Title:

Functional Complexity in Correlated Electron Matter

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Functional Complexity in Correlated Electron Matter

We have now entered an era of "complexity" being accepted as a fundamental theme which we can and must accept, understand and utilize — rather than (usually futiley) attempting to ignore or engineer away. Complexity is not merely "complicated": it has rules and structure which must be encoded in deliberate scientific methodologies. We are driven to this new and exciting situation by a confluence of remarkable advances in observational tools, high-performance computational and visualization tools, and analytical techniques. Together, these advances have forced the recognition of the functional complexity of the natural and engineered world around us; in turn, this recognition demands that we develop new theory and modeling frameworks and tools to understand, to interpret and to guide experiments, and to close the loop between experiment, theory and modeling so as to achieve not only conceptual understanding but robust predictive capabilities.

This theme of intrinsic complexity is evident in almost every traditional discipline – from particle physics to biology to fluids to plasmas to astrophysics. The field of "materials science" has been a clear beneficiary[1], driven by wonderful advances in synthesis characterization, modeling and simulation capabilities, and increasingly stringent demands of technology. The new materials and unexplained states of matter that have been revealed motivate the need for new theoretical concepts and tools which will then drive new eras of materials synthesis. The artificial boundaries between chemistry and solid-state and metallurgy, and between inorganic, organic, and biological are now eroding to define new and practical interdisciplinary fields.

The sub-field of “strongly correlated electronic materials” to which Z. Fisk has contributed so imaginatively has its own history of complexity which now has lead to a current period of fundamental change as it responds to the broader connections to complexity[2]. It is worthwhile tracing some of the origins, where we are now, and where we need to go in our research on strongly correlated electronic materials — most importantly incorporating them into a broader framework of “correlated matter”: electronic and structural; hard, soft and biological.

Some History

Regarding origins, over the last three decades, three themes were especially important to our present recognition of complexity in correlated electronic materials.

1. Organic electronic materials exhibiting low-dimensional broken-symmetry states (charge-density-wave, spin-density-wave, ferromagnetism, superconductivity, etc.) were subjected to extensive applications of prevailing solid state and manybody methodology (experimental and theoretical)[3]. The drive for technology meant that they eventually generated sufficient data and standards of accuracy to reveal the limitations of prevailing practices. In particular, studies of electronic ground, thermodynamic and photoexcited state properties, lead, (slowly) to the acceptance that: the deformability of these “soft” materials was intrinsic to their properties; that spin and charge coupled intimately to this lattice deformability; that this lead to strikingly nonlinear and nonequilibrium effects (from fractional charge, to solitons, to polarons, excitons and breathers); that functionality was embedded in multiple functional scales (from local

"hotspots" to mesoscopic patterns of them); that synthesis controlled the multiscale structures; that device performance could not be understood by traditional, e.g., semiconductor methods[4]. Accepting and using new methodologies enabled the burgeoning period of industrial organic electronic materials which we now enjoy — e.g., polymer-based light-emitting-diode displays, sensors, lasers. We need to accept[2] the same lessons now in inorganic correlated electronic materials, especially with the opportunities of nanoscale, biologically-inspired and hybrid materials before us.

2. Multiscale modeling has been the "holy grail" of materials science for many decades but limited by the scales amenable to observation or modeling. However, the science needed for control of "synthesis-structure-property" relations is precisely that of "microscopic-mesoscopic-macroscopic" relations. Here, the last twenty years of modern nonlinear science has been of great benefit, providing qualitatively new experimental and model equation tools to establish the genericity of many important lessons[1,5]. For example, soliton equations (and their precise quantum equivalent of Bethe-ansatz-solvable models) demonstrate that not all scales are equally functional: microscopic interactions in nonlinear systems result in collective, coherent, mesoscopic structures (solitons) on specific intermediate scales; it is those structures which dominate macroscopic responses. We find the same lesson in non-integrable systems; for example, those supporting topological structures on intermediate scales (dislocations, magnetic vortices, flux lines in superconductors, vortex lines in fluids, etc.); the secondary patterns formed by these primary building blocks determine macroscopic responses, from stress-strain in materials to I-V characteristics in superconductors. At the same time, experiments on fluids, plasmas, granular materials,

etc., have demonstrated the prevalence of coherent mesoscopic patterns, emerging from microscopic interactions and controlling macroscopic responses.

