) found a systematic variation with galactic longitude of $E(U-B)/E(B-V)$, the ratio of slopes in the blue to those in the visible region.

- In the 1960s and early 1970s, the extension of the extinction curve toward the middle and far UV ($\lambda^{-1} > 3 \mu\text{m}^{-1}$) was made possible by rocket and satellite observations, including the rocket-based photoelectric photometry at $\lambda = 2600 \text{ \AA}$ and 2200 \AA (Boggess & Borgman 1964); the *Aerobee* rocket spectrophotometry at $1200 \text{ \AA} < \lambda < 3000 \text{ \AA}$ (Stecher 1965); the *Orbiting Astronomical Satellite* (OAO-2) spectrophotometry at $1100 \text{ \AA} < \lambda < 3600 \text{ \AA}$ (Bless & Savage 1972); and the *Copernicus* Satellite spectrophotometry at $1000 \text{ \AA} < \lambda < 1200 \text{ \AA}$ (York et al. 1973). **By 1973, the interstellar extinction curve had been determined over the whole wavelength range from $0.2 \mu\text{m}^{-1}$ to $10 \mu\text{m}^{-1}$.**
- In 1965, the **2175 \AA extinction bump was detected** by Stecher (1965). Shortly after its detection, it was attributed to graphite (Stecher & Donn 1965).⁵ It was later found that the strength and width of this bump vary with environment while its peak position is quite invariant.
- Cardelli, Clayton, & Mathis (1989) found that the optical/UV extinction curve in the wavelength range of $0.125 \leq \lambda \leq 3.5 \mu\text{m}$ which shows considerable regional variations can be approximated by an analytical formula involving only one free parameter: the total-to-selective extinction ratio $R_V \equiv A_V/E(B - V)$, whereas the near-IR extinction curve ($0.9 \mu\text{m} \leq \lambda \leq 3.5 \mu\text{m}$) can be fitted reasonably well by a power law $A(\lambda) \sim \lambda^{-1.7}$, showing little environmental variations.⁶

From Metallic Grains to Dirty Ices: Meteoritic Origin or Interstellar Condensation?

- In the 1930s, small **metallic particles** were proposed to be responsible for the interstellar extinction, partly because meteoritic particles (predominantly metallic) and interstellar grains were then thought to have the same origin. Reasonably good fits to the λ^{-1} extinction law were obtained in terms of small metallic grains with a dominant size of $\sim 0.05 \mu\text{m}$ (Schalén 1936) or a power-law size distribution $dn(a)/da \sim a^{-3.6}$ in the size range $80 \text{ \AA} < a < 1 \text{ cm}$ (Greenstein 1938).
- In 1935, based on the correlation between gas concentration and extinction, Bertil Lindblad suggested that **interstellar grains were formed by condensation from the interstellar gas through random accretion of gas atoms**, as speculated by Sir Arthur Eddington (1926) that it was so cold in space that virtually all gaseous atoms and ions which hit a solid particle would freeze down upon it.⁷ However, it was found later that in typical interstellar conditions, the Lindblad condensation theory would result in a complete disappearance of all condensable gases and the grains would grow to sizes ($\sim 10 \mu\text{m}$) well beyond those which could account for the interstellar extinction.
- In 1946, by introducing a grain destruction process caused by grain-grain collisions as a consequence of interstellar cloud encounters, Jan H. Oort and Hendrik C. van de Hulst further developed the interstellar condensation theory and led to the **“dirty ice” model consisting of saturated molecules** such as H_2O , CH_4 , and NH_3 with an equilibrium size distribution which could be roughly approximated by a functional form $dn(a)/da \sim \exp[-5(a/0.5 \mu\text{m})^3]$ and an average size of $\sim 0.15 \mu\text{m}$. What might be the condensation nuclei was unclear at that time.

⁵ The exact nature of the carrier of this bump remains unknown. It is generally believed to be caused by aromatic carbonaceous (graphitic) materials, very likely a cosmic mixture of polycyclic aromatic hydrocarbon (PAH) molecules (Joblin, Léger & Martin 1992; Li & Draine 2001b).

⁶ Very recently, on the basis of the *FUSE* observations of 9 Galactic sightlines at $1050 \text{ \AA} < \lambda < 1200 \text{ \AA}$, Sofia et al. (2005) found that the CCM prediction for short-wavelengths ($\lambda^{-1} > 8 \mu\text{m}^{-1}$) is not valid for all sightlines.

⁷ Van de Hulst (1949) pointed out that this is not the case for H, He and Ne since they will evaporate rapidly at grain temperatures exceeding $\sim 5 \text{ K}$.

- In 1946, van de Hulst by the first time made **realistic estimations of 10–20 K for grain temperatures**. Before that, it was long thought that they had a black-body temperature of ~ 3.2 K (Eddington 1926). Van de Hulst (1946) noted that interstellar grains are much warmer than a 3.2 K black-body because they do not radiate effectively at long wavelengths.

Interstellar Polarization

- In 1949, Hall and Hiltner independently discovered the general **interstellar linear polarization** by incident – their original objective was to look for intrinsic stellar polarization from eclipsing binaries. The interstellar origin of this polarization was indicated by the correlation of the degree of polarization with reddening and the fact that the direction of polarization is generally parallel to the galactic plane. The interstellar polarization was attributed to the **differential extinction of starlight by nonspherical grains aligned to a small degree with respect to the galactic plane**.
- In 1951, Davis & Greenstein suggested that interstellar grains could be aligned with respect to the interstellar magnetic field by the paramagnetic relaxation mechanism.
- The variation of interstellar polarization with wavelength was first revealed by Behr (1959) and Gehrels (1960). It was later shown that the **wavelength dependence of polarization** is well approximated by an empirical formula, often known as the **Serkowski law** (Serkowski 1973; Coyne, Gehrels, & Serkowski 1974; Wilking et al. 1980).⁸ But the near-IR ($1.64 \mu\text{m} < \lambda < 5 \mu\text{m}$) polarization is better approximated by a power law $P(\lambda) \propto \lambda^{-\beta}$, with $\beta \simeq 1.8 \pm 0.2$, independent of λ_{max} (Martin & Whittet 1990, Martin et al. 1992).
- In 1972, the interstellar **circular polarization** which arises from the interstellar birefringence (Martin 1972) as originally predicted by van de Hulst (1957), 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).

