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The research applies a new idea, "Objective Structures", to the systematic analysis of large classes of nanostructures. Particular contributions from the research include a new method for non-equilibrium molecular dynamics and it's application to carbon nanotubes under dynamic load; the identification of fundamental invariant manifold in non-equilibrium systems with potential application to characterizing complex fluids; a strategy to compute an entropy function for a nanotube from MD; and an analogy to phonon analysis.

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Program Manager: Dr. Fariba Fahroo, AFOSR Computational Mathematics

PI: Kaushik Dayal[1], Carnegie Mellon University

**Abstract**

This is the final report for Grant Number: FA9550-09-1-0393, managed by Dr. Fariba Fahroo.

# 1 Introduction

There is a remarkable qualitative similarity of the main structures of nanotechnology. This is true of the structures – carbon nanotubes and buckyballs – that originally defined the field. But, during the period of this project, as more complex nanosheets, nanosprings, nanorings, nanoribbons, nanocapsules, and nanorods have emerged, it has become increasingly clear that both their existence and their remarkable properties are a direct result of the defining property of objective structures: that corresponding atoms in each molecule see precisely the same environment up to translation and rotation. Thus we are increasingly convinced that the mathematical theory of objective structures comprises *the quantitative, predictive* approach to nanotechnology.

Through the results of this project, it is also become increasingly clear to us that the essential aspect of Objective Structures is not the "structure" itself. Rather it is about the "invariance" – the fundamental invariance of physical theories. This is the origin of the reason that objective structures form in the first place, often by the process of self-assembly, and also the reason for their remarkable properties. Using this invariance we have been able to describe quantitatively the main instabilities of carbon nanotubes in bending and torsion.

We have also discovered a fundamental invariant manifold in the equations of molecular dynamics. This manifold can be written down explicitly and is independent of the atomic forces. If one chooses initial conditions for the equations of molecular dynamics on this manifold, then the corresponding solution rigorously stays on this manifold. The manifold has the same form for a very simple model of atomic forces like pair-potentials as it does for atomic forces coming from the Hellmann-Feynman theorem based on full Born-Oppenheimer quantum mechanics. The manifold also depends on time in an explicit way. The effect of this is that there are certain overall atomic motions that arise from solutions on this manifold. A major thrust of our work is understanding and exploiting this manifold.

While our project has focused on the development of powerful new computational methods that can apply broadly to problems in nanotechnology, we have tested these methods on problems of significant practical interest. Thus, we have achieved a comprehensive understanding of the

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mechanical behavior and instabilities in carbon nanotubes, under tension, torsion and bending. Some of our predictions in this area have motivated, and have been confirmed by, subsequent experiments. Further experiments are planned, especially in the dynamic regime. We have found an unexpected link to experimental fluid mechanics, and we believe that our predicted flows will have a paradigm changing effect on the measurement of fluid properties.

## 1.1 Summary of goals of the project

1. Dynamic properties and failure modes of nanostructures based on non-equilibrium objective molecular dynamics.
2. Stability and thermodynamics of nanostructures based on objective phonon analysis.

We have made progress on both areas. Unexpected discoveries were made on the thermoelastic properties of carbon nanotubes and also the role of boundary loads in low-dimensional nanostructures, and on applications of our methods to experimental fluid mechanics. This report is a brief summary of the highlights of our research. More details and further developments can be found in the published papers and preprints that will be shortly submitted. Preprints and reprints are available at http://www.ce.cmu.edu/~kdayal/Publications.html.

# 2 Progress

## 2.1 A fundamental invariant manifold in the equations of molecular dynamics

A main discovery of this project is an *invariant manifold* of the equations of molecular dynamics [5]. The discovery is far-reaching, because the manifold can be written down explicitly and it applies to all materials, i.e., it is independent of the atomic forces. A few very special cases were known previously – static periodic boundary conditions and Lees-Edwards boundary conditions for plane Couette flow – but the full manifold is far bigger, richer (lots of free parameters can be varied), and more useful.

