High temperature cuprate superconductivity: science puzzles and computational challenges

Peter Hirschfeld
U. Florida (Gainesville)

Maui, Jan 2008
The promise of high temperature superconductivity

Future Superconducting Power Generation, Transmission and Distribution Network

Report of DOE workshop May 2006
US:

Energy transported in powerlines per year: $\sim 3 \times 10^{12}$ kWh

Use of high-$T_c$ cables and transformers:

- reduction of transmission and distribution losses: $\sim 6 \times 10^{10}$ kWh / year
- corresponding to savings of: $\sim 1.5 \times 10^{11}$ kWh primary energy
- emissions avoided: 100 000 t $\text{NO}_x$
  200 000 t $\text{SO}_x$
  30 000 000 t $\text{CO}_2$

*R. D. Blaughter, Research and Innovation, Siemens, Vol. 1/98, March 1998*
Progress in applied SC

Generation I high-Tc conductor - in production

GB-engineered Generation II high-Tc coated conductor

Workhorse Nb-Ti low-$T_c$ conductor

Present projects include:

- 100 MVA Generator
- several >100 MVA cables
- 35 MW Ship propulsion motor
- 10 MVA transformer
Possible High $T_c$ Superconductivity in the Ba – La – Cu – O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

History: initial optimism

1987 nobel prize to Bednorz & Müller 1987
Initial optimism: MacGyver c. 1988
“Failure” to achieve technological promise: $T_c$ saturates at $\sim 150K$

Also: materials are brittle
grain boundaries limit critical current
$d$-wave nature gives rise to nonlinear $\mu$-wave response
large thermal fluctuations at higher $T$
“Failure” on theoretical front: no consensual theory of HTS

after 20 years:

- No predictive power for $T_c$ in known materials
- No predictive power for design of new SC materials
- No explanation for pseudogap phase (see later)
- No theory of unusual transport properties
- No controlled solution for proposed effective Hamiltonians
- Only partial consensus on which materials aspects are essential
Cuprate physics

\[ \text{Ba}_2\text{Sr}_2\text{CaCu}_2\text{O}_8 \]

\[ \text{YBa}_2\text{Cu}_3\text{O}_7 \]
Phase Diagram

PG: pseudogap
AF: antiferromagnet
SC: d-wave superconductor

Pseudo-Gap temperature
1. $\delta = 0$

**La$_2$CuO$_4$**

La$^{3+}$
Cu$^{2+}$ --- (3d$^9$) **one hole**  $S = 1/2$
O$^{2-}$

Half-filled band: $n = 1$

**Insulator ---- Band calculation failed !**
1 electron per Cu = 1/2 spin per Cu

**Heisenberg model on 2-Dimensional Square lattice**

$$\mathcal{H}_J = J \sum_{\langle i,j \rangle} S_i \cdot S_j,$$

$0.5 \mu_B$ per Cu

$J = 0.13 - 0.14$ eV  
for LSCO

$J = 0.130$ eV  
for Sr$_2$CuO$_2$Cl$_2$

$J = 0.125$ eV  
for BSCCO

$J = 0.10 - 0.110$ eV  
for YBCO,
**Hubbard model**

\[ H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow} \quad (U \geq 0) \]

\[ U = 10 \text{ eV} = 10,000 \text{ K} \]

No double occupancy for \( T < 300 \text{ K} \)

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \quad \text{Cu Cu Cu} \]

can not move = Mott insulator
We need effective theories at low \( T \).

But virtual states are allowed in Quantum Mechanics

\[ \uparrow \downarrow \quad E = 0 \quad t \]
\[ \uparrow \downarrow \quad E = U \quad t \]
\[ \downarrow \uparrow \quad E = 0 \quad t \]

Virtual state (second-order perturbation)

\[ \frac{2t^2}{U} S_i^- S_j^+ \quad \frac{4t^2}{U} S_i \cdot S_j \]

Super-exchange mechanism (Anderson)