From Dirty Ices to Graphite: Interstellar Condensation or Stellar Origin?

- In early 1950s – soon after the discovery of interstellar polarization, the validity of the ice model seemed doubtful since **ice grains are an inefficient polarizer**, and therefore it would be difficult for them to explain the observed rather high degree of polarization relative to extinction (van de Hulst 1950; Spitzer & Tukey 1951; Cayrel & Schatzman 1954).
- In 1954, Cayrel & Schatzman suggested that **graphite grains**, comprising a small component of the total mass of interstellar dust, could account for the observed polarization-to-extinction ratio because of their strong optical anisotropy.
- In 1962, Hoyle & Wickramasinghe proposed that **graphite grains of sizes a few times $0.01 \mu\text{m}$ could condense in the atmospheres of cool N-type carbon stars**, and these grains will subsequently be driven out of the stellar atmospheres and **injected into interstellar space** by the stellar radiation pressure. Hoyle & Wickramasinghe (1962) argued that $\sim 10^4$ N-type stars in the Galaxy may be sufficient to produce the required grain density to account for the observed interstellar extinction. They also showed that the extinction predicted from small graphite grains is in remarkable agreement with the observed reddening law (which was then limited to $\lambda^{-1} < 3 \mu\text{m}^{-1}$). It is interesting to note that the condensation of graphite grains in cool carbon stars was suggested many years earlier by O’Keefe in 1939, while as early as 1933 Wildt had already found that solid grains of carbon, Al_2O_3 , CaO , carbides (SiC , TiC , ZrC), and nitrides (TiN , ZrN) might form in N-type stars.

⁸ The “Serkowski law” $P(\lambda)/P_{\text{max}} = \exp[-K \ln^2(\lambda/\lambda_{\text{max}})]$ is determined by only one parameter: λ_{max} – the wavelength where the maximum polarization P_{max} occurs; the width parameter K is related to λ_{max} through $K \approx 1.66\lambda_{\text{max}} + 0.01$. The peak wavelength λ_{max} is indicative of grain size and correlated with R_V : $R_V \approx (5.6 \pm 0.3)\lambda_{\text{max}}$ (λ_{max} is in micron; see Whittet 2003).

- In 1966, in view of the fact that the albedo of pure graphite grains appear to be too low to be consistent with the observations, Wickramasinghe, Dharmawardhana, & Wyld proposed that interstellar dust consists of graphite cores and ice mantles. Wickramasinghe (1965) argued that graphite grains ejected from stars tend to grow ice mantles in interstellar clouds. Wickramasinghe et al. (1966) showed that graphite grains of radii $\sim 0.05\text{--}0.07\ \mu\text{m}$ coated by an ice mantle up to twice their radii could satisfy the observed interstellar extinction and albedo.
- In 1968, Wickramasinghe & Nandy argued that solid molecular hydrogen mantles may be accreted by interstellar grains in dense interstellar clouds. Wickramasinghe & Krishna Swamy (1969) showed that graphite core-solid H_2 mantle grains with core radii $\sim 0.04\text{--}0.06\ \mu\text{m}$ and mantle radii $\sim 0.15\text{--}0.25\ \mu\text{m}$ are consistent with the observed interstellar extinction in the wavelength range of $0.11\ \mu\text{m} < \lambda < 2\ \mu\text{m}$ and the albedo and phase function derived from the diffuse Galactic light.

Interstellar Silicate Dust of Stellar Origin

- In 1963, Kamijo suggested that nanometer-sized **SiO_2 grains could condense in the atmospheres of cool M-type stars**. After blown out of the stellar atmospheres and **injected into interstellar space**, they could serve as condensation nuclei for the formation of “dirty ices”.
- In 1968, Wickramasinghe & Krishna Swamy considered quartz grains covered with dirty ice mantles and found that their match to the observed extinction curve was unsatisfactory.
- In 1969, Gilman found that **grains around oxygen-rich cool giants are mainly silicates** such as Al_2SiO_5 and Mg_2SiO_4 . Silicates were first detected in emission in M stars (Woolf & Ney 1969; Knacke et al. 1969a).

Interstellar Iron, SiC, and Diamond Grains of Stellar Origin?

- In 1965, Cernuschi, Marsicano, & Kimel argued that **iron grains** could condense out of the expanding **supernova explosion ejecta**. Schalén (1965) explicitly modeled the interstellar extinction curve in the wavelength range of $0.5\ \mu\text{m}^{-1} < \lambda^{-1} < 4.5\ \mu\text{m}^{-1}$ using iron grains of radii $\sim 0.01\ \mu\text{m}$. Hoyle & Wickramasinghe (1970) also argued that a significant fraction of the mass of the heavy elements produced in supernova explosion could condense into solid particles during the expansion phase following explosion. They further suggested that supernovae may constitute a major source of silicate, iron, and graphite grains in the ISM.⁹
- In 1969, Friedemann showed that **silicon carbide grains** could condense in the atmospheres of carbon stars and then leave the star and become an interstellar dust component, although they comprise only a minor fraction of the total interstellar dust mass.¹⁰

⁹ Many years later, the idea of metallic iron grains as an interstellar dust component was reconsidered by Chlewicki & Laureijs (1988) who attributed the $60\ \mu\text{m}$ emission measured by IRAS for the Galactic diffuse ISM to small iron particles with a typical size of $a \approx 70\ \text{\AA}$ (which would obtain an equilibrium temperature of $\sim 53\ \text{K}$ in the diffuse ISM). But their model required almost all cosmic iron to be contained in metallic grains: $\sim 34.5\ \text{ppm}$ (parts per million) relative to H. Exceedingly elongated metallic needles with a length (l) over radius (a) ratio $l/a \approx 10^5$, presumably present in the intergalactic medium, have been suggested by Wright (1982), Hoyle & Wickramasinghe (1988), and Aguirre (2000) as a source of starlight opacity to thermalize starlight to generate the microwave background. Very recently, elongated needle-like metallic grains were suggested by Dwek (2004) as an explanation for the flat $3\text{--}8\ \mu\text{m}$ extinction observed by Lutz et al. (1996) toward the Galactic Center and by Indebetouw et al. (2005) toward the $l=42^\circ$ and 284° lines of sight in the Galactic plane. But these results heavily rely on the optical properties of iron needles (see Li 2003a, 2005b).