What is an invariant manifold? This concept from the theory of dynamical systems refers to a generalized surface in phase space (the space of all positions $\boldsymbol{q} = \boldsymbol{q}_1, \ldots, \boldsymbol{q}_N$ and momenta $\boldsymbol{p} = \boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$) such that, if the initial conditions for the equations of molecular dynamics lie on this manifold, the solution stays on this manifold. Our manifold is slightly different in that, in general, it depends on time. However, the time dependence is also completely explicit, and can be written down independently of the atomic forces. A schematic view is shown in Figure 1. All of the motions and static deformations described in this report, nano and macro, lie on this manifold. These are exact solutions. There are no approximations.

What is particularly compelling for multiscale methods is that *most of experimental solid and fluid mechanics*, with one major caveat described below in Section 2.1.3, *lies on this manifold*. It will therefore play a crucial future role for validation of multiscale methods.

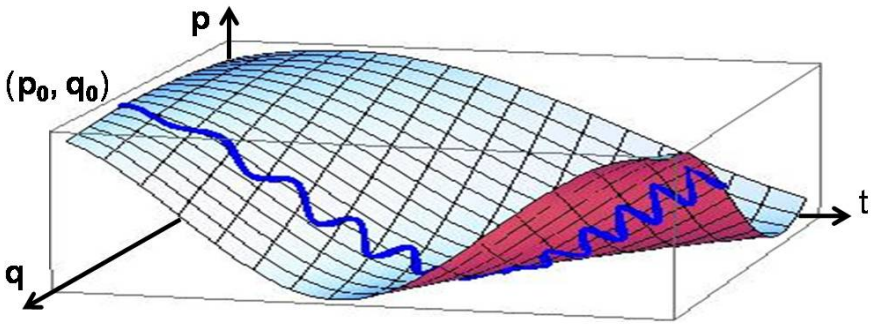


Figure 1: A schematic view of the invariant manifold of Objective Molecular Dynamics.

The reason classical experimental science evolved in such a way as to lie on this manifold goes to the heart of that subject. The main principle underlying experimental mechanics is to design the testing machine without beforehand knowing the response of the material, and still extract meaningful material properties. This principle is intimately related to the fact that the invariant manifold can be explicitly specified, without beforehand knowing the expressions for the atomic forces.

In this section we describe several examples of studies we have conducted of this manifold in the case the time dependence is nontrivial.

### 2.1.1 Failure of carbon nanotubes under dynamic loading

An example of the invariant manifold is the use of a helical group with general time dependence. A physical realization of this case is the pulling of a carbon nanotube to failure at constant macroscopic strain rate. The strain rate can be arbitrarily prescribed. We have noticed [5, 2] quite a few different failure modes.

One main lesson we have learned is about reproducibility. Even restricted to the manifold, there are still infinitely many initial conditions that correspond to a given strain rate and temperature[2]. Generally, we found a lack of reproducibility of, say, strain at failure, by choosing these initial conditions randomly. However, when we ran the dynamical system for a certain period with strain rate equal to zero, until stabilization of the temperature, and then used the stabilized initial conditions (and the measured value of temperature) for subsequent simulations at nonzero strain rate, we obtained remarkable reproducibility. For a given strain rate and temperature determined in this way, the strain at failure varied within $\pm 1/2\%$ of a value, even though this value varied from less than $1/2\%$ to more than $25\%$ with strain rate and initial temperature. Despite the generic complexity of solutions, running the dynamical system for a certain time period seems to have the effect of "preparing" the subsequent initial data, in the spirit of views of O. Penrose [8]. The prepared initial data yields reproducible macroscopic results.

We saw unexpected failure behavior. Whereas conventional wisdom would say that low strain rates and high temperatures would favor ductility, we found (Figure 2 and [5, 2]) a particular

[2]calculated as the mean time-averaged kinetic energy of atoms in the FD, after subtracting the mean motion

