



Compton Profile of Solid and Liquid Lithium from Quantum Monte Carlo

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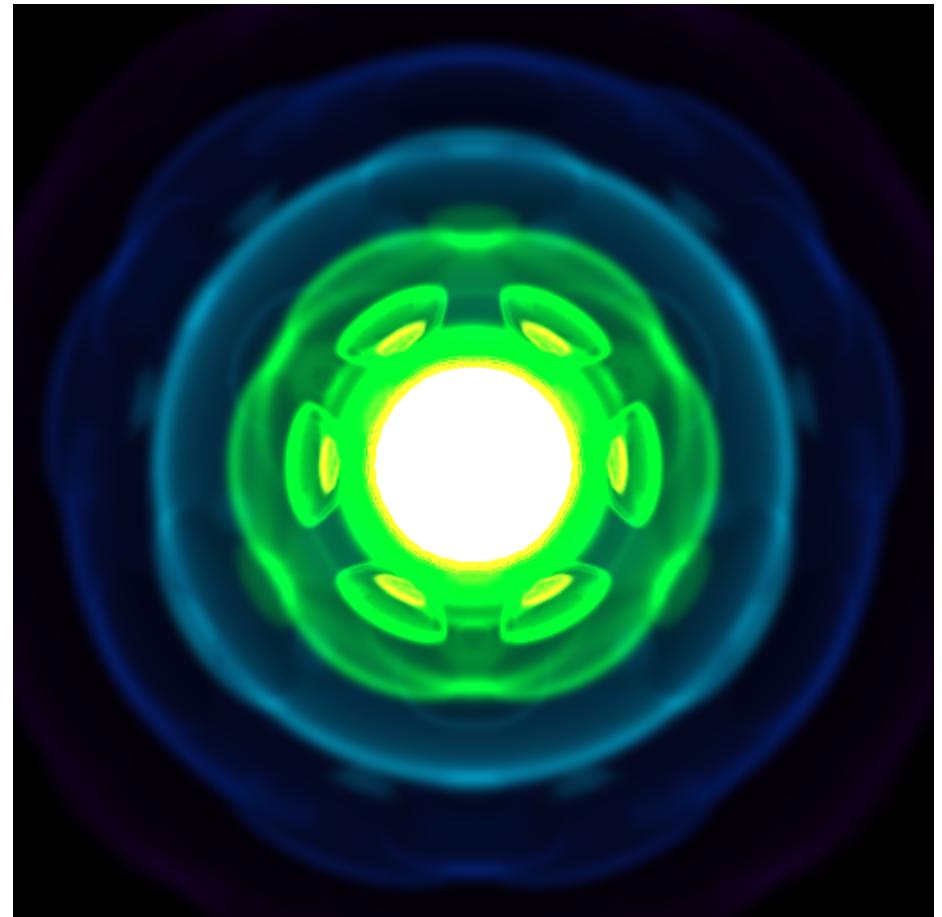
Collaborators:

Kazuhiro Matsuda, Kyoto University, Japan

Nozomu Hiraoka, NSRRC, Taiwan



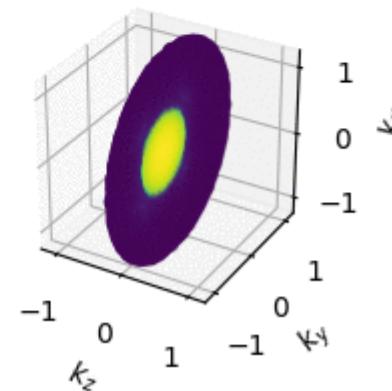
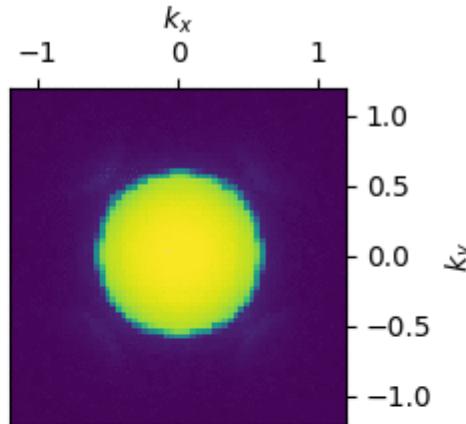
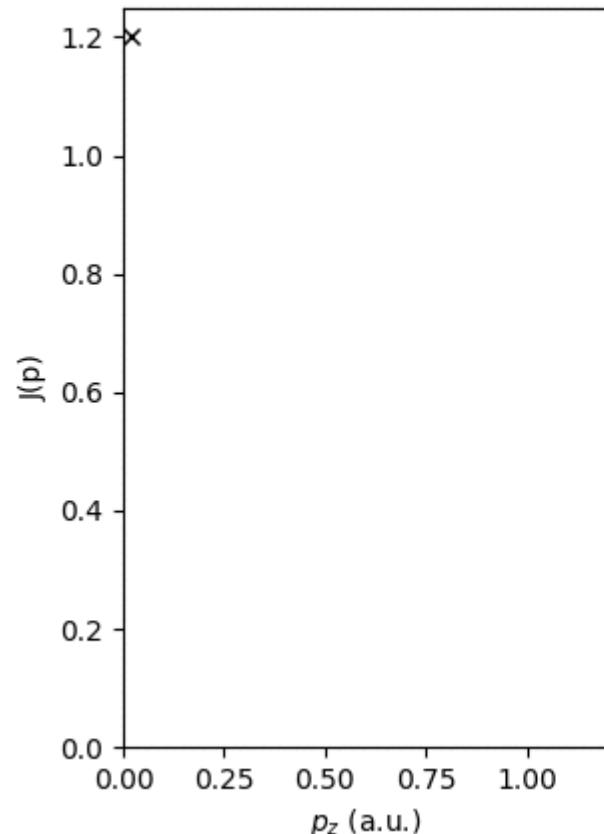
QMCPACK



What is the Compton profile?

The Compton profile is the radon transform of the electronic momentum distribution along the scattering vector p_z

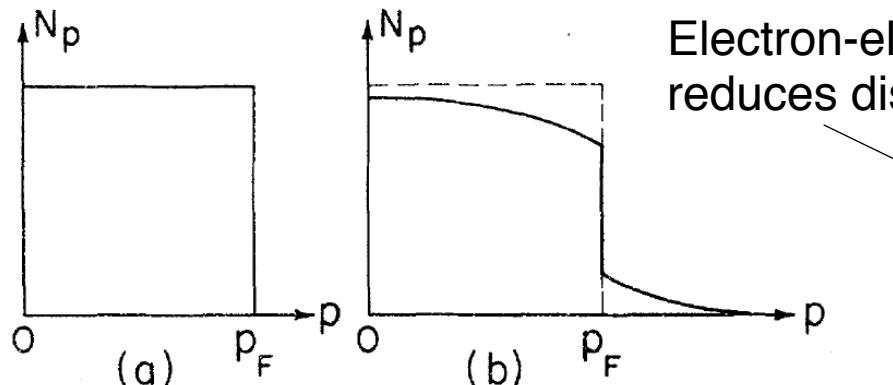
$$J(p_z) = \iint dk_x dk_y n(k_x, k_y, k_z = p_z)$$



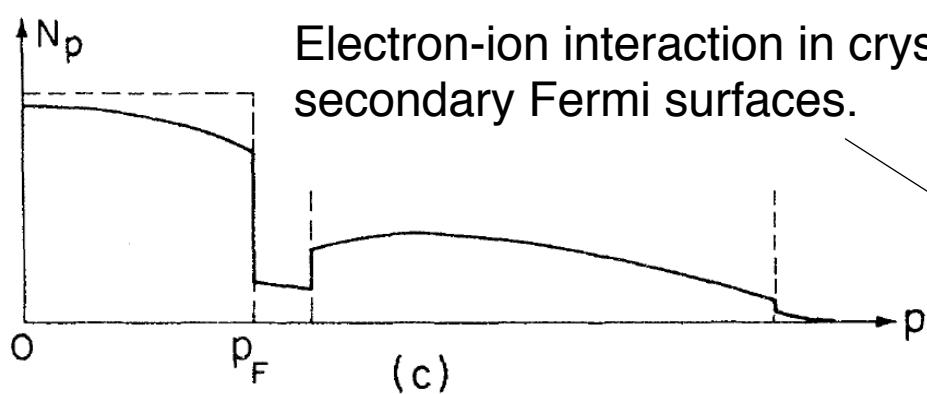
Why study the Compton profile? A measurable signature of exchange and interaction.

Exchange results in jump at p_F for metal

cusp in the Compton profile at p_F



Electron-electron interaction reduces discontinuity.



Electron-ion interaction in crystal introduces secondary Fermi surfaces.

$$J(p_z) = \iint dk_x dk_y n(k_x, k_y, k_z = p_z)$$

Take-home message:

$n(\mathbf{k})$ is a many-body observable, which contains signatures of:

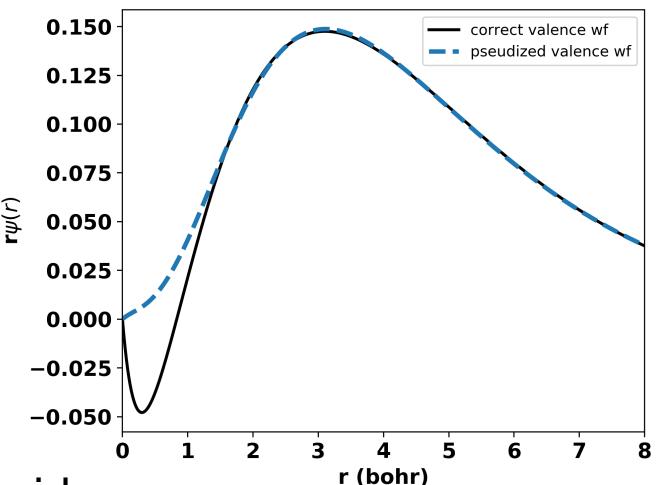
- Fermionic exchange
- Electron-electron interaction
- Electron-ion interaction

J(p) bridge expt. and sim.

Method: How to accurately calculate the momentum distribution $n(\mathbf{k})$ in QMC?