Double occupancy occurs only in virtual states

\[ U < U_c \quad \text{many double occupancies (Mott transition at } U_c) \]
2. Hole doping $\delta > 0$

large U limit of Hubbard at $d>0$: t-J model

$$H_{t-J} = \sum_{\langle i,j \rangle} \tilde{c}^+_i \tilde{c}_j + h.c. + J \sum_{\langle i,j \rangle} S_i \cdot S_j$$

But:

Oxygen site doping

U_d

$\Delta$

(hole representation)

Oxygen sites should be considered.

d-p model (Emery)

Planar cuprate
3-band Hubbard or d-p model

\[ H_{\text{dp}} = -t_{dp} \sum (d_{i\sigma}^\dagger p_{j\sigma} + \text{h.c.}) - t_p \sum (p_{j\sigma}^\dagger p_{j'\sigma} + \text{h.c.}) + t_p' \sum_{\langle jj' \rangle} (p_{j\sigma}^\dagger p_{j'\sigma} + \text{h.c.}) + \Delta \sum_{j\sigma} n_{p,j\sigma} + U_d \sum_{i} n_{d,i\uparrow} n_{d,i\downarrow} + U_p \sum_{j} n_{p,j\uparrow} n_{p,j\downarrow} + V \sum_{\{i,j\}} n_{d,i} n_{p,j}, \]

\[ t_{dp} = 1.3 \text{ eV} \] (1.5 eV)
\[ t_p = 0.65 \text{ eV} \] (0.6 eV)
\[ \Delta = 3.6 \text{ eV} \] (3.5 eV)
\[ U_d = 10.5 \text{ eV} \] (9.4 eV)
\[ U_p = 4 \text{ eV} \] (4.7 eV)
\[ V = 1.5 \text{ eV} \] (0.8 eV).


-- reduces to t-J model in realistic limit!
Remarks:

NB: These are all models of CuO$_2$ plane only!
1-layer cuprate materials have wildly different Tc’s
(Bi-2201 Tc=10K, Tl-2201 Tc=90K). Some out-of-plane physics is essential to understand!

20 years: great progress in understanding Hubbard model, 3-band model, t-J model—numerical methods:

1) QMC
2) DMFT, CDMFT
3) DMRG

But: do we even know if the model has a superconducting ground state? Not for sure. Pair susceptibilities imply strong superconducting tendency.

If we knew this, would we have solved HTS? What does it mean to solve the problem?
Solving hard problems in condensed matter physics

Schrödinger eqn. for $10^{23} \; e^-, N$ with Coulomb forces

(normal metal) \hspace{1cm} \checkmark \hspace{1cm} \downarrow \hspace{1cm} \downarrow \hspace{1cm} \text{(cuprate)}

\[
H = H_{el}^0 + H_{el-ph} + H_{Coul} \hspace{1cm} \rightarrow \hspace{1cm} \downarrow \hspace{1cm} \downarrow \hspace{1cm} H = H_{el}^0 + H_{el-ph} + H_{Coul} + H_{2DH_{Hubbard}}(?) + \text{interlayer}(?) + \text{screening}(?) + \text{phonons} (?) \hspace{1cm} \downarrow \hspace{1cm} ? \hspace{1cm} \downarrow
\]

\[
H = H_0 + V\psi^\dagger\psi^\dagger\psi\psi \; (\text{Fermi liquid}) \hspace{1cm} \downarrow \hspace{1cm} \downarrow \hspace{1cm} H = H_0 - \Delta^*\psi\psi - h.c. \; (\text{BCS}) \hspace{1cm} \downarrow \hspace{1cm} H = H_{BCS-d} + \text{pseudogap} + ?
\]
Reminder: superfluid $^3$He

- Well-defined Fermi liquid with $T_F \simeq 1K$

- Landau parameters $F_{\ell}^{s,a}$ known from experiment

- $p$-wave, spin triplet superfluid below $T_c(p) \simeq 1-3mK$.

- Subdominant pair component ($f$-wave) known from quantitative fits to BCS WC+ theory.
Theory of superfluid $^3$He

But:

- no controlled microscopic calculation of $F^{s,a}_\ell$

- no consensus on microscopic pair interaction: spin vs. density fluctuations

**Q:** Why do we think we understand $^3$He?

- Phenomenology of disordered phase (Landau thy)

- Phenomenological theory *within* each low temperature phase

Anderson Brinkman 1973

Rainer Serene 1976

- Qualitative understanding of each phase transition.
Q: By *this standard*, have we solved HTS?