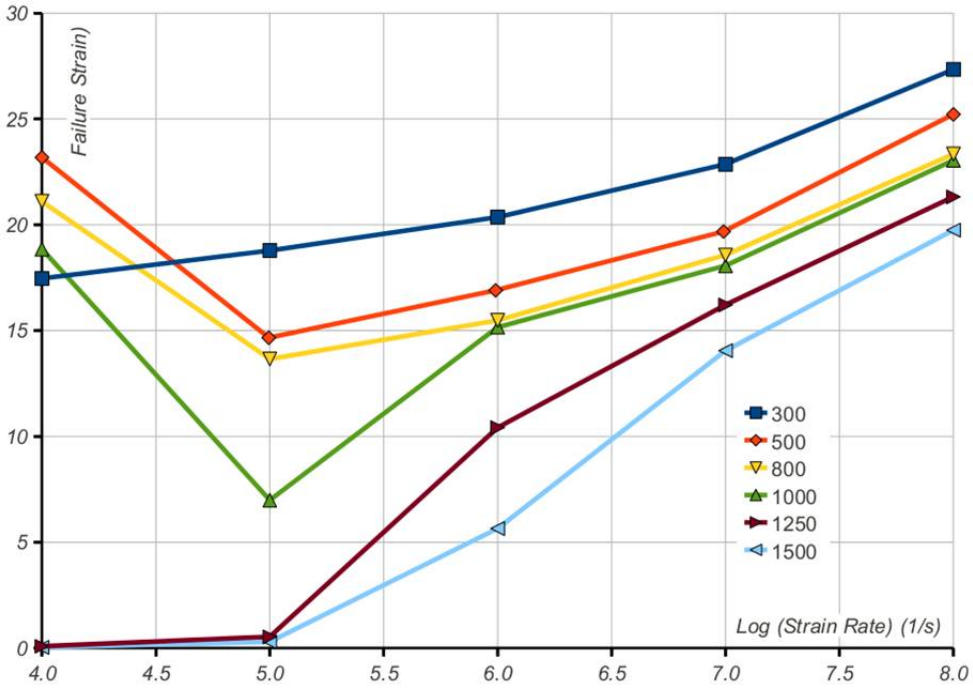


Figure 2: Failure strain as a function of strain rate and temperature measured from simulations.

regime of higher temperatures and lower strain rates where the nanotubes experienced a drastic premature failure, at strains of less than a percent! At still lower strain rates, the strain at failure appears to rise again. This highly non thermally activated failure was accompanied by large amplitude oscillations of the cross-section of the nanotube.

### 2.1.2 The entropy of a carbon nanotube

The temperature slightly decreases with time upon first stretching a carbon nanotube at constant strain rate. Thermodynamically, carbon nanotubes behave more like a crystal than a polymer. When we replot temperature, not vs. time, but vs. the current value of strain, as in Figure 3, we see a remarkable collapse of data: the blue and red curves agree over a large region. This is strong indication that, on the indicated domain of temperature and strain, a nonlinear 1D continuum thermoelasticity theory prevails [2]. From this viewpoint these collapsed curves are naturally interpreted as the level curves of entropy density $\eta(\varepsilon, \theta)$ as a function of strain and temperature. This interpretation is also consistent with the the observed evolution of forces.

The conclusion is striking: even though the carbon nanotube is being pulled a very high rates exceeding $10^6$/sec, it is behaving, *up to a point*, as a dissipationless thermoelastic material. We have used the data of Figure 3, together with a separate calculation of entropy at $\varepsilon = 0$ to fix the free function of temperature, to fully determine the entropy function of a carbon nanotube.

The red and blue curves of Figure 3 depart from each other somewhat before any obvious sign of failure. We are currently using these curves to understand the key problem of how to model dissipation and failure in carbon nanotubes. Understanding failure initiation, i.e., the point where the