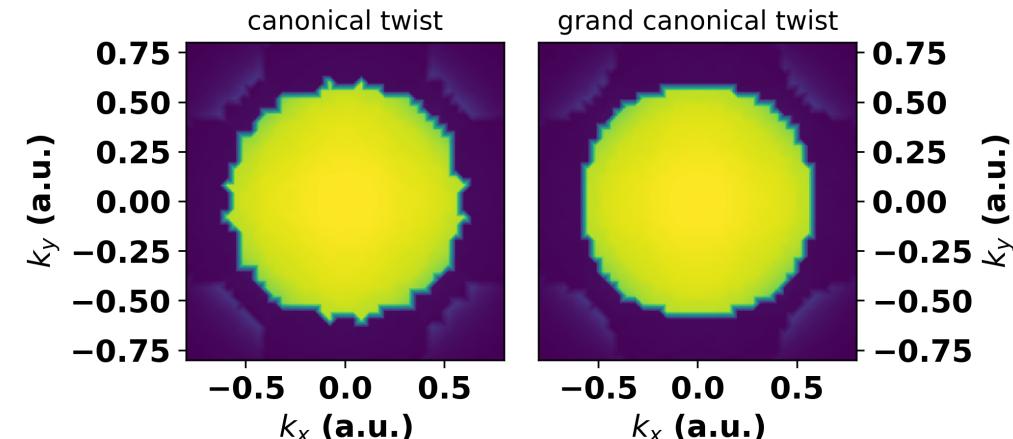
Physics:

- Density effect
- Pseudopotential bias



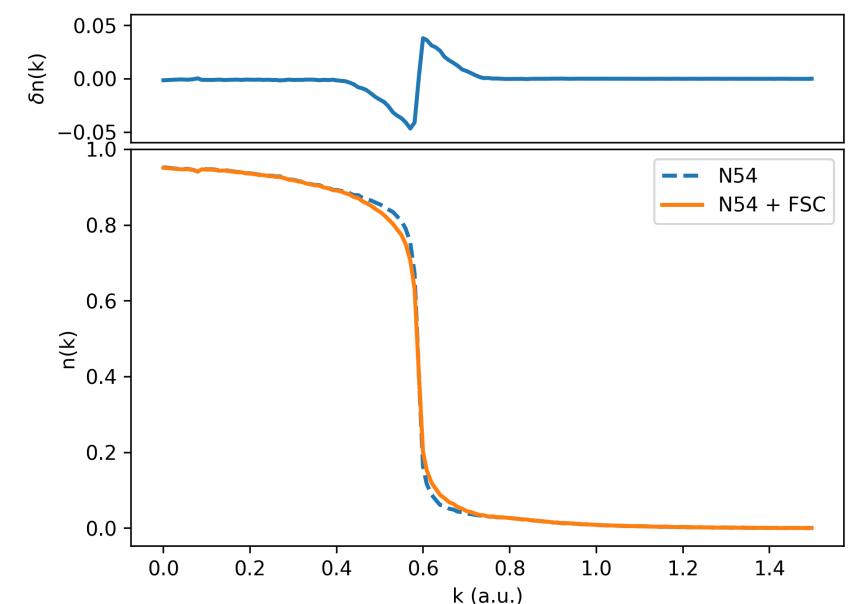
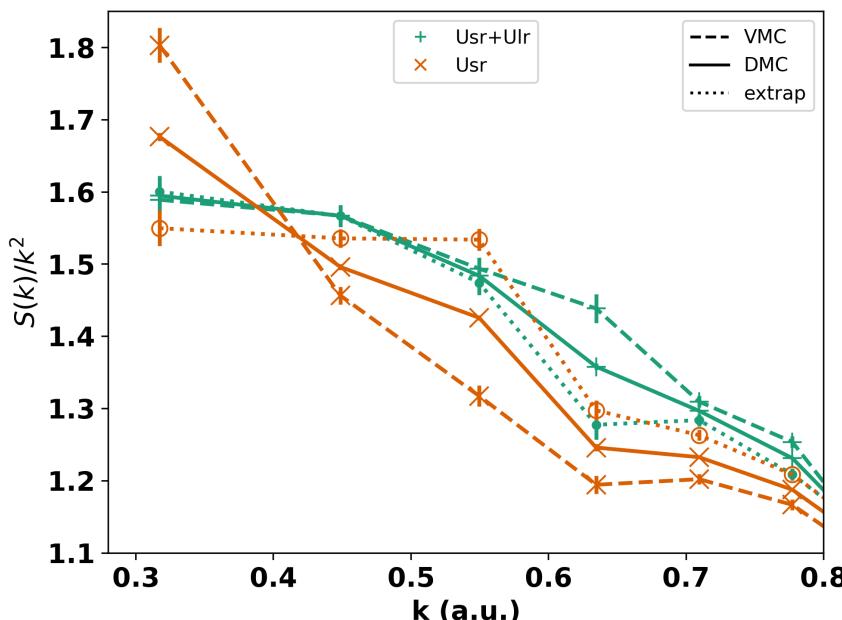
Finite-size effect:

- Independent electron: Twist grid
- Many-body: Reciprocal space correction with $S(\mathbf{k})$



Algorithm bias:

- Mixed-estimator error
- time step error
- Fixed-node error



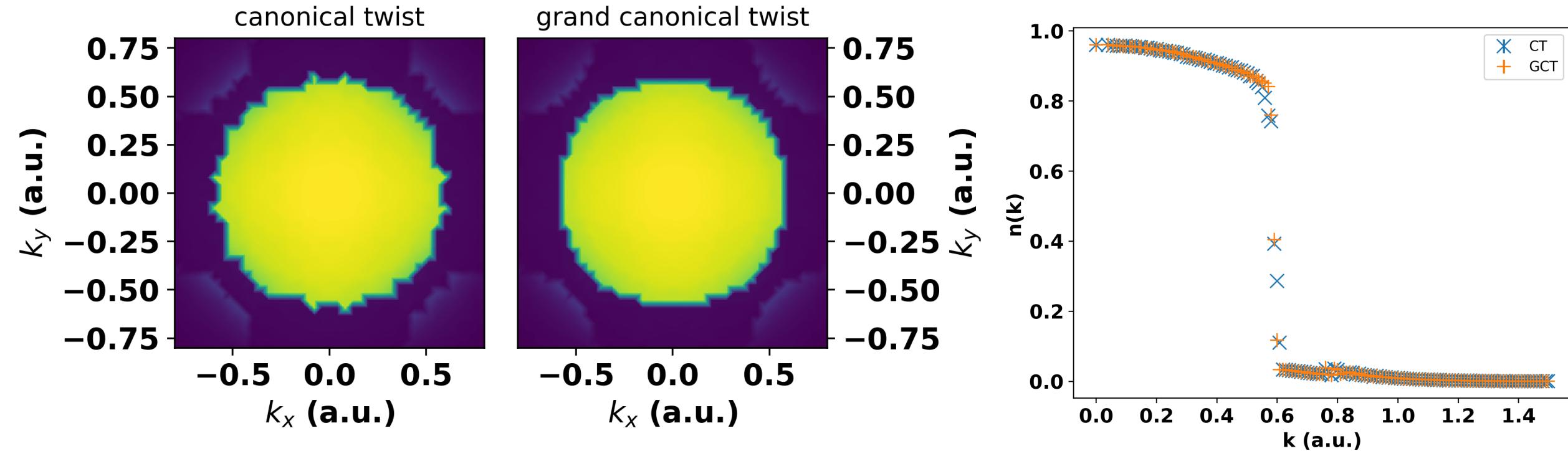
Grand canonical twist grid is crucial for sharp Fermi surface

Canonical twist (CT) grid uses the same number of electrons at all twists;

CT has occupation outside the Fermi surface → smear Fermi surface

Grand canonical twist (GCT) grid uses a varying number of electrons at each twist;

GCT prevents occupation outside the Fermi surface → sharper Fermi surface [1]



[1] C. Lin, F. H. Zhong, and D. M. Ceperley, "Twist-averaged boundary conditions in continuum quantum Monte Carlo algorithms," Phys. Rev. E **64**, 016702 (2001).

