Nanoparticles in Space and the Laboratory

Th. Henning

Max Planck Institute for Astronomy, Heidelberg, Germany

H. Mutschke

Astrophysical Institute and University Observatory, Laboratory Astrophysics, Jena, Germany

S. Schlemmer and D. Gerlich

University of Technology, Institute for Physics, Chemnitz, Germany

Abstract

Nanoparticles provide the largest fraction of solid surface in the interstellar medium. They are therefore of great importance as catalytic sites for chemical reactions. The very small grains have unique optical and radiation properties which deviate from those of bulk materials. This paper reviews observational evidence for such particles and summarizes the necessary steps to produce and characterize astronomically relevant materials in the laboratory.

1. Introduction

Small solid grains form an important component of our and other galaxies (Dorschner & Henning 1995). Although they are only a minor contributor to the total mass of these systems, they determine the thermal, dynamical, and chemical state of the cold and dense phases of the interstellar medium, thereby controlling the star formation process in molecular clouds and the mass loss from evolved stars. The coagulation of these particles in circumstellar disks is a first, but decisive step towards the formation of planetesimals.

From a chemical and physical point of view, the interstellar grains are a very interesting system of small and well-isolated particles interacting with radiation, other grains, and gas species at the low temperatures of interstellar space (Henning 1998). Therefore, many bridges to solid-state physics, quantum chemistry, and physical chemistry exist. The detection of novel forms of carbon was triggered by astrophysical studies and the investigation of polycyclic aromatic hydrocarbons (PAHs) got a new impetus from laboratory astrophysics. New computational and experimental methods for the investigation of the interaction of light with irregular, anisotropic, and fluffy grains were developed by astrophysicists.

The Infrared Space Observatory ISO demonstrated that the adequate interpretation of spectroscopic data of dusty objects in the universe requires the measurement of fundamental laboratory data of cosmic dust analogues (d’Hendecourt et al. 1999). The detection of widely distributed crystalline silicates was certainly unexpected and materials such as the Mg-rich end members of olivines and pyroxenes, forsterite and enstatite, were largely unknown to astronomers. The ISO observations and the analysis of “stardust” in meteorites and primitive

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1 Astrophysical Institute and University Observatory, Laboratory Astrophysics, Schillergässchen 3, D-07745 Jena, Germany
materials in interplanetary grains openend the new field of astromineralogy (Henning 2002). Furthermore, the presence of crystalline silicates points to annealing and mixing processes in protoplanetary disks and can be used to trace disk evolution (Bockelée-Morvan et al. 2002). SIRTF, SOFIA, Herschel and finally NGST will deliver infrared data of unprecedented sensitivity, spectral, and spatial resolution which cannot be fully exploited without laboratory data of cosmic dust analogues.

2. The Role of Nanoparticles in Space

The transition from the gas phase to solid dust grains in the interstellar medium results in the formation of solid surfaces. They provide important reaction sites for interstellar chemistry. In order to understand this phase transition, it is important to know how nanoparticles nucleate from the gas phase and grow. The formation of carbonaceous grains in space bears some similarity to soot formation by combustion processes (Frenklach & Feigelson 1997). In contrast, the formation routes of oxide particles under cosmic conditions are practically not understood.

In the interstellar radiation field, nanoparticles (in astrophysics often called “very small grains”), do not have an equilibrium temperature (Draine and Li 2001). They are stochastically heated because the time-averaged vibrational energy is smaller than the energy of the interstellar radiation field. The stochastic heating process leads to transient temperature spikes and infrared excess emission compared with larger grains of lower temperature.

Nanoparticles often have material properties different from those of bulk material. A simple example are metallic nanoparticles where the free mean path of the electrons is limited by the dimension of the grains. Surface structures are often more important for the optical behaviour of nanoparticles as this is the case for bulk materials. In addition, bulk materials with the same structure as the structure of the nanograin may not exist (and vice versa). This is especially important for carbonaceous grains where the concept of graphite nanoparticles makes no sense, but particles with graphitic basic structural units exist.

3. Observational Evidence for Nanoparticles

Direct evidence for the presence of nanoparticles comes from the analysis of primitive meteoritic material, where nanodiamonds have been found (see, e.g., Braatz et al. (2000)). Whether these particles indeed originate in the environment of evolved stars or supernovae or whether they are formed in the solar nebula remains an unsolved problem. Direct spectroscopic evidence for the presence of nanodiamonds in the environment of Herbig Ae/Be stars came from a comparison of ISO spectroscopy and laboratory data (Guillotis et al. 1999).

The first observational proof for the presence of nanoparticles was already obtained by IRAS observations. The observations with this satellite led to the detection of mid-infrared excess emission in the IRAS 12, 25, and 60 µm bands which cannot be attributed to large grains which have typical temperatures of 20 K in the interstellar medium (Boulanger & Pérault 1988). In addition, the far-UV extinction is mainly attributed to scattering by nanoparticles.
On the basis of these observations, a comprehensive dust model for the ISM has been developed which includes very small grains (Desert et al. 1990).

Another line of evidence for the presence of nanoparticles in space comes from the analysis of spectroscopic features. The UV bump at 217.5 nm and the 3.4 μm absorption feature have been attributed to carbonaceous nanoparticles (Schnaiter et al. 1998, 1999), the Extended Red Emission to silicon nanoparticles (Witt et al. 1998; Ledoux et al. 2001), and the 21 μm feature, observed in the spectra of carbon-rich post-AGB stars, to TiC nanograins or clusters (von Helden et al. 2000).