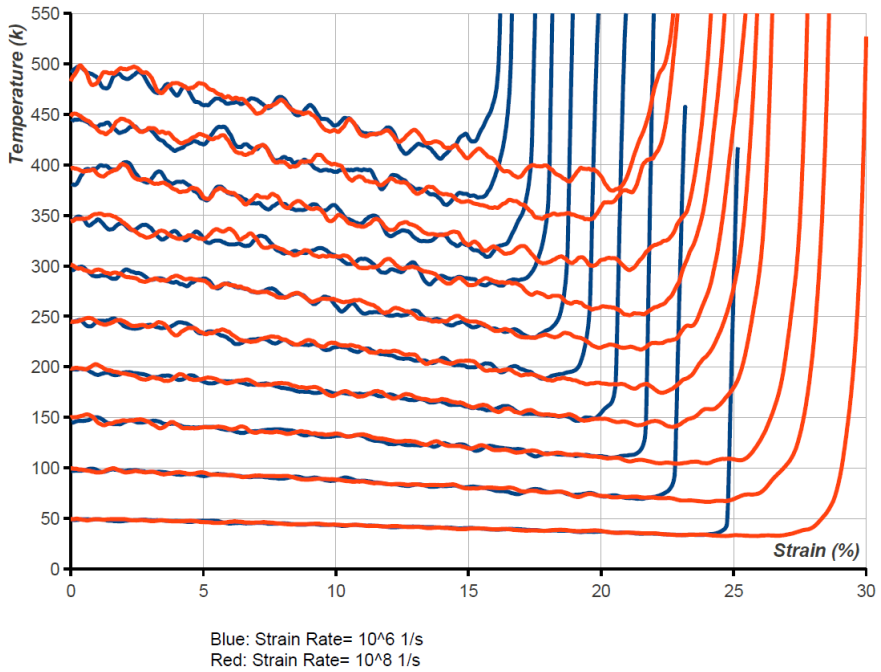


Figure 3: Temperature vs. strain plotted for two different strain rates. Blue: $10^6$ per sec. Red: $10^8$ per sec. Excellent agreement between these results and 1-D nonlinear thermoelasticity occurs in the domain where the curves overlap: in this region the curves shown are level curves of the entropy function $\eta(\varepsilon, \theta)$.

red and blue curves of Figure 3 depart from each other, will enable the use of a simple continuum thermoelasticity theory to be used to simulate up to that point, within a multiscale framework.

### 2.1.3 A new paradigm for experimental fluid mechanics

By the early 1950s it was well appreciated that the Navier-Stokes theory of fluid mechanics did not describe, even qualitatively, many of the features of complex fluids that were playing an increasingly important role in technology, particularly polymer processing. This led to models of "viscoelastic" and other "non-Newtonian" fluids, but also a reassessment of what it means to characterize a complex fluid, beyond its viscosity. On the theoretical side it led to the science of rheology and the theory of viscometry, which in turn led to designs for rheometers and standard procedures for measurement not only of viscosity, but also of normal stress differences.

We have observed that the most basic of these flows, plane Couette flow, lies on our invariant manifold [5, 6]. But we have also seen that other viscometric flows do not. On the other hand we found that there is a large family of flows, those having velocity fields of the form

$$\boldsymbol{v}(\boldsymbol{x}, t) = \boldsymbol{A}(\boldsymbol{I} + t\boldsymbol{A})^{-1}\boldsymbol{x} \tag{2.1}$$

(for any $3 \times 3$ matrix $\boldsymbol{A}$) that *are* on this manifold. This means we have an efficient molecular level simulation method for these flows. Flows of the form (2.1) include compressible as well as

a 3-parameter family of incompressible flows, with diverse physical phenomena such as unsteady motions, vortices and vortex stretching. Complex phenomena such as combustion and other chemical reactions, breakdown of polymers, dissociation and complex thermodynamics such as occurs in high speed flows are all allowed. These phenomena go far beyond what the state-of-the-art in experimental fluid mechanics is able to characterize.

Unlike viscometric flows, the flows (2.1) are exact solutions for every accepted continuum model of fluid flow, Newtonian or non-Newtonian. Together with the explicit statistics of the invariant manifold, our invariant manifold gives new solutions of the Boltzmann equation. It is our contention that these flows should be the basis of a new paradigm of experimental fluid mechanics. We have made a first attempt [6] at designing generalized rheometers based on the flows (2.1).

## 2.2 Objective Phonon Analysis of Nanostructures

Normal modes in periodic crystals, i.e. *phonons*, provide immense information into material properties, e.g. thermal transport, specific heats, etc. In the context of the proposed research, the eigenvalues and the eigenmodes provide information about stability and structural phase transformations [EST06, WR97]. Methods to detect phase transformations in coarse-grained atomic structures have been combined with multiscale methods in crystals [DELT07]. Hence, an OS analogy to phonons enables the study of structural phase transformations in OS using multiscale methods[3]. In our recent work, we have formulated and applied precisely such an analogy [ADE11], and we describe the key aspects here.