¹⁰ Whittet, Duley, & Martin (1990) estimated from the $7.7\text{--}13.5\ \mu\text{m}$ spectra (with a spectral resolution of $\sim 0.23\ \mu\text{m}$) of 10 sightlines toward the Galactic Center the abundance of Si in SiC dust to be no more than $\sim 5\%$ of that in silicates. Since about half of the dust in the ISM is injected by carbon stars in which an appreciable fraction of the stardust is SiC, it is unclear how SiC is converted to gas-phase and recondense to form silicates in the ISM.

- In 1969, Saslaw & Gaustad suggested that carbon may condense in cool stellar atmospheres in the form of **diamond grains** and are subsequently injected into interstellar space.¹¹ Presolar nanodiamonds were first detected in primitive carbonaceous meteorites based on their isotopic anomalies (Lewis et al. 1987; see §5.4 of Li & Draine 2004a and Jones & d’Hendecourt 2004 for more information regarding interstellar nanodiamonds).

Grain Mixtures with Multi-modal Size Distributions

- The extension of the wavelength base for the interstellar extinction observations into the far-UV and IR provide a strong stimulus for the development of dust models. The fact that the extinction continues to increase in the far UV (e.g., see York et al. 1973) implies that **no single grain type with either a single size or a continuous size distribution could account for the observed optical to far-UV interstellar extinction** (Greenberg 1973). This led to the abandonment of any one-component grain models and stimulated the emergence of various kinds of models consisting of multiple dust constituents, including silicate, SiC, iron, iron oxide, graphite, dirty ice, solid H₂, etc.¹² **By early 1970s, the two highly refractory components – silicates and graphite have been considered in most dust models**, supported by the detection of the conspicuous bump in the interstellar extinction curve at 2175 Å and the prominent emission feature at 10 μm of oxygen-rich stars and by the belief that graphite and silicate grains can be produced in stellar atmospheres and expelled into the ISM.
 - In 1969, Hoyle & Wickramasinghe modeled the interstellar extinction in terms of a mixture of **silicate** grains of radii $\sim 0.07 \mu\text{m}$ and **graphite** grains of radii $\sim 0.065 \mu\text{m}$.
 - Wickramasinghe (1970a) found that the interstellar extinction curve in the wavelength range $0.3 < \lambda^{-1} < 9 \mu\text{m}^{-1}$ could be reproduced by a mixture of **graphite** grains with a size distribution of $dn(a)/da \sim \exp[-0.5 \{(a - 0.06)/0.02\}^2]$ for $0.03 \mu\text{m} < a < 0.13 \mu\text{m}$ and **silicate** grains of radii $\sim 0.07 \mu\text{m}$. He also found that **silicate** grains of radii $\sim 0.03 \mu\text{m}$ with an **ice mantle** of radii $\sim 0.14 \mu\text{m}$ together with the same graphite population could fit the observed extinction curve equally well.¹³ By modeling the albedoes and phase functions derived from the diffuse Galactic light, Wickramasinghe (1970b) concluded that the graphite-silicate mixture was preferred over the graphite-(ice-coated) silicate mixture.
 - Wickramasinghe & Nandy (1970) found that a mixture of **silicate, graphite, and iron grains** also achieved a rough fair fit to the interstellar extinction curve at $\lambda^{-1} < 8 \mu\text{m}^{-1}$.
 - Huffman & Stapp (1971) found that **enstatite** grains plus 12% small ($\sim 100 \text{Å}$) **iron oxide** grains also provided a fairly good fit to the extinction curve up to $\lambda^{-1} < 8 \mu\text{m}^{-1}$.
 - Gilra (1971) performed extinction calculations for a mixture of **graphite, silicate, and SiC** and provided close fits to the observed extinction curves. But his model heavily relied on SiC: the required mass of the SiC component was ~ 4 times of that of graphite.

¹¹ Nanodiamonds were identified in the dust disks or envelopes surrounding two Herbig Ae/Be stars HD 97048 and Elias 1 and one post-asymptotic giant branch (AGB) star HR 4049, based on the $3.43 \mu\text{m}$ and $3.53 \mu\text{m}$ C–H stretching emission features expected for surface-hydrogenated nanodiamonds (Guillois, Ledoux, & Reynaud 1999; van Kerckhoven, Tielens, & Waelkens 2002).

¹² The reason why so many different materials with such a wide range of optical properties could be used to explain the observed interstellar extinction was that the number of free parameters defining the size distribution was sufficiently large.

¹³ The reason why Wickramasinghe (1970a) considered ice-coated silicate grains was that he thought that graphite grains of a typical size $\sim 0.06 \mu\text{m}$ would attain an equilibrium temperature of $\sim 40 \text{K}$ in the ISM and would be too warm to possess an ice mantle, while silicate grains would tend to take up lower temperatures because of their lower optical and UV absorptivity and therefore the condensation of ice mantles could occur on their surfaces.

- Greenberg & Stoeckly (1970) found that **ice-coated cylindrical silicate grains** together with a population of **small bare silicate grains** could reproduce the extinction curve from the IR to the UV and the wavelength dependence of polarization.
- In 1974, Greenberg & Hong suggested that interstellar grains consist of **submicron-sized silicate cores surrounded by mantles of heterogeneous molecular and free-radical mixture of O, C, N and H** (“modified dirty ices”), and a minor component of **very small bare grains** of sizes $<100 \text{ \AA}$ whose precise composition was uncertain.
- In a study of the scattering properties of interstellar dust (albedo and phase function) determined from the OAO-2 observations at $1500 \text{ \AA} < \lambda < 4250 \text{ \AA}$ of the diffuse Galactic light (Witt & Lillie 1973), Witt (1973) first explicitly suggested a bi-modal size distribution for interstellar grains: large grains with radii $>2500 \text{ \AA}$ would provide extinction in the visible region including scattering which is strongly forward directed, and small particles with radii $<250 \text{ \AA}$ would dominate the UV region and contribute nearly isotropic scattering.