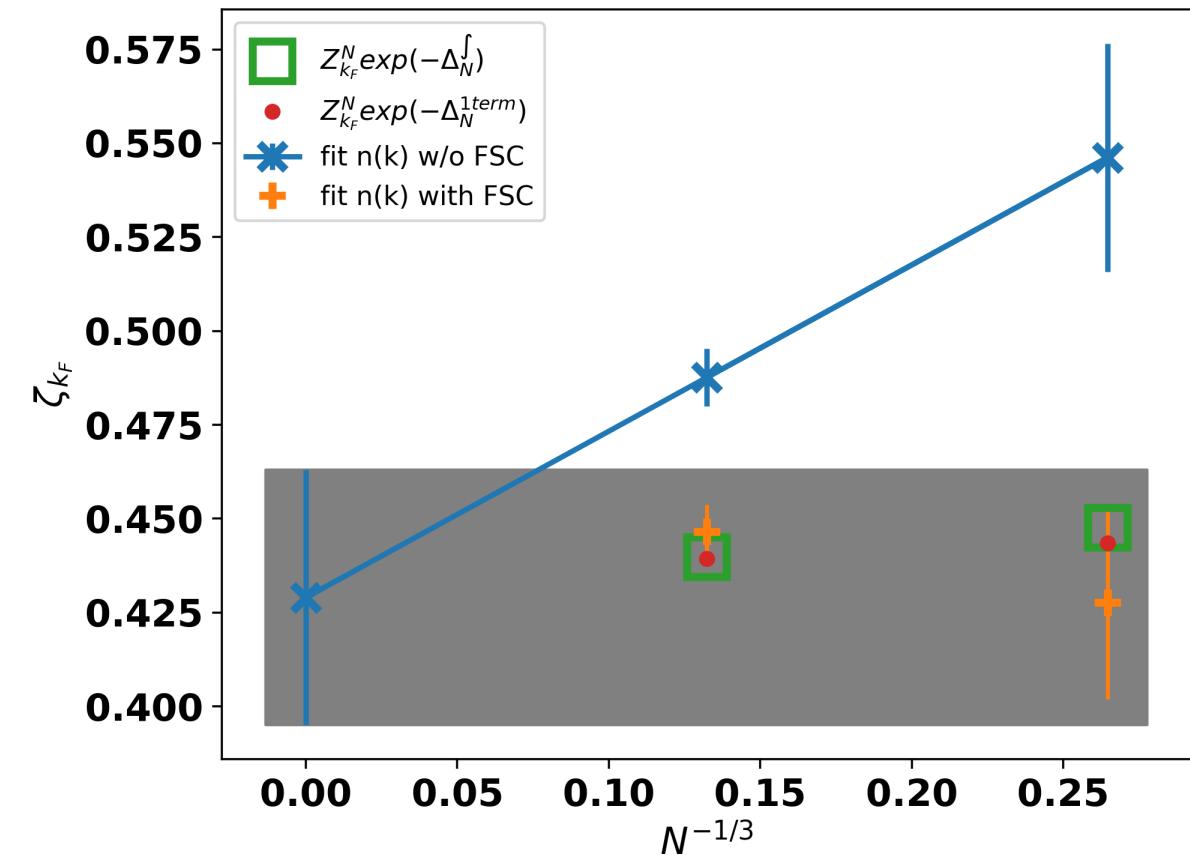
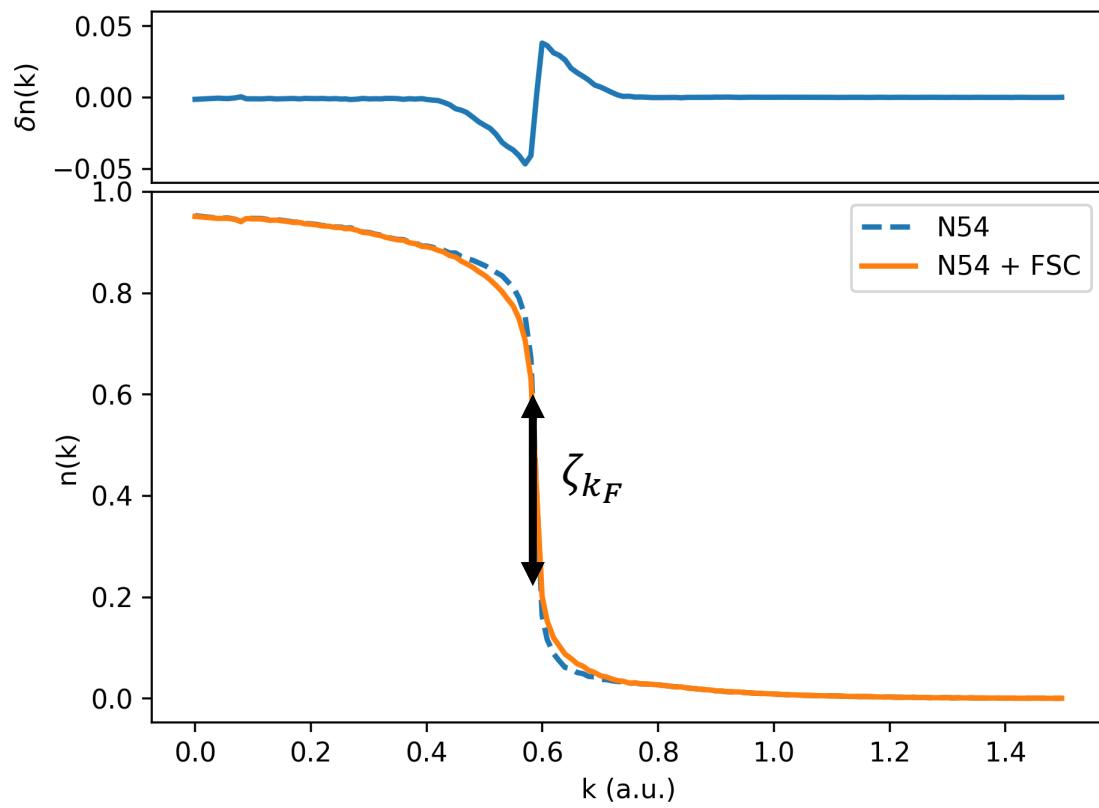
Grand canonical twist grid can be setup using nexus QmcpackInput

```
1 def set_norb(qi, norb):
2     for name in ['u', 'd', 'sposet', 'updet', 'downdet']:
3         node = qi.get(name)
4         node.set(size=norb)
5
6 if __name__ == '__main__':
7     from qmcpack_input import QmcpackInput
8     ntwist = 35
9     norb = 8
10    for itwist in range(ntwist):
11        fxml = 'qmc.g%03d.twistnum_%d.in.xml' % (itwist, itwist)
12        qi = QmcpackInput(fxml)
13        set_norb(qi, norb)
14        qi.write(fxml)
15 # end __main__
```

$n(k)$ finite size error is large near the Fermi surface

Finite-size error of $n(k)$ is large at the Fermi surface of a metal. Correct using $S(k)$. [1]

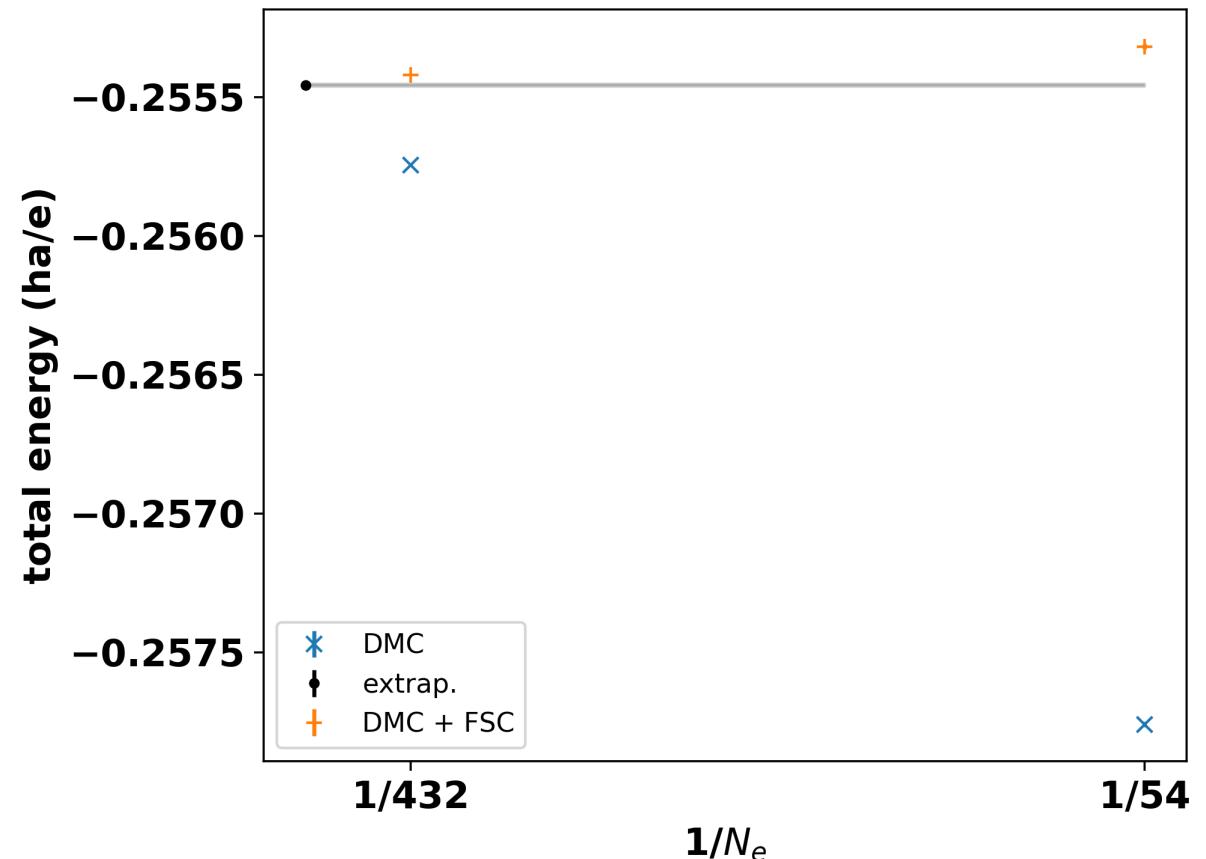
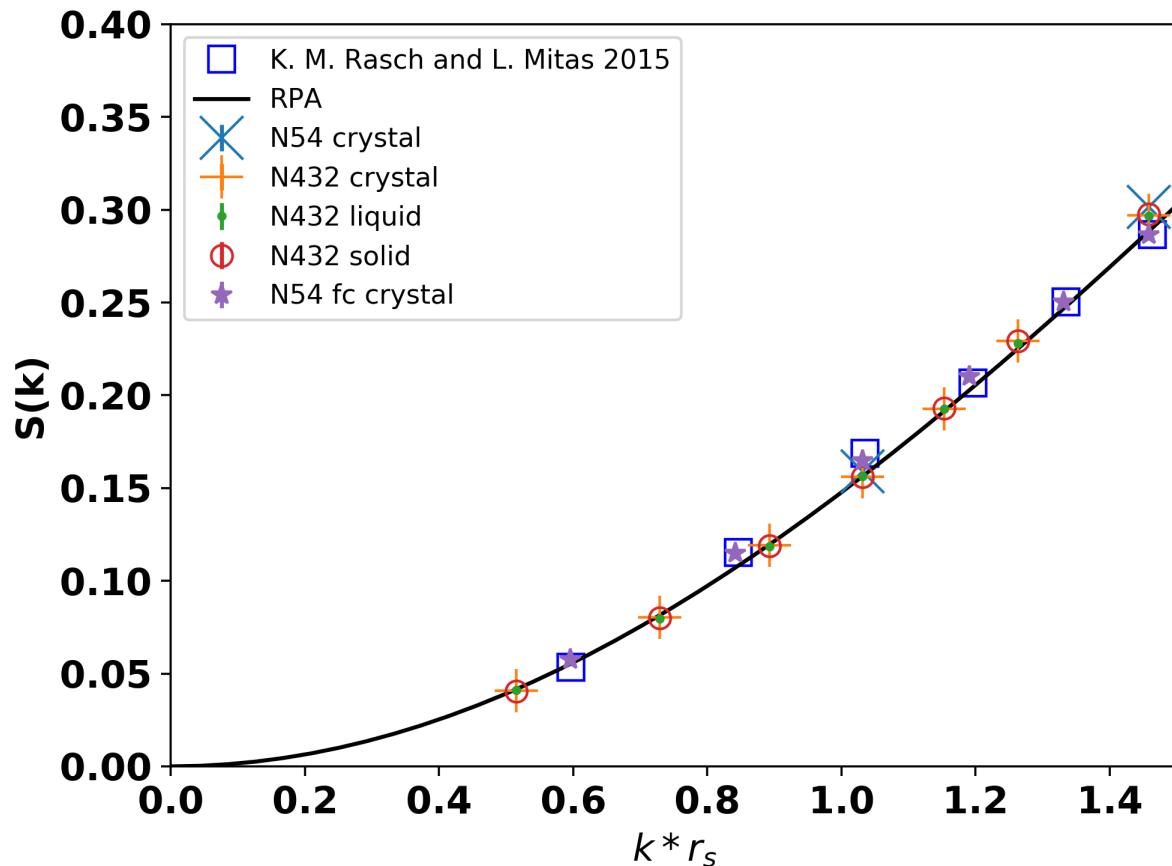
Finite-size error of $n(k)$ scales as $1/L$. Fortunately, correction is satisfactory with $N=54$ lithium atoms.