Let $\phi(\boldsymbol{x_0}, \ldots, \boldsymbol{x_j}, \ldots, \boldsymbol{x_N})$ be the energy of a configuration $\{\boldsymbol{x_i}\}$ of the OS, with the bold subscript representing a multi-index. The potential energy, whether it comes from quantum mechanics or empirical potentials, has fundamental invariances that are at the heart of the OS framework. In particular, from frame-indifference, consider perturbing atom $\boldsymbol{j}$ by $\boldsymbol{u_j}$ holding all other atoms fixed.

$$\begin{aligned}\phi(\boldsymbol{x_0}, \ldots, \boldsymbol{x_j} + \boldsymbol{u_j}, \ldots, \boldsymbol{x_N}) &= \phi(\boldsymbol{x_{j'}}, \ldots, \boldsymbol{x_0} + g_{\boldsymbol{j}}^{-1}(\boldsymbol{u_j}), \ldots, \boldsymbol{x_{j''}}) \\ &= \phi(\boldsymbol{x_0} + g_{\boldsymbol{j}}^{-1}(\boldsymbol{u_j}), \ldots, \boldsymbol{x_j}, \ldots, \boldsymbol{x_N})\end{aligned} \tag{2.2}$$

The first equality arises from frame-indifference, i.e., the energy is invariant under *any* orthogonal transformations. We choose for the transformation the OS group element $g_{\boldsymbol{j}}^{-1}$ that maps $\boldsymbol{x_j}$ to $\boldsymbol{x_0}$. From the defining properties of a group, the action of $g_{\boldsymbol{j}}^{-1}$ on the other atoms of the OS simply permutes their positions. Hence, the second equality arises by relabelling the atoms. Taking the limit of $\boldsymbol{u_j} \to \boldsymbol{0}$, we find a relation between forces acting on atoms in an atomic OS:

$$\frac{\partial \phi}{\partial \boldsymbol{x_j}} = \boldsymbol{Q_j} \frac{\partial \phi}{\partial \boldsymbol{x_0}}, \quad \frac{\partial^2 \phi}{\partial \boldsymbol{x_k} \partial \boldsymbol{x_j}} = \boldsymbol{Q_j} \frac{\partial^2 \phi}{\partial \boldsymbol{x_0} \partial \boldsymbol{x_{j-k}}} \boldsymbol{Q_j^T} \tag{2.3}$$

where $\boldsymbol{Q_j}$ is the orthogonal tensor associated with $g_{\boldsymbol{j}} = (\boldsymbol{Q_j} | \boldsymbol{c_j})$. The second derivative above comes from repeating this procedure.

[3] In the OS context, a phase transformation corresponds to changes in the structure of the isometry group of the nanostructure.

To compute the normal modes about a reference (stable or unstable) equilibrium configuration, we first linearize the energy. To second order, the change in potential energy when the OS is perturbed by $\boldsymbol{u_i}$ is:

$$\delta\phi = \sum_{\boldsymbol{i}} \frac{\partial \phi}{\partial \boldsymbol{x_i}} \cdot \boldsymbol{u_i} + \frac{1}{2} \sum_{\boldsymbol{i,j}} \boldsymbol{u_i} \cdot \frac{\partial^2 \phi}{\partial \boldsymbol{x_i} \partial \boldsymbol{x_j}} \cdot \boldsymbol{u_j} + O(|\boldsymbol{u}|^3) \ldots \tag{2.4}$$

The first term vanishes at equilibrium.

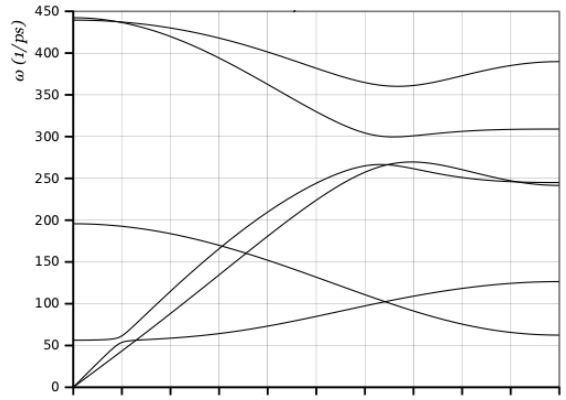


Figure 4: Phonon eigenvalue curves for a carbon nanotube parametrized by wavenumber. Wavenumber components are in the reciprocal space of the corresponding group parameter.

The essential idea in finding the normal modes is to use (2.3b) for the second derivative. In a crystal, (2.3b) holds but with the orthogonal tensors being identity and hence the second derivative is block-circulant. This enables the use of the Bloch/Floquet theorem and a subsequent linear transform to a space in which it is diagonal (or close-to-diagonal if a multilattice). This is equivalent to decoupling the large eigenvalue problem into many smaller individual problems each posed on the unit cell.