4. Production and Characterization of Nanoparticles

Various techniques have been established to produce nanoparticles from the gas phase, from solid precursors or by sol-gel chemistry. These techniques have to be applied to astronomically relevant materials (see, e.g., Colangeli et al. (2002)). A particularly promising technique is laser pyrolysis which allows the production of size-selected nanoparticles of well-defined composition. Spectroscopy of the nanoparticles can be performed by conventional powder techniques, matrix isolation spectroscopy or with new intensive infrared light sources such as free electron lasers and synchrotron facilities. In addition, the luminescence properties of nanoparticles can be extremely important as it is the case for silicon nanoparticles. In order to reach a deeper understanding of the spectral behaviour of nanoparticles, a comprehensive analytic characterization of their internal structure by high-resolution electron microscopy and other techniques is absolutely necessary. This has been performed in many of the investigations of the Jena group (see, e.g., Jäger et al. (1999)).

5. Particles in Traps

Much of the present information on the role of dust as an active chemical component originates from bulk experiments. For example the interaction of gas phase species with grains is simulated by surface science experiments with macroscopic surfaces (Pironello et al. 1999). For experiments with grains, e.g. extinction measurements, large quantities of dust are necessary to obtain sufficient signal. Therefore most experimental results are congested by size and shape variations or variations in the chemical composition.

In order to overcome this problem and to characterize individual particles, a new approach has been developed in the Chemnitz group which uses the electrodynamical trapping technique. The benefit of the trapping device lies in the combination of the following features: (i) long time trapping of a single particle; (ii) isolation of the particle with respect to disturbing surfaces and gases, i.e., UHV and variable temperature conditions; (iii) very good localization (micrometre range) of the particle. The corresponding density can be as high as 10^{12} cm^{-3}, which makes it perfectly suited for optical experiments, and (iv) non-destructive and high resolution mass determination.
These features are operational in a 3D-quadrupole trap with an optical detection scheme for scattered light. The light signal is modulated by the particle’s secular motion, the frequency of which is proportional to the particle’s Q/M ratio. Frequency determination is achieved by Fourier analysis. A thorough description of the apparatus and first results have been published recently (Schlemmer et al. 2001). Controlled charging/discharging of the particle in steps of single elementary charges leads to the determination of the absolute charge and thus also of the absolute mass. Presently a mass resolution ($\Delta m/m$) of about $10^{-4}$ for a single 500 nm SiO$_2$ particle in a 10 second measurement is routinely obtained. Integration over longer periods of time improve the resolution to the ppm regime.

Due to the long term stability of the rather robust experimental setup, the particle’s Q/M ratio can be followed over weeks and makes the trap an ideal tool for systematic studies of the adsorption and desorption of molecules. As an example the adsorption of C$_{60}$ molecules has been recorded with sub-monolayer resolution. Temperature programmed desorption (TPD) is a standard surface technique in order to determine the binding energies (or sublimation temperatures) of molecules to a surface (Fraser et al. 2001). In the nanoparticle experiment TPD has been utilized by IR-laser heating of the trapped particle (Schlemmer et al. 2002a).

The quadrupole trap for nanoparticles is more than just a scale. Thanks to the non-destructive high-resolution mass and charge determination, processes changing the mass as well as the charge can be monitored online. As a first example of such an experiment, the emission of secondary electrons upon electron bombardment of a 500 nm SiO$_2$ particle has been observed (Schlemmer et al. 2002b). Future experiments make use of the good localization of the particle in the trap. Light scattering experiments on particles and agglomerates are presently performed in the Jena group. The interaction of particles with synchrotron radiation is studied in a new experiment. Light scattering in the VUV and soft X-ray regime from a well characterized trapped particle is one future objective. Fluorescence upon X-ray absorption (EXAFS and NEXAFS) will give information on the chemical and structural composition of the particle. Using short wavelengths Mie-scattering can be extended to much smaller particles and will reveal information on the size, shape and composition of dust particles.

6. Conclusions

The investigation of the spectral features of nanoparticles is a relatively new field in the context of astronomical missions with spectroscopic capabilities. It requires new initiatives to get the necessary fundamental data. An example is the identification of the ERE with silicon nanoparticles. This identification was recently questioned on the basis of the lack of observational evidence for a feature at 20 $\mu$m which would be produced by an oxide mantle around the silicon nanoparticles (Li & Drake 2002). However, the surface of silicon nanoparticles in space is more likely saturated by hydrogen atoms (no oxide feature) or the particles can be embedded in a larger matrix environment (no emission feature because of the lack of transient heating). In addition, it is not clear at all if the emission of the small oxide layer can be treated with
bulk optical properties. Progress in this area can only be reached with additional dedicated measurements.

The investigation of nanoparticles is a major future direction for quadrupole trapping. Production, isolation, trapping, and detection of very small particles is the technical challenge which has to be solved in coming years. One way of producing isolated carbon nanoparticles and measuring their optical emission was described in the pioneering work by Rohlfing (1988).

Acknowledgments

The experimental research is supported by the DFG grant “Research Group Laboratory Astrophysics Chemnitz/Jena”.

REFERENCES