The Infrared Era: Ices, Silicates, PAHs and Aliphatic Hydrocarbons

- In the 1960s, **the first attempt to search for the $3.1 \mu\text{m}$ feature of H_2O ice in the diffuse ISM was unsuccessful** (Danielson, Woolf, & Gaustad 1965; Knacke, Cudaback, & Gaustad 1969b), although it had long been considered to be a possible constituent of interstellar grains. This was the strongest objection against the dirty-ice model of Oort & van de Hulst (1946).
- In 1973, the $3.1 \mu\text{m}$ H_2O ice feature was finally detected (Gillett & Forrest 1973). But it was recognized that **water ice is present only in dense regions** (usually with $A_V > 3$ mag).
- By early 1970s, **silicates had been detected in the ISM**, first in emission in the Trapezium region of the Orion Nebula (Stein & Gillett 1969), then in absorption toward the Galactic Center (Hackwell, Gehrz, & Woolf 1970), and toward the Becklin-Neugebauer object and Kleinmann-Low Nebula (Gillett & Forrest 1973).
- In 1973, Gillett, Forrest, & Merrill (1973) detected prominent emission features at 8.6 , 11.3 , and $12.7 \mu\text{m}$ in the planetary nebulae NGC 7027 and BD+30°3639. These features together with the 3.3 , 6.2 , and $7.7 \mu\text{m}$ features were collectively known as the “*unidentified infrared*” (**UIR**) **bands**, which are now often attributed to polycyclic aromatic hydrocarbon (PAH) molecules (Duley & Williams 1981; Léger & Puget 1984; Allamandola, Tielens, & Barker 1985; Allamandola, Hudgins, & Sandford 1999).¹⁴
- Willner et al. (1979) detected a strong absorption band at $3.4 \mu\text{m}$ in the Galactic Center toward Sgr A W. Wickramasinghe & Allen (1980) detected this feature in the Galactic Center source IRS 7. 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 (see Pendleton & Allamandola 2002, Pendleton 2004 for recent reviews). 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.

¹⁴ Since the “UIR” emission bands were initially found to be associated with UV-rich objects, it had been thought that they were pumped primarily by UV photons. Li & Draine (2002b) demonstrated that the excitation of PAHs does not require UV photons – since the PAH electronic absorption edge shifts to longer wavelengths upon ionization and/or as the PAH size increases (see Mattioda, Allamandola, & Hudgins 2005 for their recent measurements of the near-IR absorption spectra of PAH ions), therefore long wavelength (red and far-red) photons are also able to heat PAHs to high temperatures so that they emit efficiently at the “UIR” bands (also see Smith, Clayton, & Valencic 2004). Li & Draine (2002b) have modeled 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).

Interstellar Depletion: Where Have All Those Atoms Gone?

- In 1973, Morton et al. found that **the gas-phase abundances of some heavy elements** (relative to hydrogen) measured by the *Copernicus* UV satellite for interstellar clouds are **significantly lower than in the Sun**.
- In 1974, Field noted that **the depletions of certain elements observed by Morton et al. (1973) correlate with the temperatures for dust condensation** in stellar atmospheres or nebulae. He suggested that these elements have condensed into dust grains near stars and other elements have accreted onto such grains in interstellar space after they enter the ISM, forming a mantle composed of H, C, N and O compounds.
- In 1974, Greenberg found that the observed depletion of C, N, and O is significantly greater than could be accommodated by the dust under any reasonable models, using the gas-phase abundances measured by *Copernicus* for the ζ Ophiuchi sightline (Morton et al. 1973) and the solar abundances as the reference abundances.
- Twenty years later, Sofia, Cardelli, & Savage (1994) found that the interstellar depletions are lowered for C, N, and O if B stars are used as the reference standard. They argued that the solar system may have enhanced abundances of many elements, and therefore the solar abundances are not representative of the interstellar abundances.
- Snow & Witt (1996) analyzed the surface abundances of B stars and field F and G stars and found that not only C, N, and O but also Si, Mg, and Fe and many other elements are underabundant in these stars. This led them to suggest that the **interstellar abundances are appreciably subsolar** ($\sim 60\%$ – 70% of the solar values).¹⁵

Dust Luminescence: The “Extended Red Emission”

- In 1980, Schmidt, Cohen, & Margon (1980), detected in the Red Rectangle a far-red continuum emission in excess of what would be expected from simple scattering of starlight by interstellar dust. This continuum emission, known as the “**extended red emission**” (ERE), consists of a broad, featureless emission band between $\sim 5400 \text{ \AA}$ and 9500 \AA , peaking at $6100 < \lambda_p < 8200 \text{ \AA}$, and with a width $600 \text{ \AA} < \text{FWHM} < 1000 \text{ \AA}$.¹⁶ 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 & Vijh 2004 for a recent review).
- 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 unity (Gordon, Witt, & Friedmann 1998). \rightarrow **The ERE carriers are very likely in the nanometer size range** because nanoparticles are expected to luminesce efficiently through the recombination of the electron-hole pair

¹⁵ The most recent estimates of the solar C ($[\text{C}/\text{H}]_{\odot} \approx 245$ ppm; Allende Prieto, Lambert, & Asplund 2002) and O abundances ($[\text{O}/\text{H}]_{\odot} \approx 457$ ppm; Asplund et al. 2004) are also “subsolar”, just $\sim 50\%$ – 70% of the commonly-adopted solar values (e.g. those of Anders & Grevesse 1989) and close to the “subsolar” interstellar abundances originally recommended by Snow & Witt (1996). **If the interstellar abundances are indeed “subsolar”, there might be a lack of raw material to form the dust to account for the interstellar extinction. Mathis (1996) argued that this problem could be solved if interstellar grains have a fluffy, porous structure** since fluffy grains are more effective in absorbing and scattering optical and UV starlight than compact grains (on a per unit mass basis). However, **using the Kramers-Kronig relation, Li (2005a) demonstrated that fluffy dust is not able to overcome the abundance shortage problem.** The abundances of refractory elements in *stellar photospheres* may under-represent the composition of the interstellar material from which stars are formed, resulting either from the possible underestimation of the degree of heavy-element settling in stellar atmospheres, or from the incomplete incorporation of heavy elements in stars during the star formation process.