3. Competing interactions were recognized early as the source of much complexity in space and time — from spatio-temporal intermittency to chaos. In solid state and materials science[1] we can trace this to early modeling of competing length scales, e.g. in expitaxy or ANNI (axial-next-nearest-neighbor Ising spin) models. The competitions were found to lead to long-period, superlattice orderings, frustration ("solid state chaos"), spatio-temporal intermittency and glassy responses etc. Some attempts to extend this to charge- and spin-density wave materials followed. A parallel line of research focused on "spin glasses" from the competition of extrinsic disorder and frustration, leading to hierarchial "glassy" phases[7]. We now understand[2] (below) that such competing lengthscale problems do not need to be externally engineered in strongly correlated matter — the interactions among the coupled degrees-of-freedom themselves generate self-consistent nonlinearity and their own "intrinsic (dynamic) disorder", leading to all the phenomena of competing/coexisting ground states, hierarchial patterns and multiscale features, coupled in space and time (glassiness, hysteresis, metastability, intermittency, etc).

Where Are We?

Turning to what have been traditional "strongly correlated electronic materials" — actinides, heavy electron materials, Laves Phase systems, mixed-valence compounds, charge-transfer salts, transition-metal oxides, etc — we can recently observe major changes in philosophy emerging (or at least competing with each other!), driven by the discovery of high-temperature superconductors, colossal magneto-resistance manganites, more modern characterization of organic charge-transfer salts, new generations of heavy-electron superconductors, etc.

The reduction to minimal model Hamiltonians such as Hubbard, Kondo, Double-Exchange, framed many-body intellectual challenges in their own right — and resulted in elegant advances in mathematical physics, field theory, and many body computations, which have their own spin-off benefits. However, the intense experimental scrutiny (across a very broad range of properties and controlled syntheses) and dramatic advances in experimental resolution (HRM, ARPES, STM, XAFS, etc) have clearly established[2] that such models are, at best, too minimal if the aim is to explain either a broad range of properties (electronic ground and excited state; structural; thermodynamic), or fundamental collective states (superconductivity, magnetoresistance, ferroelectricity, etc). However, the massive focus (akin to that in earlier organic electronic materials above, but on a much accelerated timescale) has now provided the elements of the next level of “minimal models” sufficient to capture the intrinsic and functional complexities of classes of correlated materials.

A personal view on lessons learned (shared with the “soft” organic materials above) includes:

1. The strong electronic correlations attributed to d- and f-shell materials leads to narrow electronic bands and localization tendencies, as much research has established. However, this same localization tendency then admits coupling to degrees-of-freedom which might otherwise be ignored — hence the importance of spin-charge-lattice (and

orbital) degrees-of-freedom.[2] For instance, as found in, e.g., single- and multi-band Hubbard[8], Kondo[9], and Double Exchange[26,10] models, even weak electron-lattice coupling results in strong local coupling of spin, charge and lattice. This is the origin of self-trapped "magnetoelastic" polarons, bipolarons and excitons, and important in their secondary assembly[8] into mesoscopic patterns (stripes, clusters, etc).

2. A second consequence of localized d- and f-orbitals is their directionality. Much as covalently bonded materials, this constitutes a source of constraints and potential frustration. One manifestation is the multiple structural "phases" of Pu and related actinides. On closer examination (e.g. with XAFS, PDF and diffuse scattering, HR microscopies) these phases exhibit much substructure on a hierarchy of scales (twinning, tweed, etc) and extremely anomalous elastic, phonon, thermodynamic properties. Similar effects are observed or anticipated in all transition metal oxides[11] (e.g. LTT, LTO phases in cuprates).

3. This "multiscale complexity" can be understood[12] in terms the coupling, in sufficiently complex unit cell materials (including "correlated electronic materials") between intra- and inter-unit cell distortions. In turn (as implied by Zener in 1948[13] this is the microscopic origin of elasticity from coupled zone-center and zone-edge modes. The constraint on unit cell distortions from one unit cell to the next is the symmetry origin of long-range, anisotropic elasticity, as explained in Refs: (12). This long-range field directly leads to statistically predictable hierarchical patterns of lattice distortion — missed in average or periodic experimental or theoretical approaches. These are "intrinsic landscapes" of nearby phases with all the attendant properties — glassy, hysteric, memory, sensitivity to small/local internal or extend fields/impurities. This is in

fact, the origin of large parameter regions of “finescale structure” accompanying solid-solid transformations[14], and in the sub-class of these materials exhibiting “shape memory”.

