SUMMARY AND PROGRESS REPORT
Joint Theory Institute Project
MASTERING DYNAMICS ON THE ENERGY LANDSCAPE
Principal Investigators: R. Stephen Berry, The University of Chicago, and Julius Jellinek, Argonne National Laboratory
22 June 2007

PROJECT DESCRIPTION

The broad objective of this project is relating the dynamics and kinetics of nanoscale particles and atomic and molecular clusters to the interparticle forces between the components and especially to the topographies of the multidimensional energy landscapes of the systems. One of the major questions about such systems is "How is it that some systems find their way to specific, selective structures while others take on random, usually amorphous forms?" Associated with this is the possibility of using knowledge about the dynamics and kinetics of a system to develop control procedures to guide it to a particular structure or morphology. This kind of information will be crucially relevant in such systems as nanoscale alloys intended to be used as catalysts because the catalytic behavior of a nanoscale alloy depends not only on its composition but on its structure. A minority species typically behaves very differently when it is on a surface or corner site than when it is in the interior of a cluster.

The project depends heavily on computation, including simulation of dynamics, kinetics of complex interconnected reactions and exploration and characterization of the topographies of potential energy landscapes. The basic computational tools exist and are familiar to the principal investigators. Several approaches are involved in the project. One is relating the nature, especially the range, of interparticle forces to the degree of structure-seeking or glass-forming character of a system. Another is determining how best to sample the topography of a potential in order to construct a statistical-sample-based master equation whose eigenvalues, especially for slow processes, mirror those of the full system. This, if successful, would be a powerful tool for understanding and eventually controlling the behavior of nanoscale materials. The systems studied in this project include a range from quite realistic representations such as those for metal alloy clusters to idealized models designed to give insights into basic principles, e.g. the model binary system analogous to alkali halides but with interparticle potentials whose ranges can be varied continuously.

PROGRESS REPORT

The announcement of the Joint Theory Institute Award for the project "Mastering Dynamics on the Energy Landscape" was made to the Principal Investigators, R. Stephen Berry and Julius Jellinek, on 5 February 2007. The PIs immediately began a search for candidates for the two postdoctoral openings that this award is intended to support. Announcements were posted in various publications, and a number of applications came, some as a result of the announcement and some, from general inquiries. The search

extended from February until late April. After examining several of the potentially promising applications, the PIs decided in May to make offers to two particularly promising young scientists. One is currently doing postdoctoral research at Brown University in the group of Professor Richard Stratt. This is Dr. Chengju Wang. The other, Jason Green, is completing his doctorate at Purdue University under the direction of Professors Graham Cooks (for experimental work) and Igal Szleifer (for theoretical research). Both have outstanding recommendations and backgrounds that are particularly appropriate for this project. Both have experience with computers and complex computations, and with kinetics of complex systems.

Both Chengju Wang and Jason Green have now made several visits to The University of Chicago and have met and talked extensively with both PIs. Dr. Wang will presumably leave his current position approximately one month earlier than its formal termination, and, assuming his visa application is approved on schedule, will arrive to take on his new position on 1 July 2007. (As of the date of this writing, this approval is moving on schedule.) Likewise, Jason Green will have submitted his doctoral thesis and completed all the requirements for his Ph.D. in Chemistry and will also arrive on 1 or 2 July. Both will have offices in the Gordon Center for Integrative Science, 929 East 57th Street, at the University of Chicago and at Argonne National Laboratory.

Both Wang and Green have taken on well-defined research problems and have been carrying out the background reading and preparation for computation that their projects will entail. Wang is undertaking a study whose goal is finding a scale to characterize the degree to which any given nanoscale system is either a "glass-former" or a "structure-seeker." The two extreme cases have been identified and characterized in a qualitative way, but there is currently no precise or quantitative way to place a system between the limiting cases. At one extreme are systems that, when cooled from the melt or allowed to relax from a random structure, simply "get caught" in some random, amorphous structure. At the other are systems that find their way to rare, specially ordered structures such as crystalline forms or native structures of foldable proteins. Wang has begun work on a model set of systems, binary clusters much like alkali halide clusters such as $(NaCl)_n$, but with a *shielded* Coulomb or Yukawa potential, instead of a classical Born-Mayer Coulomb potential. In this way, he is studying how systems change character as the range of the interaction between particles changes from the infinite range of the Coulomb case, which yields extremely effective structure-seeking character, to the very short range characteristic of glass-formers. He will carry out both molecular dynamics calculations and explorations of the potential energy surfaces. At present, he is learning to use the programs he will be using and probably adapting for his own problem. He will be participating in an international workshop in Colorado in August of 2007, under the auspices of the Telluride Science Research Center, where he will be presenting his first results.