$S(k)$ converge is satisfactory

$S(k)$ is converged with as few as 54 lithium atoms →

finite-size error on the total energy can be satisfactorily corrected [1]



Long-range Jastrow can minimize mixed-estimator error of $S(k)$

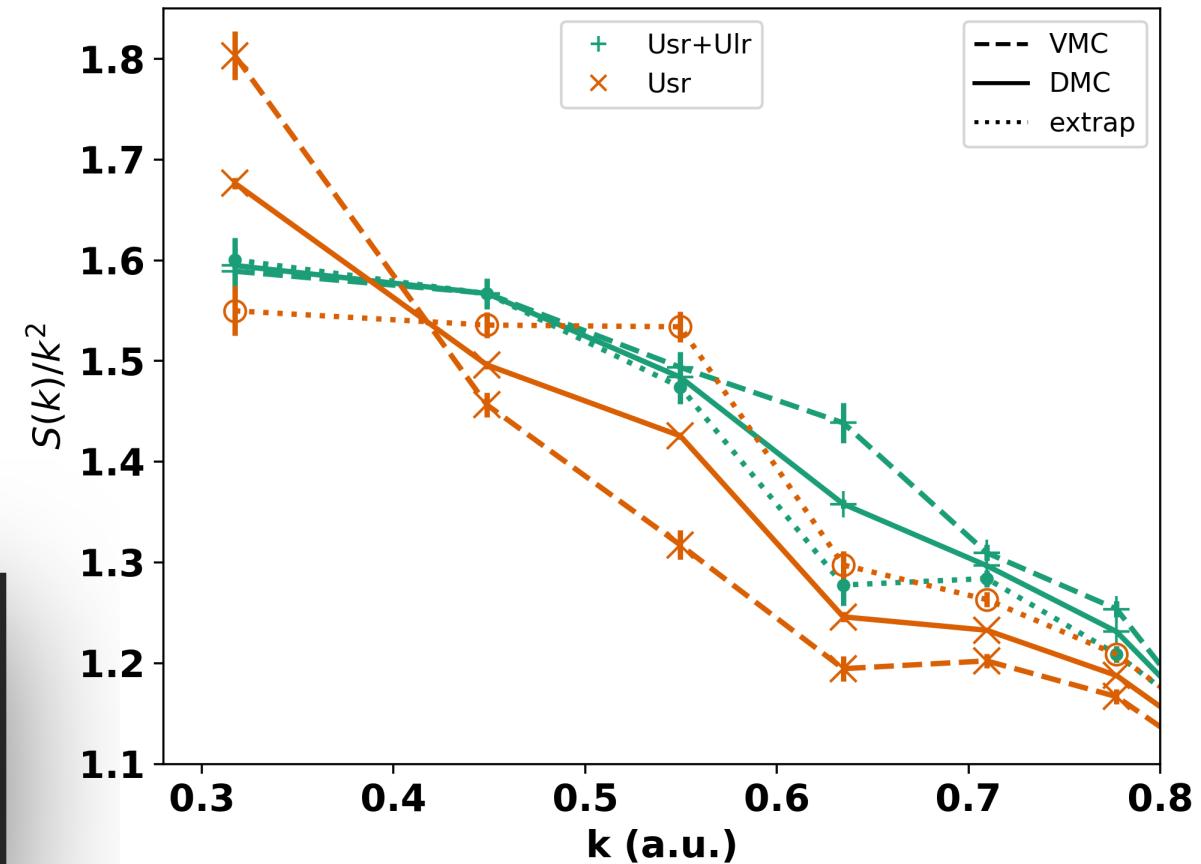
K-space Jastrow can impose correct long-wavelength behavior of wavefunction

⇒ faster DMC convergence

⇒ minimize mixed-estimator error

Mixed-estimator extrapolation does less work

```
1 <jastrow type="kSpace" name="Jk" source="ion0">
2   <correlation kc="0.8" type="Two-Body" symmetry="isotropic">
3     <coefficients id="cG2" type="Array">
4 -68.0 16.0 21.0 32.3 20.1 14.8
5   </coefficients>
6 </correlation>
7 </jastrow>
```



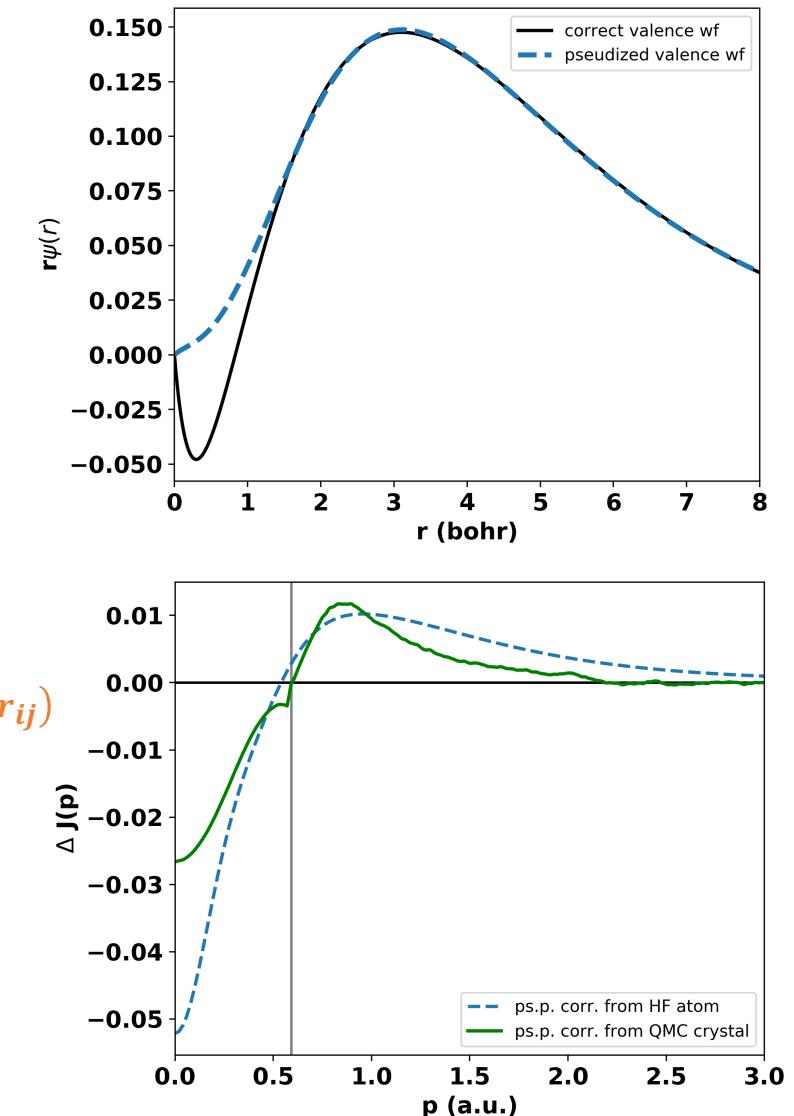
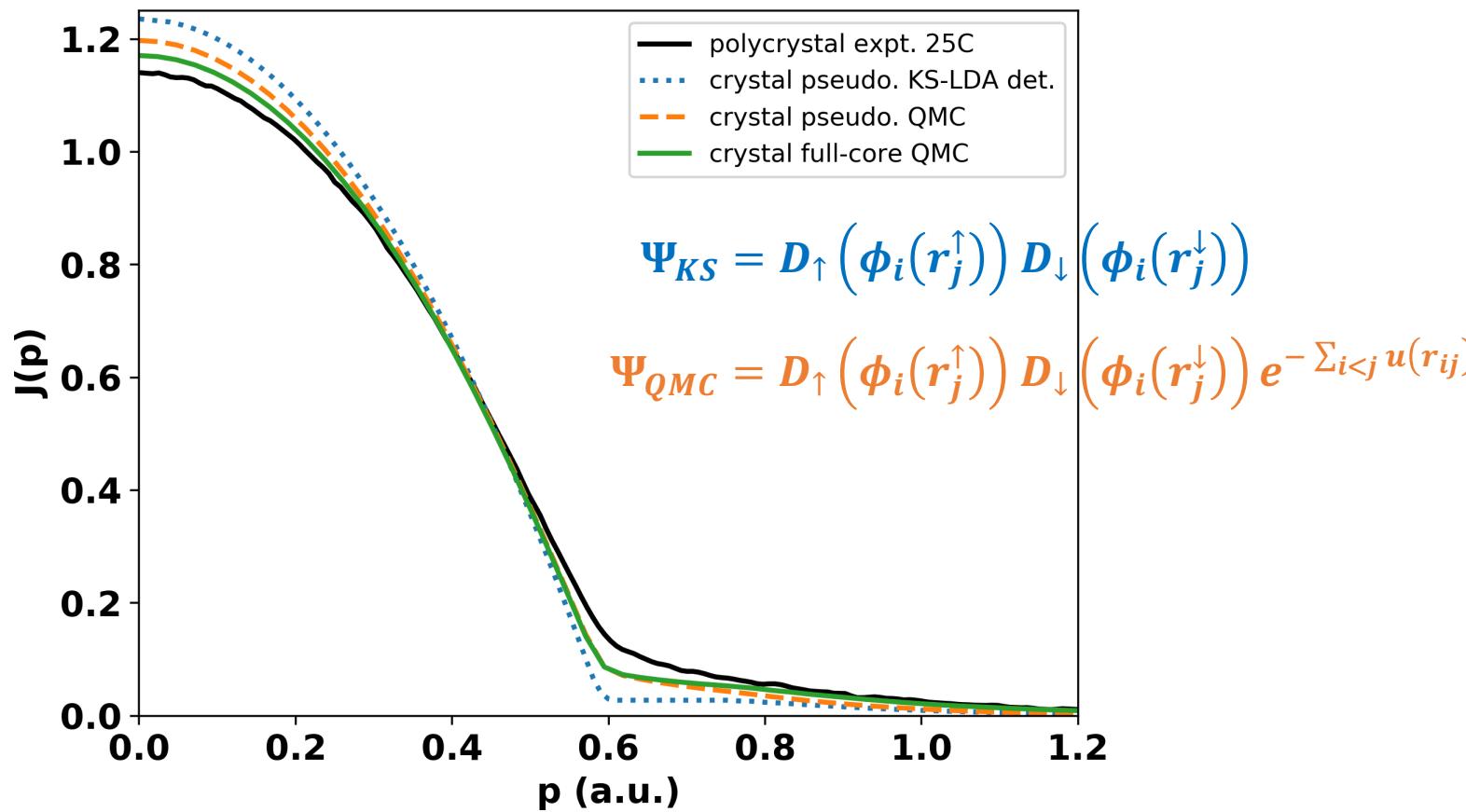
Custom wavefunction can be injected into QmcpackInput

```
1  sdmc = generate_qmcpack(**dmc_inputs)
2  # read custom jastrow
3  from nexus import QmcpackInput
4  qi_opt = QmcpackInput(opt_xml)
5  jas_opt = qi_opt.qmcsystem.wavefunction.jastrows
6  # swap the jastrow
7  qi = sdmc.input
8  qi.simulation.qmcsystem.wavefunction.jastrows = jas_opt
```