¹⁶ Very recently, Vijh, Witt, & Gordon (2004) reported the discovery of blue luminescence at $\lambda < 5000 \text{ \AA}$ in the Red Rectangle and identified it as fluorescence by small three- to four-ringed PAH molecules. Nayfeh, Habbal, & Rao (2005) argued that this blue luminescence could be due to hydrogen-terminated crystalline silicon nanoparticles.

created upon absorption of an energetic photon, since in such small systems the excited electron is spatially confined and the radiationless transitions that are facilitated by Auger and defect related recombination are reduced (see Li 2004a).

- **The ERE carrier remains unidentified.** Various candidate materials have been proposed, but most of them appear unable to match the observed ERE spectra and satisfy the high-PL efficiency requirement (Li & Draine 2002a; Li 2004a; Witt & Vijh 2004). Promising candidates include PAHs (d’Hendecourt et al. 1986) and silicon nanoparticles (Ledoux et al. 1998, Witt, Gordon, & Furton 1998, Smith & Witt 2002), but both have their own problems (see Li & Draine 2002a).

Stochastically Heated Ultrasmall Grains or “Platt” Particles

- In 1956, **John R. Platt first suggested that very small grains or large molecules of less than 10 Å in radius** grown by random accretion from the interstellar gas could be responsible for the observed interstellar extinction and polarization. Platt (1956) postulated these “Platt” particles as quantum-mechanical particles containing many ions and free radicals with unfilled electronic energy bands.
- In 1968, Donn further proposed that **PAH-like “Platt particles” may be responsible for the UV interstellar extinction.**
- In 1968, Greenberg first pointed out that very small grains with a heat content smaller than or comparable to the energy of a single stellar photon, cannot be characterized by a steady-state temperature but rather are subject to **substantial temporal fluctuations in temperature.**
- Andriessse (1978) by the first time presented observational evidence for the existence of **“Platt” particles in a dust cloud near M17**, as indicated by its near-invariant 8–20 μm spectral shape over a distance of $\sim 2'$ through the source and by its broad spectral energy distribution characterized by a combination of widely different color temperatures. He found that the the observed IR spectrum of M17 could be explained by a population of large grains and a population of “Platt” particles of $\sim 10 \text{ \AA}$ in size which exhibit temperature fluctuations.
- Sellgren, Werner, & Dinerstein (1983) found that the color temperatures of the 2–5 μm near-IR continuum ($\sim 1000 \text{ K}$) and the spectral shapes of the 3.3 μm emission features of three visual reflection nebulae NGC 7023, 2023, and 2068 show very little variation from source to source and within a given source with distance from the central star. They attributed the near-IR continuum emission to ultrasmall grains of radii $\sim 10 \text{ \AA}$ undergoing large excursions in temperature due to stochastic heating by single stellar photons.
- The presence of a population of ultrasmall grains in the diffuse ISM was explicitly indicated by the 12 μm and 25 μm “cirrus” emission detected by the *Infrared Astronomical Satellite* (IRAS) (Boulanger & Péroult 1988), which is far in excess (by several orders of magnitude) of what would be expected from large grains of 15–25 K in thermal equilibrium with the general interstellar radiation field. Subsequent measurements by the *Diffuse Infrared Background Experiment* (DIRBE) instrument on the *Cosmic Background Explorer* (COBE) satellite confirmed this and detected additional broadband emission at 3.5 μm and 4.9 μm (Arendt et al. 1998). More recently, spectrometers aboard the *Infrared Telescope in Space* (IRTS) (Onaka et al. 1996; Tanaka et al. 1996) and the *Infrared Space Observatory* (ISO) (Mattila et al. 1996) have shown that the diffuse ISM radiates strongly in emission features at 3.3, 6.2, 7.7, 8.6, and 11.3 μm .

Interstellar Grain Models: Modern Era

- The modern era of interstellar grain models probably began in 1977 with the paper by Mathis, Rumpl, & Nordsieck (1977). By fitting the interstellar extinction over the

wavelength range of $0.11 \mu\text{m} < \lambda < 1 \mu\text{m}$, Mathis et al. derived a power-law size distribution of $dn/da \sim a^{-3.5}$ for a mixture of **bare silicate and graphite grains**.¹⁷ With the substantial improvements made by Draine & Lee (1984), this model became one of the standard interstellar grain models with well-characterized chemical composition, size distribution, optical and thermal properties. Modifications to this model were later made by Draine & Anderson (1985), Weiland et al. (1986), Sorrell (1990), Siebenmorgen & Krügel (1992), Rowan-Robinson (1992), Kim, Martin, & Hendry (1994), Dwek et al. (1997), Clayton et al. (2003), and Zubko, Dwek, & Arendt (2003) by including new dust components (e.g., amorphous carbon, carbonaceous organic refractory, and PAHs) and adjusting dust sizes (e.g., deriving dust size distributions using the “Maximum Entropy Method” or the “Method of Regularization” rather than presuming a certain functional form).

Recent developments were made by Draine and his coworkers (Li & Draine 2001b, 2002b,c; Weingartner & Draine 2001a) who have extended the silicate-graphite grain model to explicitly include a PAH component as the small-size end of the carbonaceous grain population. It has been shown that the IR emission spectrum calculated from this model closely matches that observed for the Milky Way (Li & Draine 2001b), the Small Magellanic Cloud (SMC; Li & Draine 2002c), and more recently the ringed Sb galaxy NGC 7331 (Regan et al. 2004; Smith et al. 2004), including the “UIR” emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm .

- In contrast to the bare silicate-graphite model, Greenberg (1978) proposed that interstellar grains could be **coated by a layer of organic refractory material** derived from the photoprocessing of ice mantles acquired in molecular clouds and repeatedly cycled into and out of diffuse and molecular clouds. The organic refractory mantles would provide a shield against destruction of the silicate cores. Since the rate of production of silicate dust in stars is about 10 times slower than the rate of destruction in the ISM (mostly caused by sputtering and grain-grain collisions in interstellar shock waves; Draine & Salpeter 1979a,b, Jones et al. 1994), the silicates would be underabundant if they were not protected and thus it would be hard to explain the observed large depletions of Si, Fe and Mg and the strength of the observed 9.7 μm silicate absorption feature, unless most of the silicate mass was condensed in the ISM as suggested by Draine (1990). The most recent development of this model was that of Li & Greenberg (1997), who modeled the core-mantle grains as finite cylinders (to account for the interstellar polarization). In addition, a PAH component and a population of small graphitic grains are added respectively to account for the far-UV extinction rise plus the “UIR” emission bands and the 2175 Å extinction bump.