Jason Green's situation begins much as Chengju Wang's. He is already doing the background reading and preparation, and will begin studying dynamics, presumably first of metal alloy clusters, using molecular dynamics and potential surface exploration. His project received a somewhat unexpected enrichment when he was awarded a two-year

fellowship for a collaborative project which formally involves Dr. David Wales of the Chemistry Department, Cambridge University, and R. Stephen Berry, one of the PIs of this project. Of course Julius Jellinek will be very much involved in this collaboration as well. Wales is probably the world's expert on energy landscapes, having published a definitive treatise recently with that title. He had done postdoctoral work with R.S.B. at The University of Chicago and the two have continued to collaborate since the early 1990's. This will enable Green to spend much of 2008-2009 in Cambridge while he continues his work on this project as well as on whatever new studies he begins in the U.K.

An aspect of progress that involves both this project and prior research deals with the construction of statistically-based master equations to describe the kinetics of relaxation of clusters and nanoscale particles. The problem, broadly stated, is this: the amount of information regarding the potential energy landscape of an assembly of, say, 20 or more particles is far too vast to be used. One must find ways to construct small statistical samples of those data from which one can extract useful, important information. The most important is the set of rates of the slow relaxation processes that bring the system to any of its final configurations. We have made considerable progress in learning how to construct such samples for systems large enough to provide the extensive databases one needs to sample, yet still small enough that one can compare results from full data sets with the results from various statistical samples. At least one very promising sampling method emerged. However we have now to test this method on much larger systems; the largest systems treated in the preliminary work consisted of fewer than 15 atoms.

One other aspect of the progress of this project is important to include here. One of us (R.S.B.) received an award from the Dreyfus Foundation for undergraduate research support. Consequently, both Wang and Green will immediately have the opportunity to work with and mentor at least one undergraduate, and perhaps two beginning in the Fall term of 2007. A University of Chicago undergraduate, Kelly Olenyik, has begun research on a topic directly related to those of Wang and Green, specifically examining the behavior and potential energy landscape of certain relatively small clusters such as Ar_{17} that pass freely between liquid and solid forms. She is working at The University and will interact on essentially a daily basis with the two postdoctorals.

PROPOSAL FOR 2007-2009

The next steps of this project will include several components. One will be completion of the first major stage of study now underway of the relationship between the range of the interparticle interaction and the degree of structure-seeking or glass-forming character. This will lead to a second major stage, namely relating the structure-seeking character to the topography of the energy landscape, in terms of such aspects as the asymmetries of the energy barriers separating adjacent local minima of the surface. One further stage will then be open, namely determining the factors that govern passage of systems between large basins on the potential energy landscape. With these three, we

will have a new level of understanding of the behavior of complex systems of tens to millions of atoms or molecules.

A second major component of the study, establishing how to construct model master equations based on statistical samples of the topography of the potential energy surface, will provide a powerful tool to predict the behavior of nanoscale materials at a level currently inaccessible. This will be used, as soon it gets developed, to describe the behavior of catalytic metal alloy clusters.

Related to the second component is a natural step to simulate catalytic reactions of metal alloy nanoparticles. This will apply the findings of Jason Green's work to determine how to design structures that have specific desired catalytic properties. The master equations obtained by the most successful sampling method found until now give us confidence to move to systems too large to treat in their entirety, systems whose master equations are necessarily constructed from statistical samples of the energy landscape structure. The results of this work will enable one to develop sets of master equations for arbitrary temperatures. These in turn can be used, by methods we had developed earlier, to carry out optimal control analyses that allow one to prepare nanoparticles with desired structures by controlling the temperature profile of their passage from liquid to final solid form.

Because Jason Green will be supported for only one year on the JTI project, we will begin looking for another equally-promising postdoctoral associate who would be with this effort for two years.

BUDGETS FOR 2007-2008 AND 2008-2009

	Year 2, 2007-08	Year 3, 2008-09

Items I, II and III to be funds delivered to The University of Chicago; Item IV remains with Argonne National Laboratory. This is based on the distribution of funds in Year 1.

I. Personnel: Two postdoctoral associates,, half time at each institution		
Salaries & benefits	**76,220**	**78,500**
II. Materials and supplies	**3,500**	**4,000**
III. Travel	**4,000**	**4,500**
Total direct costs	**83,720**	**87,000**
IV. Institutional, to Argonne (Including O/H and expendable)	**27,520**	**27,577**
Total (3% increase per year)	**111,240**	**114,577**