Quantitative Compton profile of lithium crystal: pseudopotential bias

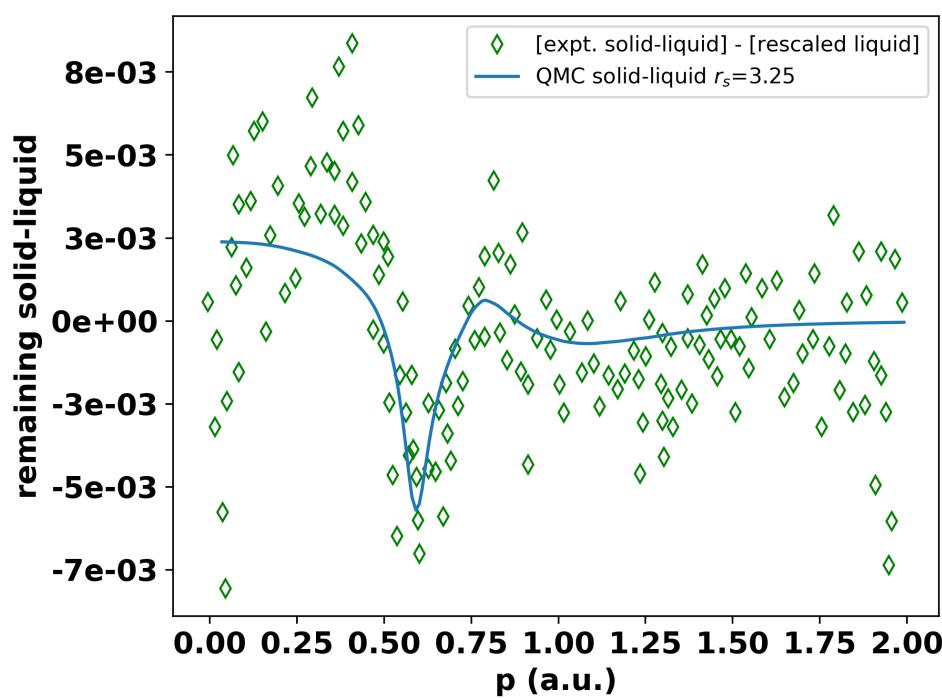
Valence Compton profile from all-electron QMC simulation agrees well with experiment away from p_F

Valence orbital is smoothed out when building pseudopotential
⇒ removed high-momentum components

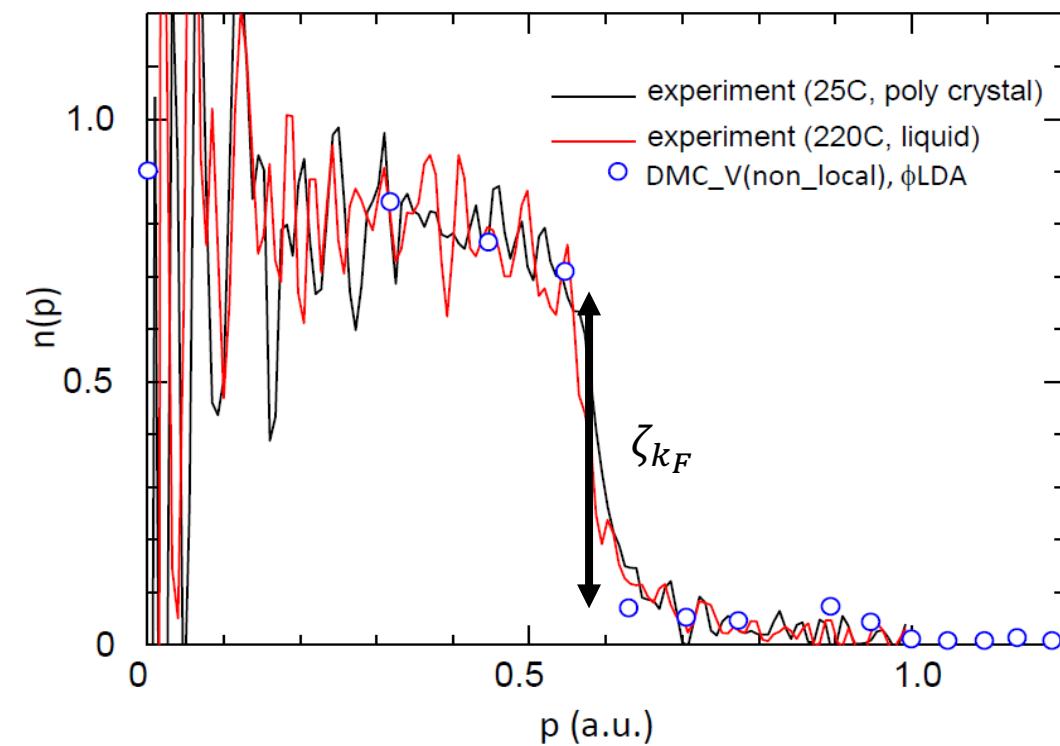


Results: How does QMC help experiment?

I. Disentangle density and crystal effects
in liquid and solid $J(p)$ difference



II. Extract the magnitude of $n(k)$ discontinuity at Fermi surface (related to the renormalization factor Z_{k_F})

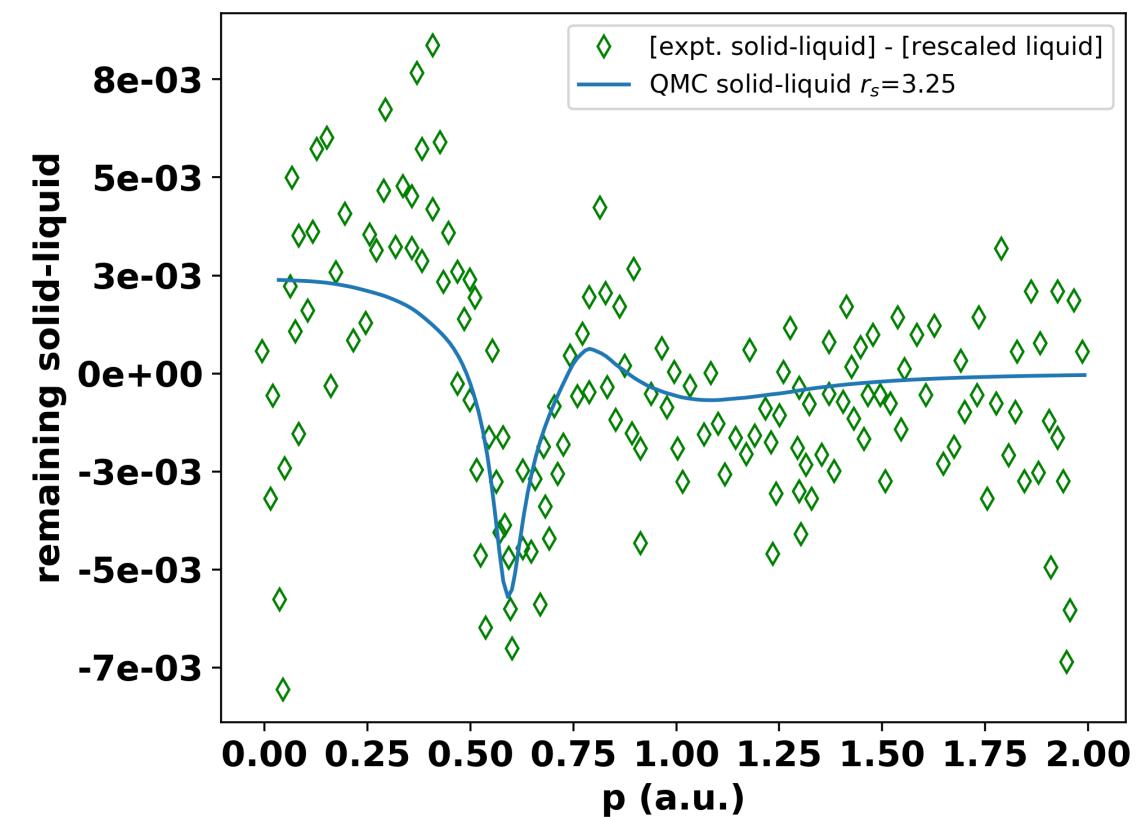
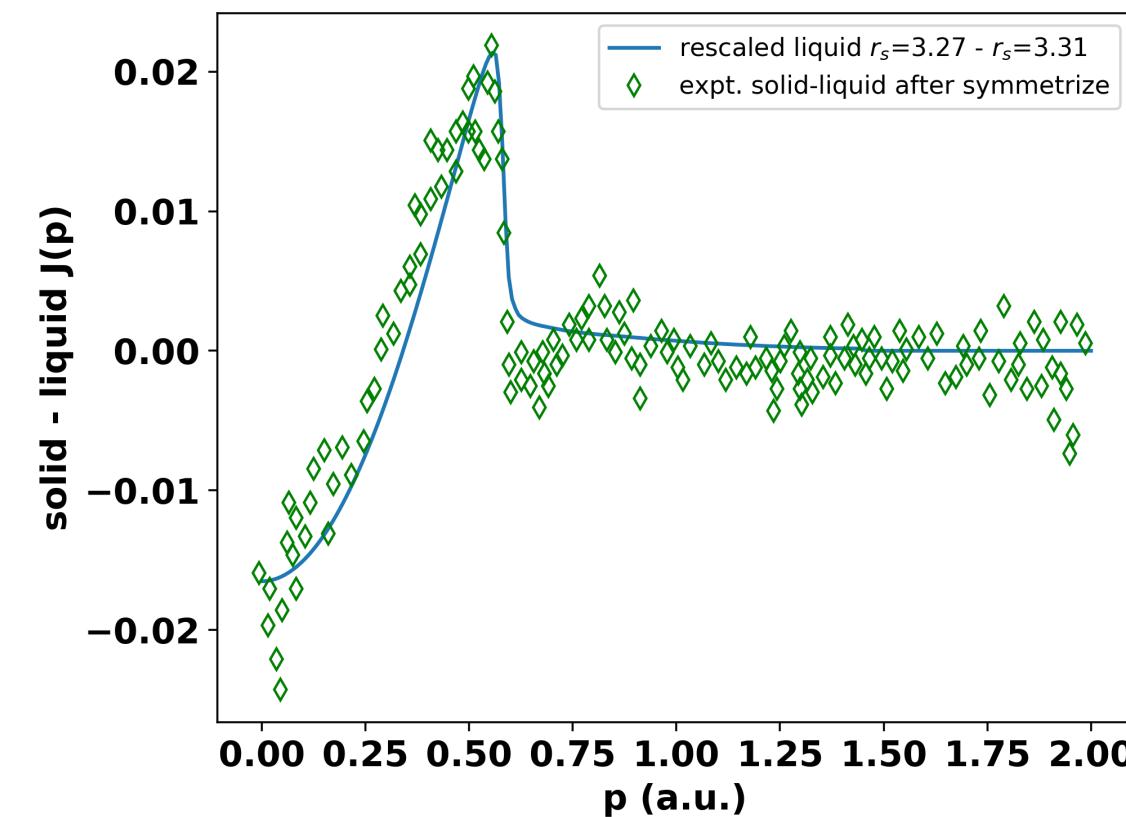