For OS, the key idea is to first apply an intermediate similarity transform to "cancel" the orthogonal tensors in (2.3b) and then proceed as in crystals. Specifically, we use the similarity transformation based on

$$\begin{bmatrix} [\boldsymbol{Q_1}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{0}] \\ [\boldsymbol{0}] & [\boldsymbol{Q_2}] & \cdots & [\boldsymbol{0}] \\ \vdots & \vdots & \ddots & \vdots \\ [\boldsymbol{0}] & [\boldsymbol{0}] & \cdots & [\boldsymbol{Q_N}] \end{bmatrix} \tag{2.5}$$

Fig. 4 shows the eigenvalues obtained from such a procedure for a deformed nanotube, and Fig. 5 some of the corresponding normal modes. Many structural transformations, both in crystals and in OS, can be detected and predicted using the phonon spectrum. In particular, a zero eigenvalue indicates a "soft mode" or a deformation mode that costs no energy. Hence, these provide an indicator of the structural transformation. By path-following algorithms and successive linearizations around incremented (unstable) equilibrium states, the structural transformation can be tracked [EST06].

In addition to the insight into structural transformations, the similarity transformation above enables analogies of other wave-nanostructure/crystal interactions. For example, interactions between OS and light waves, electromagnetic waves, and electrons, can provide new analogs of photonics, X-ray diffraction and nanoscale antennas, and electronic bandstructures respectively.

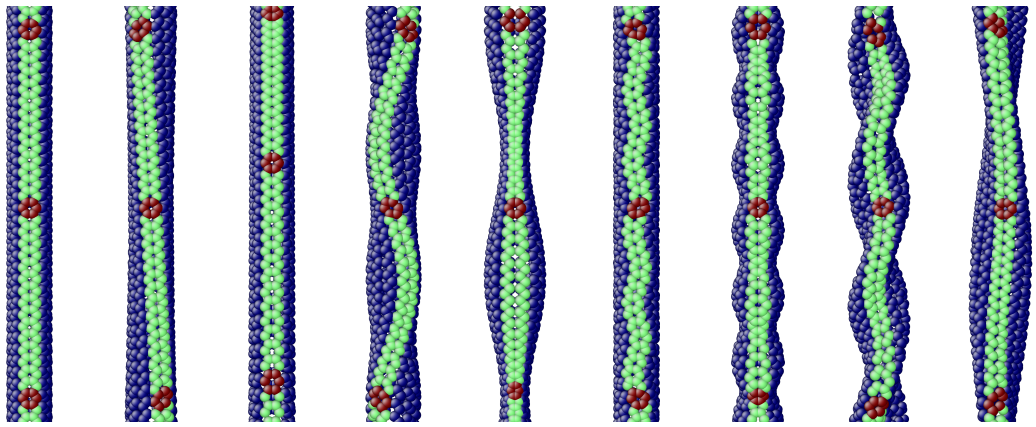

Figure 5: Selected phonon deformation modes of a carbon nanotube. First figure is the reference state. The colors of the atoms have no significance and are only to enable easy visualization.

# 3 Practical implications of our research for Air Force applications

In our dynamic studies of failure at high strain rates we have noticed an unusual regime of premature failure. This has implications for the structural integrity of composites made with carbon nanotubes. This is an active area of research within AFRL, particularly related to the problem of getting the stryength of the composite to benefit from the strength of the nanotube.

Our results have implications for experimental fluid mechanics. We have given a universal method of molecular level simulation that can be used to simulate, with a few atoms, certain large scale flows. This has major potential implications for the Air Force and its contractors. Instead of testing full scale vehicles in elaborate wind tunnel facilities[4] it may be possible to design much simpler, much less expensive, experimental facilities that produce our flows. These can then be used directly to validate an array of computational fluid mechanics and multiscale methods. Of particular interest to the Air Force are flows with chemical reactions (combustion), and high speed flows involving processes like complex thermodynamics, dissociation and excited states.

**References including Dayal as co-author were supported by this project. Preprints and reprints are available at http://www.ce.cmu.edu/~kdayal/Publications.html**

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