4. The coexistence of short- and long-range interactions is now found, in many cases, to be responsible for landscapes of energetically nearby mesoscopic patterns — particularly clusters and filamentary “stripes”.[15] This is common to observations in hard (e.g. transition metal oxides), soft (e.g., gels, liquid crystals, block copolymers) and biological (polyelectrolytes, membranes, etc) matter. The long-range forces can appear at mesoscopic scales from the creation of topological textures (e.g. vortices, dislocations) even if microscopic interactions are purely short-range.[16] In “correlated electronic materials”, the short-range forces originate from doping locally destroying broken symmetry (CDW, AF, spin-Peierls, Jahn-Teller) and inducing patches of neighboring metastable symmetries.[8] The discreteness of the lattice is essential. The long-range forces come from Coulomb or, equally importantly, from elastic interactions (above). Although short-range correlated electron models alone (e.g. Hubbard, Dorlde-Exchange) can produce tendencies toward phase separation, this is unlikely to be the realistic source of the skeleton mesoscopic patterns. Rather, these models determine the local structure and excitations aroused around the skeleton filaments. The real-space spin, charge, lattice separation on fine scales accompanying this mesoscopic pattern formation has direct signatures in local excitations in those fields (local “phonons”, “spinwaves”, etc) but also in ARPES, thermodynamic and nonequilibrium (e.g. relaxor glassy) behaviors. These new timescales and local electro-elastic

couplings can be the origin for local pairing, local metallicity, etc, resulting in filamentary superconductivity, magnetism and so forth.[26,8,10]

5. Textured phases, coexisting phases, competing phases and frustrated phases can occur <u>without</u> doping in broken-symmetry materials (i.e. in models of stoichiometric materials). Two major sources are: anistropic coupling — e.g. intra- and inter-chain/plane (organic change-transfer salts are a good example); and competing field strengths, e.g. electron-electron and electron-lattice. In the latter category, phases intermediate between CDW and AF are possible[8,17] (long period insertions of one phase in the other, spin-Peierls, etc. Similarly, adding weak electron-lattice coupling to the periodic Anderson lattice[9] is sufficient to induce lattice disorder without magnetic disorder, which can explain persistent evidence for "disorder" in several "pure" heavy-electron materials. These examples can be mapped to ANNI-like models, or models with coupled wave-vectors, because of effective and competing nearest – and next-nearest neighbor interactions in, e.g., spin, due to the coexistence of the lattice coupling, and multiple bands or orbitals.[8] The ground and metastable phases are not independent of each other and their coupling allows mixed phases to lower energy beyond a pure phase in extended parameter regions, or for local regions of nearby phases to be induced by local perturbations.

In all the cases 4 and 5 above, a common feature is that weak perturbations in one ground state (Af, CDW, spin-Peierls superconductivity, etc) readily induce regions of neighboring metastable phases — perturbations such as dopants, charges (resulting in multicomponent polarons, excitons), interfaces, surfaces, electric or magnetic fields.

Where is The Future?

As we move beyond the examples of intrinsic functional complexity in complex “strongly correlated” electronic materials acquired over the last decade, both experimentally and theoretically, the burden now is to seek organizing principles which can provide interpretative frameworks for experiments and guide new materials searches and designs. This is imperative as we move beyond academic studies of “single crystals “ of inorganic materials to device configurations with thin film, interfaces, and hybrids with other inorganic, organic and biological matter. The coupled deformability (elasticity) and electronic polarizability of all these materials will dominate field-injection, photo-injection, spin charge-transport, coherence and decay. Additionally, as we move to the finite systems of nanoscale science and technology, quantum information, etc. the intrinsic competitions and metastabilities referred to above are even more pronounced, just as in biological macromolecules and cellular structures.

The essential issues for functional inhomogeneity (a.k.a. “multiscale materials modeling”) are: (a) Determining what “microscopic” forces control emergent “mesoscopic” spatio-temporal patterns; (b) Measuring and characterizing the mesoscale patterns controlling (various) “macroscopic” properties; (c) Identifying (hierarchies of) functional scales and how formation is passed between them up to macroscopic scales.

We offer the following observations and speculations:

1. In “traditional” simple materials we have been accustomed to one set of forces determining “ground state” structure and another set controlling function (fluctuations around the ground state). In “soft” matter, be it inorganic, organic or biological, structure determines function, which in turn determines structure in cycles — because multiscale structure is itself determined by delicate force balances (as above) which change (often qualitatively) with function.