Theory contribution 1: explain liquid v.s. solid Compton profiles $J(p)$

Solid and liquid Compton profile difference is mostly due to density change

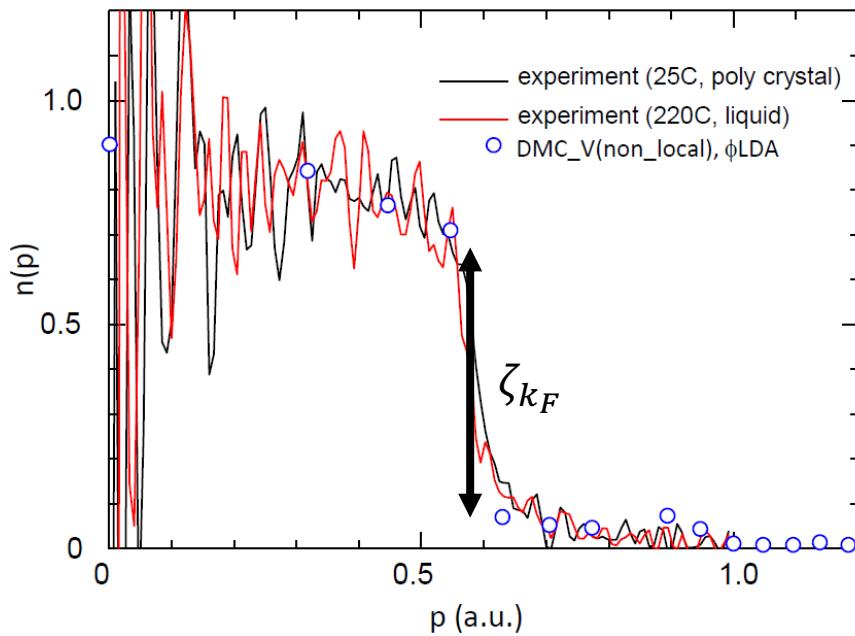
Solid to liquid **density** change induces
 $O(0.01 \text{ a.u.})$ change in Compton profile

Solid to liquid *structure* change induces
 $O(0.001 \text{ a.u.})$ change in Compton profile



Theory contribution 2: calculate discontinuity ζ_{k_F} of $n(k)$ in disordered system

Q/ How to measure the magnitude of the discontinuity in disordered system?



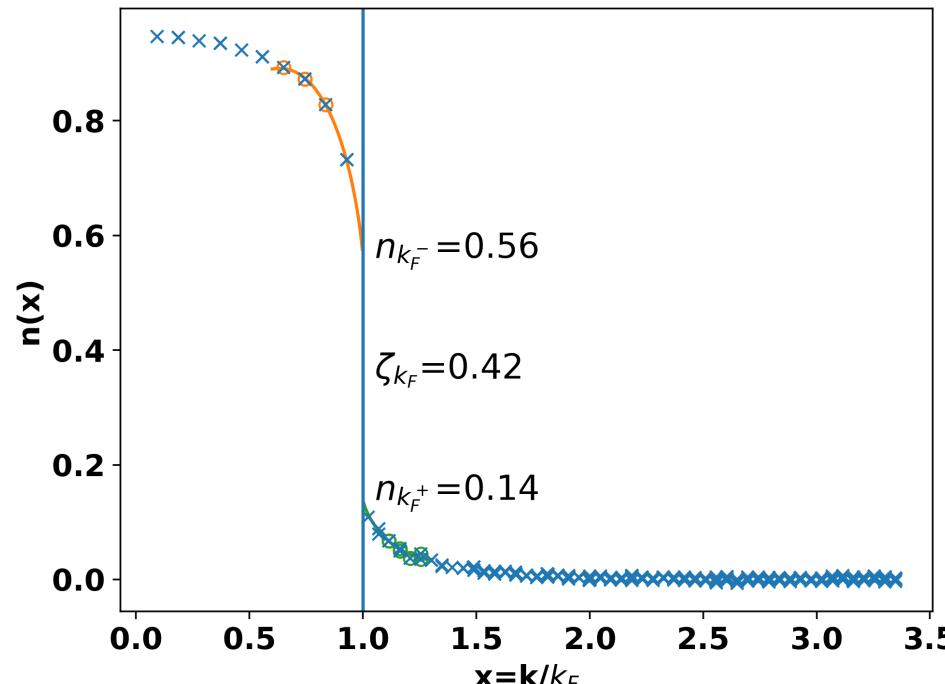
Easier in simulation:

ζ_{k_F} is finite along **one** direction in
one disorder realization.

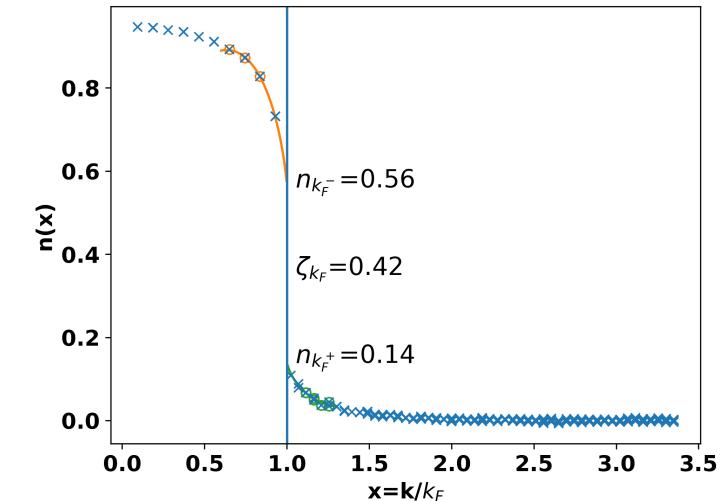
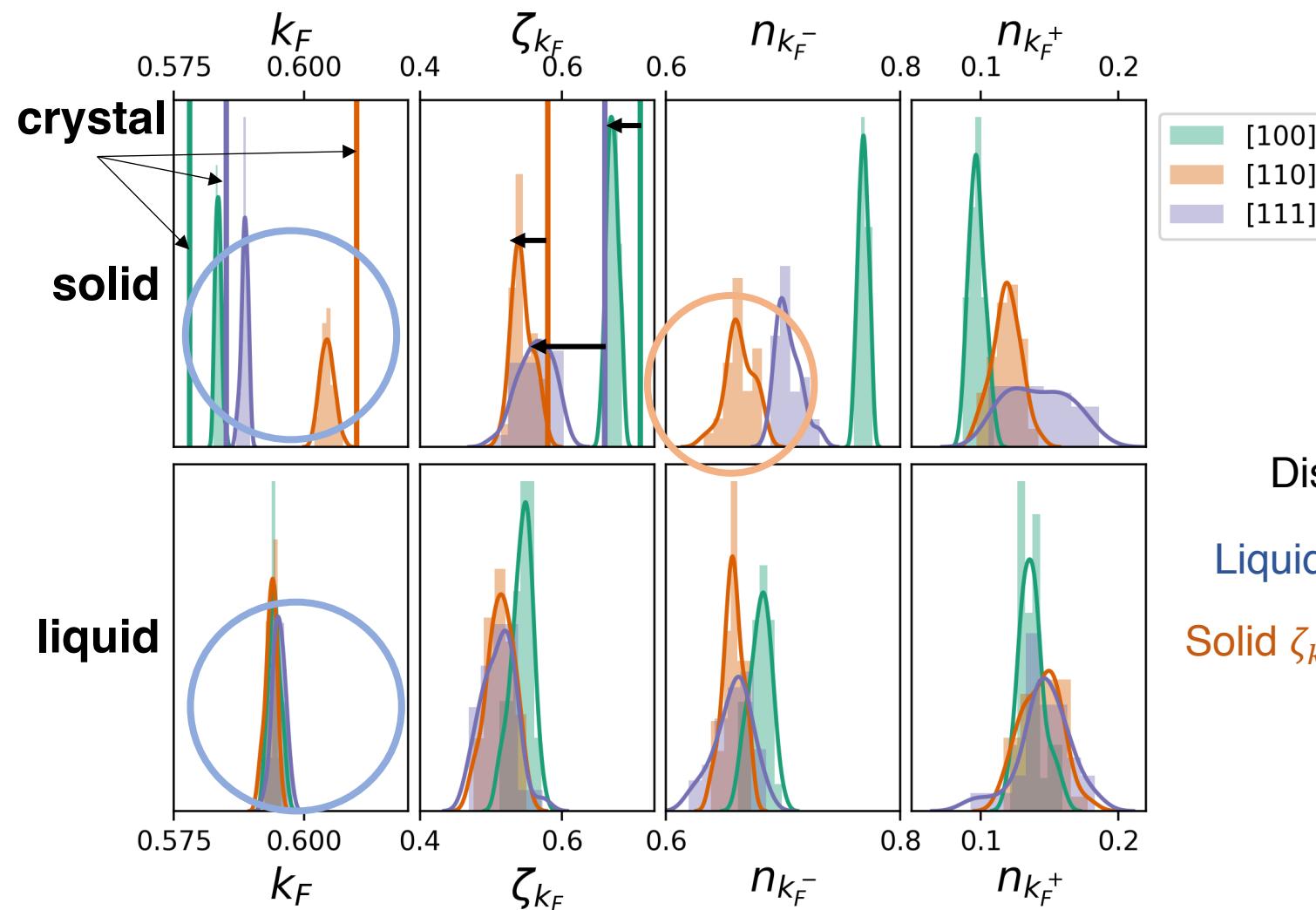
Fit $n(k)$ near k_F to obtain the jump ζ_{k_F}

A/ Very difficult from experimental data alone

1. $J(p) \rightarrow n(k)$ requires taking derivative of noisy data
2. Expt. $J(p)$ is smeared at k_F due to disorder, final state interaction, instrument resolution etc.