- SC phase symmetry understood
  phenomenology available (BCS)
- AF phase symmetry understood,
  quantitative calculations possible
- (claim) spin glass phase understood
  as disorder-induced magnetic correlations
  (stripes at special fillings)
- nature of pseudogap, strange metal unknown, many proposals

A: not quite, but close!

But: to make materials-specific predictions, to aid discovery or
engineering of new, higher $T_c$ compounds, we need a higher standard!
Avenues to further progress

• Understanding origin of pairing in Hubbard, \( t/J \) type effective models

• Adding correlations to DFT

• “Bridges” between ab initio and model calculations

• New paradigms to study and engineer pairing interaction: spatial inhomogeneities

All will require petascale computing power!
Pairing in Hubbard-type models

Maier, Jarrell, & Scalapino 2006 et seq.

Dynamic cluster QMC calculations

Strong tendency to pair in $d_{x^2-y^2}$ channel!
Inclusion of correlations in Density Functional Theory

- **LDA** = local density approximation
- **GGA** = generalized gradient approximation
  - Include the density gradient for the higher order correction
  - Preserving the sum rule for the exchange-correlation hole
- **GW** = Green's function + screened interaction potential
  - Self-energy correction by
    \[ \Sigma(r, r'; \omega) \approx G(r, r'; \omega) \epsilon^{-1}(r, r'; \omega)V_{\omega}(r, r') \]
- **LDA+U**
  - Unrestricted Hartree-Fock treatments for the localized orbital states

Eschrig et al 2003  LDA+U  Sr$_2$CuO$_2$Cl$_2$
**“Bridges” between ‘DFT+’ and effective models**

Pavarini et al 2001 – 1) calculate spaghetti:

2) then “downfold” onto effective model with small set of orbitals

3) show how model parameters depend on atomic positions…

4) …which are linked to macroscopic observables ($T_c$!)

---

**La$_2$CuO$_4$**  
**Tl$_2$Ba$_2$CuO$_6$**

![Energy diagrams](image)
Combining “downfolding’ and strong correlations

Kent et al 2008: try to use downfolded band structure for different materials to obtain systematics of $T_c$ within 3-band Hubbard model.

**FIG. 2:** (Color online) Calculated in-layer hoppings for five single-layer cuprates with different $T_c^{\text{max}}$. 
Combining ‘DFT+’ with experiments

- Measure correlations of pairing with spatial perturbations
- Determine actual atomic displacements
- Figure out how to make a higher temperature superconductor
Nanoscale Inhomogeneity in BSCCO-2212

Spectral gap in LDOS varies by factor of 2-3 over distances 20-30 Å

A.A.A. : “can you please make the resolution less?”
Out-of-plane defects, e.g. interstitial oxygen

-960mV peak with 300meV FWHM

K. McElroy et al. Science 05
Relation: spectra ↔ oxygen dopants

Fantastic possibility to correlate dopants and energy gap!

K. McElroy et al., 2005

\[ C_{fg}(j) = \frac{1}{N} \sum_i \frac{\langle \delta f(i) \delta g(i+j) \rangle}{\sqrt{\langle \delta f \rangle \langle \delta g \rangle}} \]

Oxygen ↔ gap positively correlated
contradicts local doping picture

Charge modulations almost disappear when integrated up to -900meV
Simple disorder model(s)

Mean field Hamiltonian for inhomogeneous d-wave superconductor (BdG):

\[
H = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_{i\sigma} V_i c_{i\sigma}^+ c_{i\sigma} + \sum_{\langle ij \rangle} (\Delta_{ij} c_{i\uparrow}^+ c_{j\downarrow} + H.c.)
\]

with:

\[
\varepsilon_k = -2t \left( \cos k_x + \cos k_y \right) - 4t' \cos k_x \cos k_y - \mu \quad t' = -0.3t, \quad \mu = -1.0t
\]

(d-wave ground state \(\Delta_k \sim \cos k_x - \cos k_y\) in homogeneous case)

Self-consistency condition for order parameter:

\[
\Delta_{ij} = g_{ij} \left\langle c_{i\uparrow} c_{j\downarrow} - c_{i\downarrow} c_{j\uparrow} \right\rangle
\]

Allow for dopant-modulated coupling constant:
How could O-dopants modulate pair interaction?