2. Complex matter embeds several functional scales — not all scales are functional — coupled together as “engines” (“machines”), much as we can imagine biological systems accomplish. Thus the task of complex materials and of nanoscience is not simply to package more functions on ever-smaller devices, but rather to control how they couple to each other. Unavoidably, this leads to essential nonlinear, nonadiabatic, stochastic (from the influence of slaved scales) and nonequilibrium properties. Multiple length scales determine multiple timescales.

In correlated electron materials, coupling spin, charge and lattice inevitably leads to nonlinear (e.g. nonlinear Schrodinger) effective equations if one field is slaved to another. This is the expression of feedback between fields responsible not only for spatio-temporal complexity, but for polarons, excitons, and multiquantum bound states (“breathers”).[18] However, the multiple lengthscales which result then introduce new timescales which may require nonadiabatic connections to the slaving.

3. The coupling of spin, charge and lattice in correlated electronic materials leads to new classes of “electro-elastic” materials (elasticity coupled to secondary order-parameters — magnetic, electric dipoles, etc), with coupled intrinsic inhomogeneities and functions in electronic and structural degrees-of-freedom. This is the underlying

framework in HTC and CMR perovskites, but can now rationalize older puzzles in ferroelectrics, Laves phase materials, heavy-electron superconductors, organic electronic materials, etc. (From "ghost" modes to relaxor dynamics.) For example, light doping into narrow band transition metal oxides produces "landscapes" of filamentary patterns in elastic textures mediating interactions between the charges, whose patterns (self-consistently) modify the global elastic patterns.[8,15,20]

4. The tunability of soft inorganic, organic and biological matter derives from the deformability of unit cells and large molecules and the constraints on how these elementary building blocks can pack. The <u>local</u> constraints control <u>long</u>-range and <u>directional</u> "polarizability" and "elasticity" fields. This coexistence of short- and long-range fields defines a very broad class of intrinsically inhomogeneous electronic soft matter.[15,16,19] Lattice scale effects are as essential as long-range fields. The tunability is then not only of global (average) phases but also of the hierarchies of multiscale functional textures.

5. Competing interactions and constraints are responsible for landscapes of phases, which can be tuned by varying parameters and conditions (temperature, magnetic fields, pressure, anisotrophy, doping, etc). The landscapes include pure phases, coexistence, frustration; and imply metastability, hysteresis, memory, noise and sensitivity to local/small, internal/external perturbations. A further refinement is that the landscapes may themselves be dynamic, as in, e.g., spatio-temporal intermittency. (This is typical of many relevant nonlinear equations). A particularly intriguing prospect is that patterns may be adopted transiently for a given function (in response to some internal or external stimulus), and then transitioned to another pattern for a subsequent

function. In this way, the same system "engine" can assume a sequence of structures for a series of functional steps. This appears to be a modality in biological matter (e.g. protein or DNA substates[21], or so-called rafts[22] in membranes), efficiently using the same complex system for multiple functions.

6. Perhaps the most important change of philosophy is the need to move beyond the solid state traditions of Bloch states and a linear wave-vector basis. These were themselves radical concepts last century and a magnificent heritage of quantum mechanics. However, the assumption of lattice periodicity, sufficient for simpler materials and average properties, fails for the intrinsically inhomogeneous, multiscale patterns of strongly correlated matter — and cannot be ignored if the functionalities reside in those scales. This is hardly radical in soft polymeric or biological matter, but in solid state means we must revise our operational definition of "single crystal", and apply fresh concepts to notions of, e.g., "quantum critical points" or "non-Fermi-liquid" behavior. Quantum fluctuations can restore translational symmetries in simple models (e.g. periodic lattice or one-polaron bands), but in inhomogeneous environments, multi-polaron situations etc, they can at best induce tunneling between phases and smooth out the lowest barriers. Likewise, electronic structure or manybody computational schemes are incomplete if restricted to periodicity assumptions. The lessons are equally important for experimental probes. Thermodynamic, Fermi surface, crystallography, etc. measurements need to be interpreted carefully and provide incomplete data. New generations of probes at local and mesoscopic scales, and with related scales of time-resolution, are essential. For strongly correlated electron materials, new local probes such as XAFS, neutron PDF, STM are already affective.

Seeking novel elasticity and polarizability signatures and using nonlinear susceptibilities, time-resolved spectroscopies, and noise measurements are directions which need more emphasis. Similarly, correlating high-energy “electronic” and low-energy “lattice” signatures of inhomogeneity are essential.[8] The new concepts we must seek will only be successful if they can explain all these kind of data for spin, charge and lattice degrees-of-freedom, and in a common integrating framework.

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