Extract Fermi momentum k_F and jump ζ_{k_F} from disorder realizations



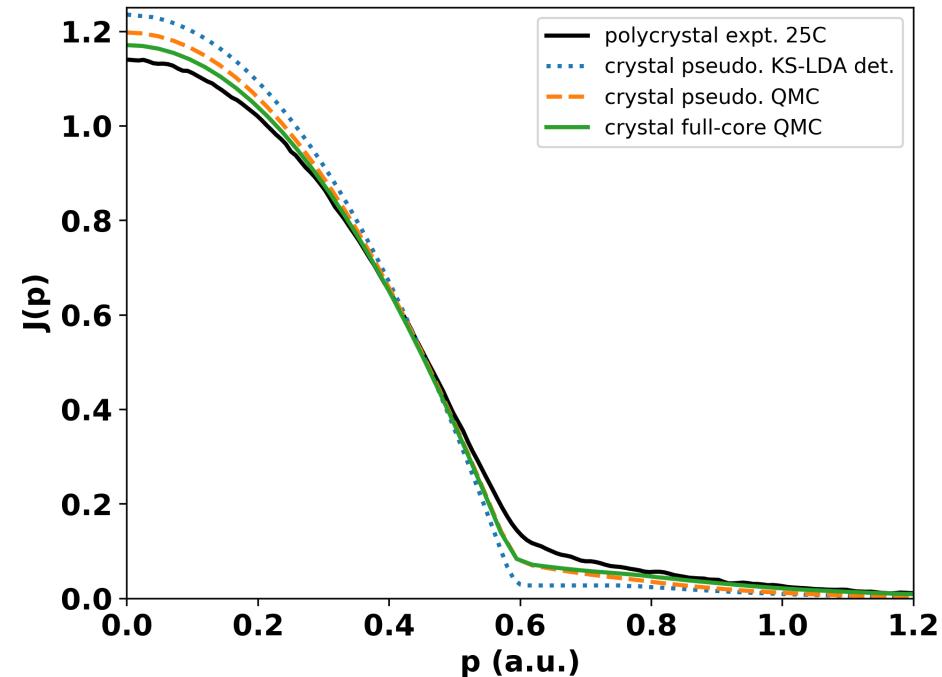
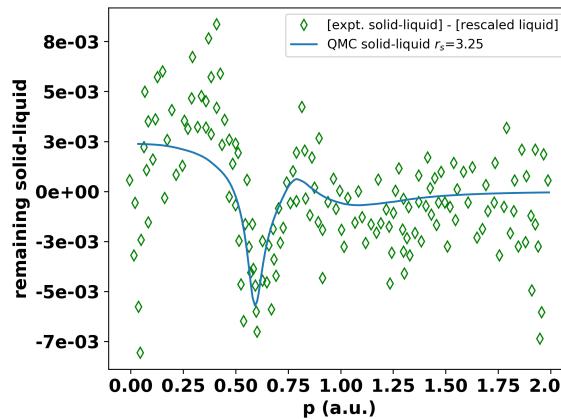
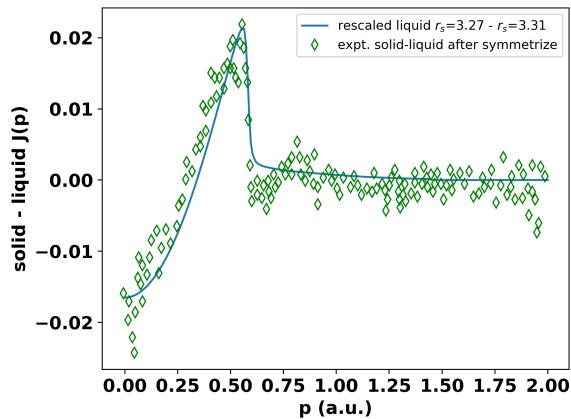
Disorder reduces ζ_{k_F} compared to perfect crystal
 Liquid Fermi surface (FS) is isotropic, solid FS is not.
 Solid ζ_{k_F} is lowest along [110], and is caused by low $n_{k_F^-}$

Conclusions:

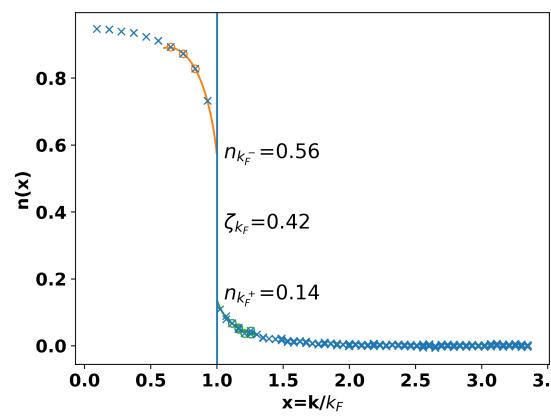
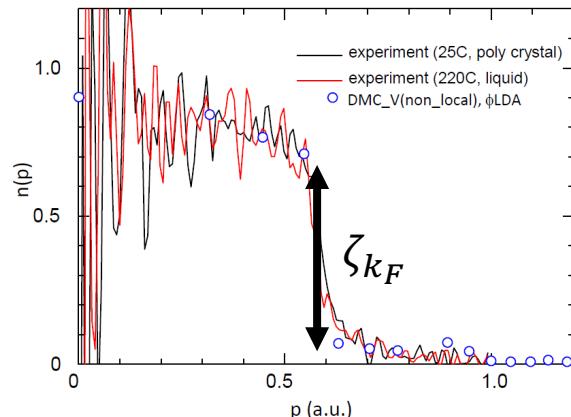
All-electron QMC Compton profile $J(p)$ agrees very well with experiment away from the Fermi momentum.

QMC can satisfactorily explain the difference between solid and liquid $J(p)$.
QMC shows the change in $J(p)$ from liquid to solid is mostly density-induced.

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QMC can extract the discontinuity ζ_{k_F} with disorder.

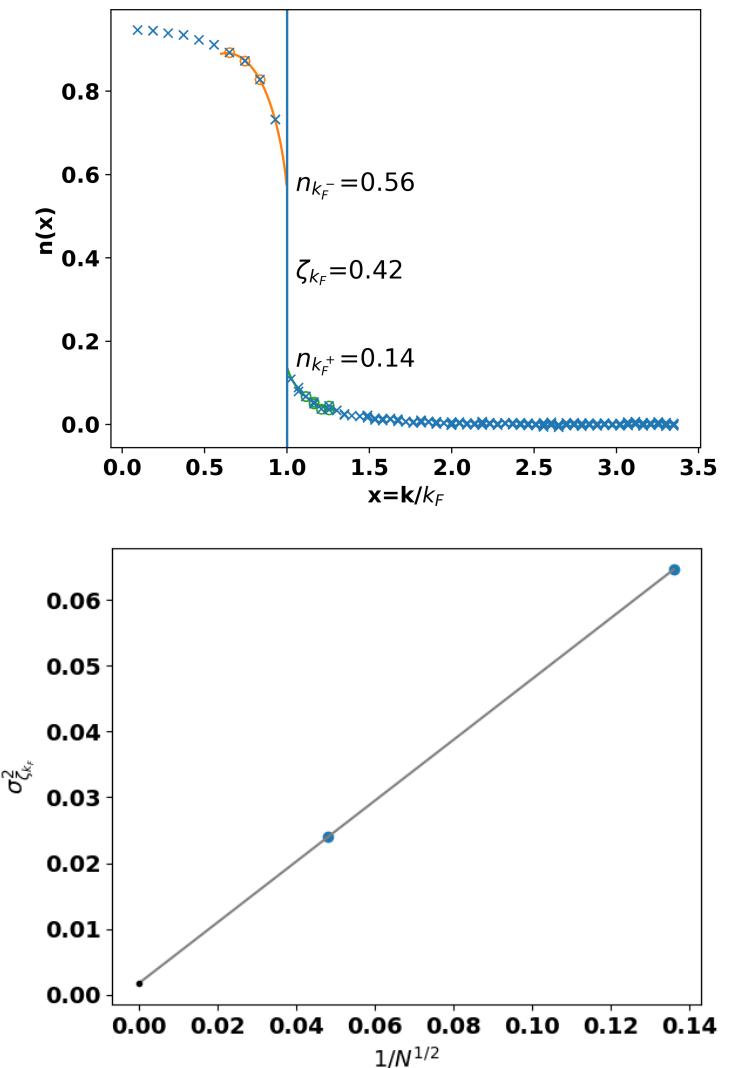
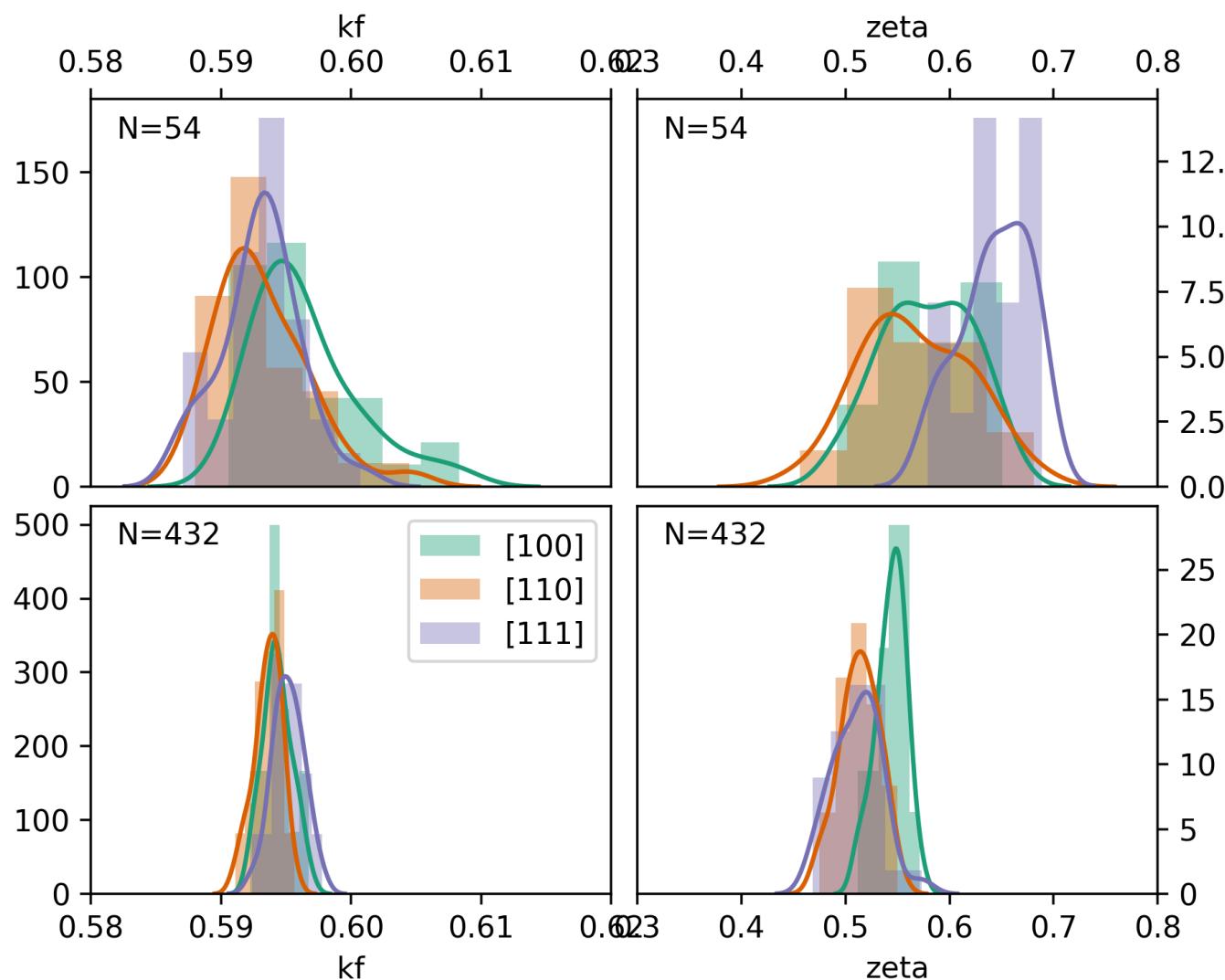