Modifications to this model were also made by considering different coating materials (e.g., amorphous carbon, hydrogenated amorphous carbon [HAC]), including new dust type (e.g., iron, small bare silicates), and varying dust size distributions (Chlewicki & Laureijs 1988; Duley, Jones, & Williams 1989; Désert, Boulanger, & Puget 1990; Li & Greenberg 1998; Zubko 1999). In particular, Duley et al. (1989) speculated that the silicate cores are coated with a mantle of HAC material arising from direct accretion of gas-phase elemental carbon on the silicate cores in the diffuse ISM.

- Recognizing that grain shattering due to grain-grain collisions and subsequent reassembly through agglomeration of grain fragments may be important in the ISM, Mathis & Whiffen (1989) proposed that interstellar grains may consist of a **loosely coagulated structure built up from small individual particles of silicates and carbon of various kinds** (amorphous carbon, HAC, and organic refractories). Further developments of this

¹⁷ Such a power-law size distribution is a natural product of shattering following grain-grain collisions (e.g. see Hellyer 1970, Biermann & Harwit 1980, Dorschner 1982, Henning, Dorschner, & Gürtler 1989).

composite model were made by Mathis (1996), Itai et al. (2001, 2004), Saija et al. (2001, 2003), and Zubko, Dwek, & Arendt (2003) (see §2 of Li 2004a for more details).

2. Interstellar Grains, What Do We Know?

Our knowledge of interstellar dust regarding its size, shape and composition is mainly derived from its interaction with electromagnetic radiation: attenuation (absorption and scattering) and polarization of starlight, and emission of IR and far-IR radiation. Presolar grains identified in meteorites and interplanetary dust particles (IDPs) of cometary origin also contain useful information regarding the nature of interstellar grains. The principal observational keys, both direct and indirect, used to constrain the properties of dust were summarized in recent reviews of Draine (2003) and Li (2004b).

- **(1) Grain Sizes.** From the wavelength-dependent interstellar extinction and polarization curves as well as the near, mid and far IR emission, we know that there must exist a distribution of grains sizes, ranging from a few angstroms to a few micrometers.
 - The interstellar extinction curve contains important information regarding the grain sizes since generally speaking, a grain absorbs and scatters light most effectively at wavelengths comparable to its size $\lambda \approx 2\pi a$. The extinction curve rises from the near-IR to the near-UV, with a broad absorption feature at about $\lambda^{-1} \approx 4.6 \mu\text{m}^{-1}$ ($\lambda \approx 2175 \text{ \AA}$), followed by a steep rise into the far-UV $\lambda^{-1} \approx 10 \mu\text{m}^{-1}$. → **There must exist in the ISM a population of large grains with $a > \lambda/2\pi \approx 0.1 \mu\text{m}$ to account for the extinction at visible wavelengths, and a population of ultrasmall grains with $a < \lambda/2\pi \approx 0.016 \mu\text{m}$ to account for the far-UV extinction at $\lambda = 0.1 \mu\text{m}$** (see Li 2004a for details).
 - The interstellar polarization curve rises from the IR, has a maximum somewhere in the optical and then decreases toward the UV. → **There must exist a population of aligned, nonspherical grains with typical sizes of $a \approx \lambda/2\pi \approx 0.1 \mu\text{m}$ responsible for the peak polarization at $\lambda \approx 0.55 \mu\text{m}$.**
 - Interstellar grains absorb starlight in the UV/visible and re-radiate in the IR. The IR emission spectrum of the Milky Way diffuse ISM, estimated using the IRAS 12, 25, 60 and 100 μm broadband photometry, the DIRBE-COBE 2.2, 3.5, 4.9, 12, 25, 60, 100, 140 and 240 μm broadband photometry, and the FIRAS-COBE 110 $\mu\text{m} < \lambda < 3000 \mu\text{m}$ spectrophotometry, is characterized by a modified black-body of $\lambda^{-1.7} B_\lambda(T=19.5 \text{ K})$ peaking at $\sim 130 \mu\text{m}$ in the wavelength range of $80 \mu\text{m} < \lambda < 1000 \mu\text{m}$, and a substantial amount of emission at $\lambda < 60 \mu\text{m}$ which far exceeds what would be expected from dust at $T \approx 20 \text{ K}$. In addition, spectrometers aboard the 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 μm . → **There must exist a population of “cold dust” in the size range of $a > 250 \text{ \AA}$, heated by starlight to equilibrium temperatures of $15 \text{ K} < T < 25 \text{ K}$ and cooled by far-IR emission to produce the emission at $\lambda > 60 \mu\text{m}$ which accounts for $\sim 65\%$ of the total emitted power (see Li & Draine 2001b); there must also exist a population of “warm dust” in the size range of $a < 250 \text{ \AA}$, stochastically heated by single starlight photons to temperatures $T \gg 20 \text{ K}$ and cooled by near- and mid-IR emission to produce the emission at $\lambda < 60 \mu\text{m}$ which accounts for $\sim 35\%$ of the total emitted power (see Li & Draine 2001b; Li 2004a).**
 - The scattering properties of dust grains (albedo and phase function) provide a means of constraining the optical properties of the grains and are therefore indicators of their size and composition. The albedo in the near-IR and optical is quite high (~ 0.6), with a clear dip to ~ 0.4 around the 2175 \AA hump, a rise to ~ 0.8 around $\lambda^{-1} \approx 6.6 \mu\text{m}^{-1}$, and a

drop to ~ 0.3 by $\lambda^{-1} \approx 10 \mu\text{m}^{-1}$; the scattering asymmetry factor almost monotonically rises from ~ 0.6 to ~ 0.8 from $\lambda^{-1} \approx 1 \mu\text{m}^{-1}$ to $\lambda^{-1} \approx 10 \mu\text{m}^{-1}$ (see Gordon 2004). \longrightarrow **An appreciable fraction of the extinction in the near-IR and optical must arise from scattering; the 2175 Å hump is an absorption feature with no scattered component; and ultrasmall grains are predominantly absorptive.**

