SUPERCRITICAL FLUIDS AND NANOTECHNOLOGY

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The intersection of nanotechnology with technologies employing supercritical fluids provides an exciting platform to launch novel materials and processes for the specialty chemicals, materials and pharmaceutical industries. Nanotechnology is focused on the ability to manipulate matter at the atomic, molecular and supramolecular levels in order to create novel materials, devices and systems. Supercritical fluids offer tunable solvent properties and desirable transport properties leading to significant improvements in various reactions, separations and processing strategies. The potential for new discoveries and products based on utilizing the synergy between nanotechnology and supercritical fluid technologies is extremely promising.

Definition of Nanotechnology

The emerging fields of nanoscale science and engineering (NSE) focus on building new materials atom-by-atom, molecule-by-molecule by controlling their chemistry, order and structure. The ability to control the synthesis and processing of man-made materials and to understand the complex structure and functions of natural materials have paved the way to discovery of new materials and functions with many exciting applications in a wide range of industries. The recognition of the potential of nanoscale phenomena has generated significant global investments in nanoscale science and engineering.

International Investments in Nanotechnology

The worldwide nanotechnology research and development investments reported by government organizations have increased approximately seven-fold in the last seven years (Figure 1), from $432 million in 1997 to about $3 billion in 2003. 30 countries have initiated national programs covering a very broad net of topics in physical, chemical, biological and engineering sciences (Table 1).

Table1: Nanotechnology R&D expenditures 1997-2004 in $ millions/year. W. Europe includes EU and Switzerland. Others include Australia, Canada, China, Eastern Europe, Israel, Korea, Singapore, Taiwan and all other countries that report R&D in nanotechnology.

Region	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**
W. Europe	126	151	179	200	225	400	650	
Japan	120	135	157	245	465	720	800	
USA	116	190	255	270	465	697	862	960
Other	70	83	96	110	380	550	800	
Total	432	559	687	825	1535	2367	3112	

In the 2001 fiscal year, the United States initiated a multidisciplinary strategy for development of science and engineering fundamentals through the National Nanotechnology Initiative (NNI). This strategy of setting a collaborative model at the national level has received international acceptance. Japan and Western Europe have broadly based programs combining academic and industrial R&D. Other countries have focused on certain areas of strength and potential markets. For example, Korea has allocated funds for nanoelectronics and memory chips. Australian government investments target photonics. Russia and Ukraine concentrate on advanced materials synthesis and processing.

US National Nanotechnology Initiative (NNI)

The US Government's National Nanotechnology Initiative (NNI) has grown significantly in last five years. The National Science Foundation (NSF) is the lead agency in charting the NNI directions and investments. In 2001, the inaugural year, the NNI was funded in six federal departments and independent agencies in US. In 2004, ten federal departments and agencies have requested NNI funds as summarized in Table 2.

Table 2: NNI funding in USA in $millions. NSF-National Science Foundation; NIH-National Institutes of Health; NIST-National Institute of Standards and Technology; NASA-National Aeronautics and Space Administration; EPA-Environmental Protection Agency; DHS-Department of Homeland Security; USDA-Department of Agriculture; DOJ- Department of Justice

US Department/Agency	**2000**	**2001**	**2002**	**2003**	**2004**
NSF	97	150	204	221	254
Dept. of Defense (DOD)	70	125	224	322	315
Dept. of Energy (DOE)	58	88	89	134	203
NIH	32	40	59	78	80
NIST	8	33	77	64	63
NASA	5	22	35	36	37
EPA		6	6	5	5
DHS/TSA			2	1	1
USDA		1.5	0	1	1
DOJ		1.4	1	1	1
Total	270	466.9	697	863	960

Nanoscale Science and Engineering (NSE) Priority Area at NSF

In line with the mission of NSF, the NSE priority area emphasizes long-term fundamental research addressing a set of grand challenges, supports interdisciplinary centers and networks including shared instrumentation facilities, and education and research programs on societal implications of nanotechnology. The principal areas of current NSF funding targets:

Biosystems at the nanoscale
Nanostructured materials with unique physical, chemical, biological, electronic, optical and magnetic properties
Device and system architecture and integration
Environmental processes
Multiscale and multiphenomena modeling
Manufacturing at the nanoscale
Education and societal implications

Development of Supercritical Fluids Technologies

The fascination in the universality of the critical point of pure liquids and model systems was at its peak in the decades of 1960-1980. Scientists in liquid-state physics, physical chemistry and statistical mechanics were interested in critical phenomena of pure and binary systems. The discovery of second-order phase transitions and the development of scaling laws governing thermodynamic and transport properties formed the basis of the renormalization group theory. While the scientists' interests in pure systems continued, in the later decades, 1970-1980, engineers started getting involved with their interests focused on multi-component real systems. Engineering research on thermodynamics of non-ideal mixtures, categorization of the complicated phase behavior of binary systems, and new methods for measuring transport properties at non-ambient conditions were developed. As the fundamental knowledge of the thermodynamics and transport properties of fluids in the vicinity of the critical point grew, scientists and engineers started envisioning many exciting applications of supercritical fluids.

In the last decade of the 20th century, burgeoning applications of supercritical fluids, particularly supercritical carbon dioxide, were proposed based on desirable properties of supercritical fluids. These properties include tunable density or solvent power, high diffusivity and low viscosity while supercritical carbon dioxide is also an environmentally benign and recyclable solvent. Most of the applications capitalize on supercritical solvents as replacement of organic solvents in separations and reactions. In some cases, replacing water with a supercritical fluid might be advantageous if dry steps follow wet steps in a process. In the last ten years, materials synthesis and processing with supercritical fluids have produced many exciting products and have led to the formation new companies.

The Intersection of Nanotechnology and Supercritical Fluid Technologies

The growth of supercritical fluid technologies with focus on materials synthesis and processing coincides with very exciting discoveries of new materials and properties at the nanoscale. The intersection of these two blossoming fields is a fertile ground for innovation. The future challenges will be the synthesis and processing of the new materials with unique properties into useful products with unprecedented attributes. The supercritical fluid technologies can play a significant role in several industrial sectors that are positioned to benefit from advances in nanotechnology.

Chemical Industry: Catalysis is at the heart of chemical industry and is based on understanding nanoscale phenomena. It is possible to envision that the discovery of new catalysts combined with reactor design that utilizes the fast transport processes in supercritical fluids will lead to breakthroughs.

Pharmaceutical Industry: Drug synthesis is predominantly nanoscale science. Supercritical fluids are successfully used in processing of drugs into designed particles and powders.

Electronics Industry: Nanoscale lithography used in the manufacture of electronic devices involves wet and dry processes. Supercritical fluid technologies have tremendous potential for improvements in the transfer from wet to dry or vacuum processing in the electronics fabrication.