Previous works on spatial modulations of pair interactions by impurities, grain boundaries, …:

H. Suhl et al 1962
A.I. Larkin 1970
Weinkauf Zittartz 1975
I. N. Khlyustikov and A. I. Buzdin 1987

(modulation of e-ph couplings by impurities or interfaces)

For HTS, maybe similar, or possibly:

atomic-scale modulation of local electronic structure which affects pairing via exchange of electronic excitation

Atomic scale pairing disorder

- Homogeneous low-energy Ldos
- Positive correlation: dopants $\leftrightarrow$ gap magnitude
- Anti-correlation: “coherence” peak height $\leftrightarrow$ gap magnitude
- Small charge modulations

Results:

McElroy et al 2005

Theory: Nunner et al 2005

Note small scale

$\approx 430\text{Å}$
Can STM tell us about *local causes* of pairing?

Logic:

- O dopants enhance pairing *locally* around themselves
- Find out what O dopants do to local electronic structure
- See how these changes affect models of pair interaction

Part of more general program:

Systematic investigation of *local* perturbations which correlate positively with superconducting gap: constrain pair theories

**Grand challenge for theory:** give up old prejudice that atomic scale information is irrelevant for superconductivity
DFT calculations of O interstitials: structure

Calculations performed by Y. He and H-P Cheng, U. Florida

DFT good for calculations of high-energy (impurity) states, structure

<table>
<thead>
<tr>
<th>#</th>
<th>Location (Å)</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.09,1.09,-0.83</td>
<td>-6.560172</td>
</tr>
<tr>
<td>2</td>
<td>2.11,0.00,-0.38</td>
<td>-3.914803</td>
</tr>
<tr>
<td>3</td>
<td>2.59,0.00,-0.38</td>
<td>4.378865</td>
</tr>
<tr>
<td>4</td>
<td>2.59,0.00,-4.81</td>
<td>14.968390</td>
</tr>
</tbody>
</table>

Stable positions of O interstitial, energies relative to crystal w/o interstitial
Interstitial creates unhybridized O 2p\textsubscript{z} state at -1eV
BSCCO “supermodulation” also correlates with gap (pairing?)

Bi-2212 topograph (Davis group)

BSCCO-2212 supermodulation correlates with gap (Slezak et al 07)
DFT calculations of supermod structure agree with x-ray data!

He et al arXiv:0709.0662

same displacement of apical oxygen sideways as in O defect case correlates positively with gap!
Combining “DFT+” and calculations of critical current to solve grain boundary problem?


\[ J_c(\theta) = J_0 \exp\left(-\frac{\theta}{\theta_0}\right) \]

Conclusion - strong texture is needed!
Approach in PH group: 1) reconstruct CuO$_2$ plane using MD simulation (à la Zhang and Catlow 1992)

Molecular dynamics approach

Final structures
2) Calculate hoppings in grain boundary via overlap of Cu 3d and O2p orbitals, include charging of defects
3) Use hopping and electrostatic potentials thus determined in Bogoliubov-de Gennes calculation of critical current $J_c(\theta)$ including d-wave order parameter and Hubbard $U$.

110 junction with magnetic correlations in leads (Andersen et al 2008)

Next: DFT+ calculations of grain boundaries?
Conclusions

higher standard needed to make materials-specific predictions, to aid discovery or engineering of new, higher $T_c$ compounds

• Most important theory and simulation problems remaining in HTS physics/materials science will require large-scale computers from here on

• Progress is being made in:
  - refining of electronic structure methods towards true ab initio method to study correlated systems (LDA+U, GW, CDMFT…)
  - calculating pairing interactions accurately within effective models
  - downfolding electronic structure to determine parameters of effective models
  - understanding and using data on inhomogeneity to study pairing