- The “anomalous” Galactic foreground microwave emission in the 10–100 GHz region (Draine & Lazarian 1998a,b), the photoelectric heating of the diffuse ISM (Bakes & Tielens 1994, Weingartner & Draine 2001b), and (probably) the ERE (Witt & Vijh 2004) also provide direct or indirect proof for the existence of **nanometer-sized grains** in the ISM (see §2 in Li 2004a for details).
- Both **micrometer-sized presolar grains** (such as graphite, SiC, corundum Al_2O_3 , and silicon nitride Si_3N_4) and **nanometer-sized presolar grains** (such as nanodiamonds and titanium carbide nanocrystals)¹⁸ of interstellar origin as indicated by their anomalous isotopic composition have been identified in primitive meteorites (see Clayton & Nittler 2004 for a recent review). Presolar silicate grains have recently been identified in IDPs (Messenger et al. 2003). Submicron-sized GEMS (Glass with Embedded Metals and Sulfides) of presolar origin have also been identified in IDPs and their 8–13 μm absorption spectrum were similar to those observed in interstellar molecular clouds and young stellar objects (see Bradley 2003 for a recent review).
- Very large interstellar grains (with radii $a > 1 \mu\text{m}$) entering the solar system have been detected by the interplanetary spacecraft *Ulysses* and *Galileo* (Grün et al. 1993, 1994). Huge grains of radii of $a \sim 10 \mu\text{m}$ whose interstellar origin was indicated by their hyperbolic velocities have been detected by radar methods (Taylor et al. 1996). But Frisch et al. (1999) and Weingartner & Draine (2001a) argued that the amount of very large grains inferred from these detections were difficult to reconcile with the interstellar extinction and interstellar elemental abundances.
- **(2) Grain Shape.** The detection of interstellar polarization clearly indicates that **some fraction of the interstellar grains must be nonspherical and aligned.** The fact that the wavelength dependence of the interstellar polarization exhibits a steep decrease toward the UV suggests that **the ultrasmall grain component responsible for the far-UV extinction rise is either spherical or not aligned.**
 - The 9.7 and 18 μm silicate absorption features are polarized in some interstellar regions, most of which are featureless.¹⁹ Polarization has also been detected in the 3.1 μm H_2O , 4.67 μm CO and 4.62 μm OCN^- absorption features (e.g. see Chrysostomou et al. 1996). Hough et al. (1996) reported the detection of a weak 3.47 μm polarization feature in the Becklin-Neugebauer object in the OMC-1 Orion dense molecular cloud, attributed to carbonaceous materials with diamond-like structure. \longrightarrow The detection of polarization in both silicate and ice absorption features is consistent with the assumption of a core-mantle grain morphology (e.g. see Lee & Draine 1985).
 - 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

¹⁸ von Helden et al. (2000) proposed that TiC nanocrystals could be responsible for the prominent 21 μm emission feature detected in over a dozen carbon-rich post-AGB stars which remains unidentified since its first detection (Kwok, Volk, & Hrivnak 1989). Based on the Kramers-Kronig relations (Purcell 1969), Li (2003b) found that the TiC proposal is not feasible because it requires at least 50 times more Ti than available.

¹⁹ The only exception is AFGL 2591, a molecular cloud surrounding a young stellar object, which displays a narrow feature at 11.2 μm superimposed on the broad 9.7 μm polarization band, generally attributed to annealed silicates (Aitken et al. 1988). However, its 3.1 μm ice absorption feature is not polarized (Dyck & Lonsdale 1980, Kobayashi et al. 1980).

alignment and/or polarizing ability of the carrier should be very small (see §2.1.2.1 in Li & Greenberg 2003 for details). → The 2175 Å bump carrier is a very inefficient polarizer (i.e. it is either nearly spherical or poorly aligned).

- So far, no polarization has been detected for the DIBs (see Somerville 1996 for a review), the 3.4 μm absorption feature (Adamson et al. 1999),²⁰ and the “UIR” emission bands (Sellgren, Rouan, & Léger 1988). → Their carriers do not align or lack optical anisotropy.

- **(3) Grain Composition.** It is now generally accepted that interstellar grains consist of amorphous silicates and some form of carbonaceous materials; the former is inferred from the 9.7 μm Si–O stretching mode and 18 μm O–Si–O bending mode absorption features in interstellar regions as well as the fact that the cosmically abundant heavy elements such as Si, Fe, Mg are highly depleted; the latter is mainly inferred from the 2175 Å extinction hump (and the ubiquitous 3.4 μm C–H stretching vibrational band) and the fact that silicates alone are not able to provide enough extinction (see Footnote-14 of Li 2004b).

- The 9.7 μm and 18 μm absorption features are ubiquitously seen in a wide range of astrophysical environments. These features are almost certainly due to silicate minerals: they are respectively ascribed to the Si–O stretching and O–Si–O bending modes in some form of silicate material (e.g. olivine $\text{Mg}_{2x}\text{Fe}_{2-2x}\text{SiO}_4$). In the ISM, these features are broad and relatively featureless. → **Interstellar silicates are largely amorphous rather than crystalline.**²¹
- The strength of the 9.7 μm feature is approximately $\Delta\tau_{9.7\mu\text{m}}/A_V \approx 1/18.5$ in the local diffuse ISM. → **Almost all Si atoms have been locked up in silicate dust, if assuming solar abundance for the ISM** (see Footnote-9 of Li 2004b).²²
- The 3.4 μm absorption feature is also ubiquitously seen in the diffuse ISM (but never in dense regions) of the Milky Way and other galaxies (e.g. Seyfert galaxies and ultraluminous infrared galaxies, see Pendleton 2004 for a recent review). This feature is generally attributed to the C–H stretching mode in **aliphatic hydrocarbon dust**, although its exact nature remains uncertain.²³
- In principle, we could estimate the volume ratio of the silicate component to the

²⁰ So far spectropolarimetric measurement of this feature has been performed only for one sightline – the Galactic Center source IRS 7 (Adamson et al. 1999). Unfortunately, no such measurements have been carried out for the 9.7 μm silicate absorption feature of this sightline. Spectropolarimetric measurements for both these two bands of the same sightline would allow a direct test of the silicate core-hydrocarbon mantle interstellar dust model (Li & Greenberg 1997), since this model predicts that the 3.4 μm feature would be polarized if the 9.7 μm feature (for the same sightline) is polarized (Li & Greenberg 2002).

²¹ Li & Draine (2001a) estimated that the amount of $a < 1 \mu\text{m}$ crystalline silicate grains in the diffuse ISM is $< 5\%$ of the solar Si abundance. Kemper, Vriend & Tielens (2004) placed a much tighter upper limit of $\sim 0.2\%$ on the crystalline fraction of the interstellar silicates along the sightline toward the Galactic Center.

²² The silicate absorption feature (relative to the visual extinction) along the path to the Galactic Center is about twice that of the local ISM: $\Delta\tau_{9.7\mu\text{m}}/A_V \approx 1/9$ (Roche & Aitken 1985). It was originally thought that there were very few carbon stars in the central regions of the Galaxy so that one would expect a much larger fraction of the dust to be silicates than is the case further out in the Galactic disk (Roche & Aitken 1985). However, this explanation was challenged by the fact that the 3.4 μm aliphatic hydrocarbon dust absorption feature for the Galactic Center sources (relative to the visual extinction: $\Delta\tau_{3.4\mu\text{m}}/A_V \approx 1/150$) is also about twice that of the local ISM ($\Delta\tau_{3.4\mu\text{m}}/A_V \approx 1/250$; Pendleton et al. 1994; Sandford, Allamandola, & Pendleton 1995).

²³ Over 20 different candidates have been proposed (see Pendleton & Allamandola 2002 for a summary). So far, the experimental spectra of hydrogenated amorphous carbon (HAC; Schnaiter, Henning & Mutschke 1999, Mennella et al. 1999) and the organic refractory residue, synthesized from UV photoprocessing of interstellar ice mixtures (Greenberg et al. 1995), provide the best fit to both the overall feature and the positions and relative strengths of the 3.42 μm, 3.48 μm, and 3.51 μm subfeatures corresponding to symmetric and asymmetric stretches of C–H bonds in CH₂ and CH₃ groups. Pendleton & Allamandola (2002) attributed this feature to hydrocarbons with a mixed aromatic and aliphatic character.

aliphatic hydrocarbon component (1) if we know the band strength of the carrier of the $3.4\ \mu\text{m}$ absorption feature (see Li 2004b), or (2) if we know the total abundances of interstellar elements (see Li 2005a). However, neither is precisely known.

- (4) **Distribution of Dust and its Association with Gas.** Interstellar grains are unevenly distributed but primarily confined to the galactic plane with an effective thickness of ~ 200 pc. On average, the “rate of extinction” (the amount of visual extinction per unit distance) $\langle A_V/L \rangle$ is about $\sim 1.8\ \text{mag kpc}^{-1}$ for the sightlines close to the galactic plane and for distances up to a few kiloparsecs from the Sun (Whittet 2003). Assuming a mean grain size of $\sim 0.1\ \mu\text{m}$ and a typical mass density of $\sim 2.5\ \text{g cm}^{-3}$ for the interstellar grain material, we can estimate the mean dust number density and mass density in the solar neighbourhood ISM respectively to be $n_{\text{dust}} \approx 1.1 \times 10^{-12}\ \text{cm}^{-3}$ and $\rho_{\text{dust}} \approx 1.2 \times 10^{-26}\ \text{g cm}^{-3}$ from the “rate of extinction”.²⁴

The association of interstellar dust and gas had been demonstrated by Bohlin, Savage, & Drake (1978) who found that the color excess and the total hydrogen column density (determined from the observations of HI Lyman- α and H₂ absorption lines with the *Copernicus* satellite) were well correlated: $E(B - V)/N_{\text{H}} \approx 1.7 \times 10^{-22}\ \text{mag cm}^2$ for the diffuse ISM in the solar neighbourhood. This correlation has recently been confirmed by the observations with the *Far Ultraviolet Spectroscopic Explorer* (FUSE) up to $E(B - V) \approx 1.0$ (Rachford et al. 2002),²⁵ suggesting that **the dust and gas are generally well mixed in the ISM**. From this ratio of $E(B - V)$ to N_{H} one can estimate the gas-to-dust mass ratio to be ~ 210 in the diffuse ISM if we take $R_V \approx 3.1$ (see Footnote-2 in Li 2004b); together with the “rate of extinction” $\langle A_V/L \rangle \approx 1.8\ \text{mag kpc}^{-1}$, one can estimate the hydrogen number density to be $n_{\text{H}} = R_V \langle A_V/L \rangle N_{\text{H}}/E(B - V) \approx 1.1\ \text{cm}^{-3}$ and a gas mass density of $\rho_{\text{gas}} \approx 2.6 \times 10^{-24}\ \text{g cm}^{-3}$.

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²⁴ Let interstellar grains be approximated by a single size of a (spherical radius) with a number density of n_d . The visual extinction caused by these grains with a pathlength of L is $A_V = 1.086 \pi a^2 Q_{\text{ext}}(V) n_d L$, where $Q_{\text{ext}}(V)$ is the dust extinction efficiency at V-band ($\lambda = 5500\ \text{\AA}$). The dust number density can be derived from

$$n_{\text{dust}} \approx \frac{\langle A_V/L \rangle}{1.086 \pi a^2 Q_{\text{ext}}(V)} \approx 1.1 \times 10^{-12} \left(\frac{\langle A_V/L \rangle}{1.8\ \text{mag kpc}^{-1}} \right) \left(\frac{1.5}{Q_{\text{ext}}[V]} \right) \left(\frac{0.1\ \mu\text{m}}{a} \right)^2 . \quad (1)$$

The dust mass density is approximately $\rho_{\text{dust}} = n_{\text{dust}} (4/3) \pi a^3 \rho_d \approx 1.2 \times 10^{-16}\ \text{g cm}^{-3}$ if we take $a \approx 0.1\ \mu\text{m}$, $Q_{\text{ext}}(V) = 1.5$, and $\rho_d = 2.5\ \text{g cm}^{-3}$.

²⁵ Dark clouds (e.g. the ρ Oph cloud) seem to have lower $E(B - V)/N_{\text{H}}$ values, suggesting grain growth through coagulation (Jura 1980; Vrba, Coyne, & Tapia 1993; Kim & Martin 1996).

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