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Fermi momentum k_F and jump ζ_{k_F} exhibit self-averaging as N increases

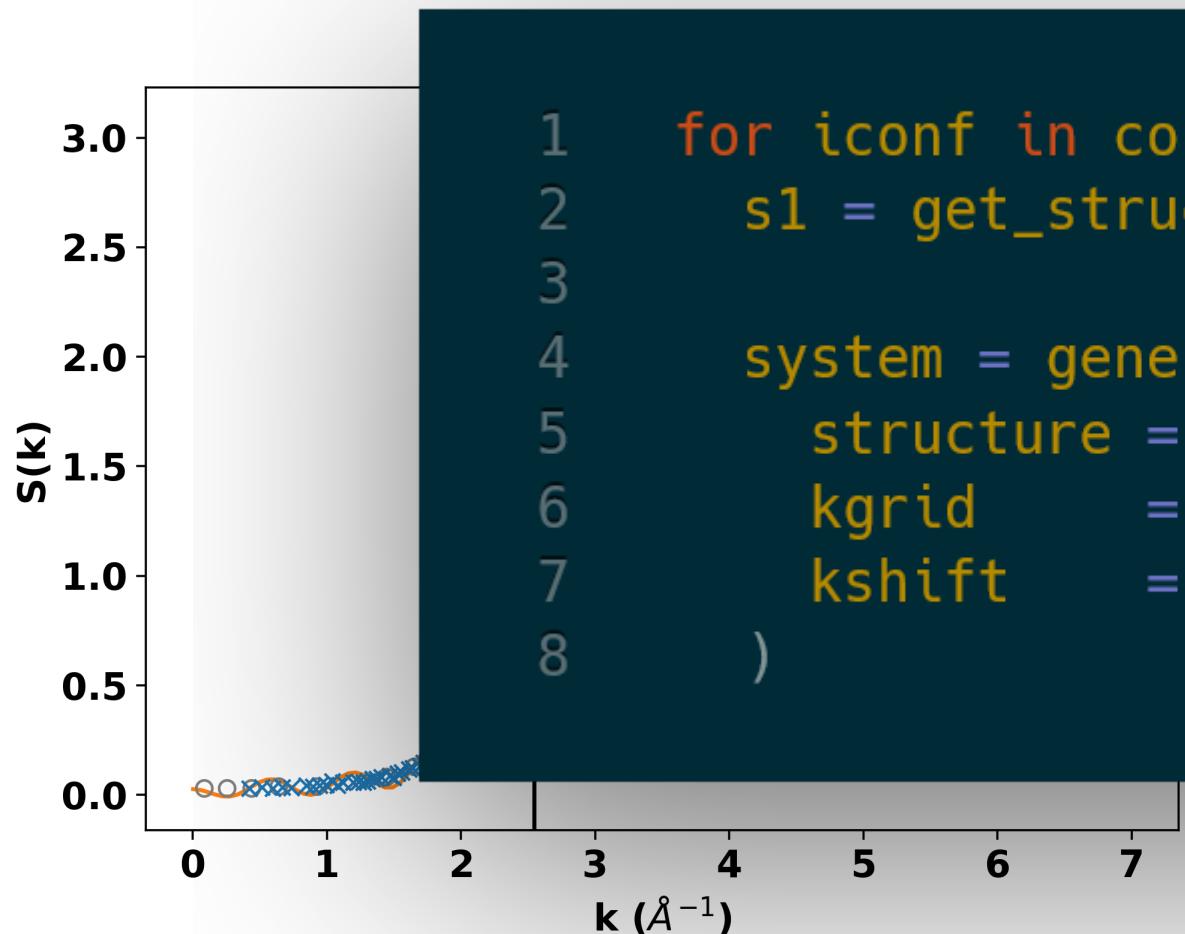


Disorder realizations generated using molecular dynamics (MD)

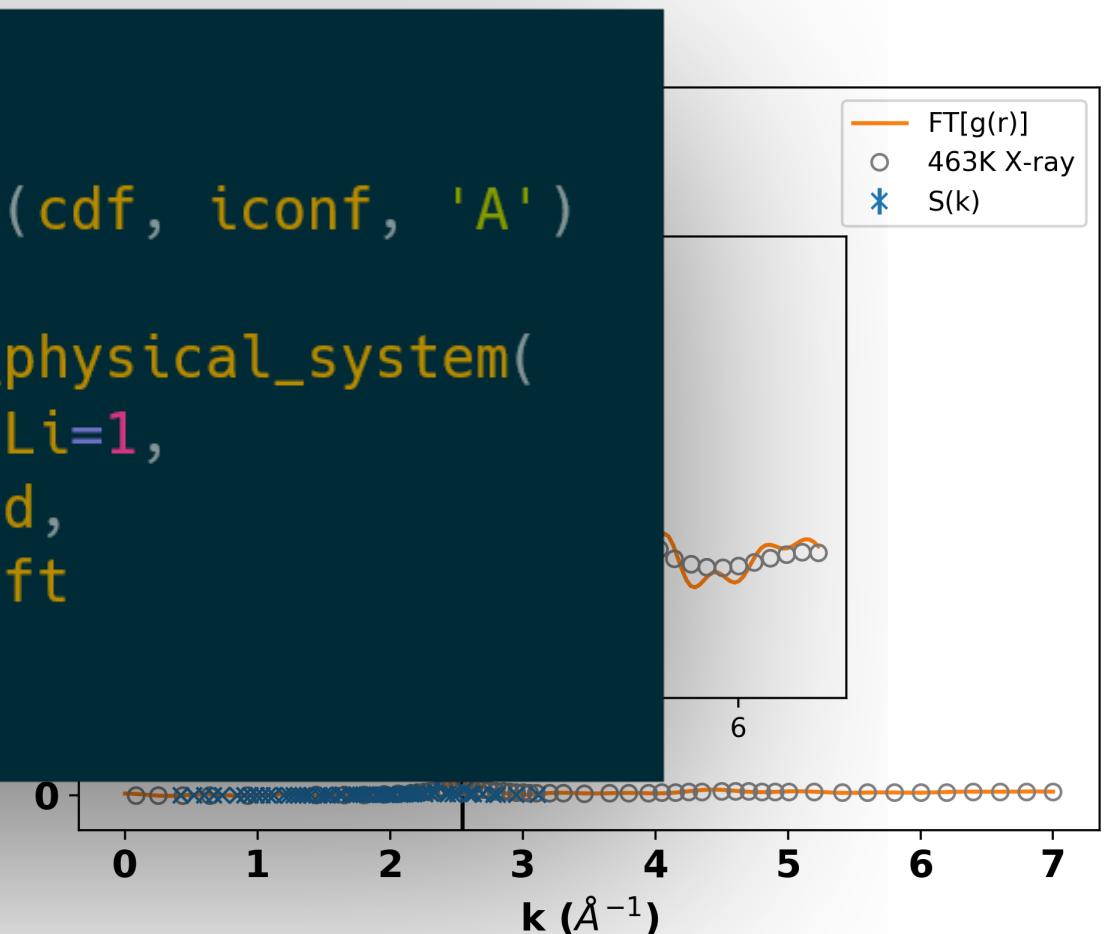
Generate static disorder realizations using molecular dynamics (MD) near expt. temperatures

Modified embedded-atom potential (MEAM) as implemented in LAMMPS

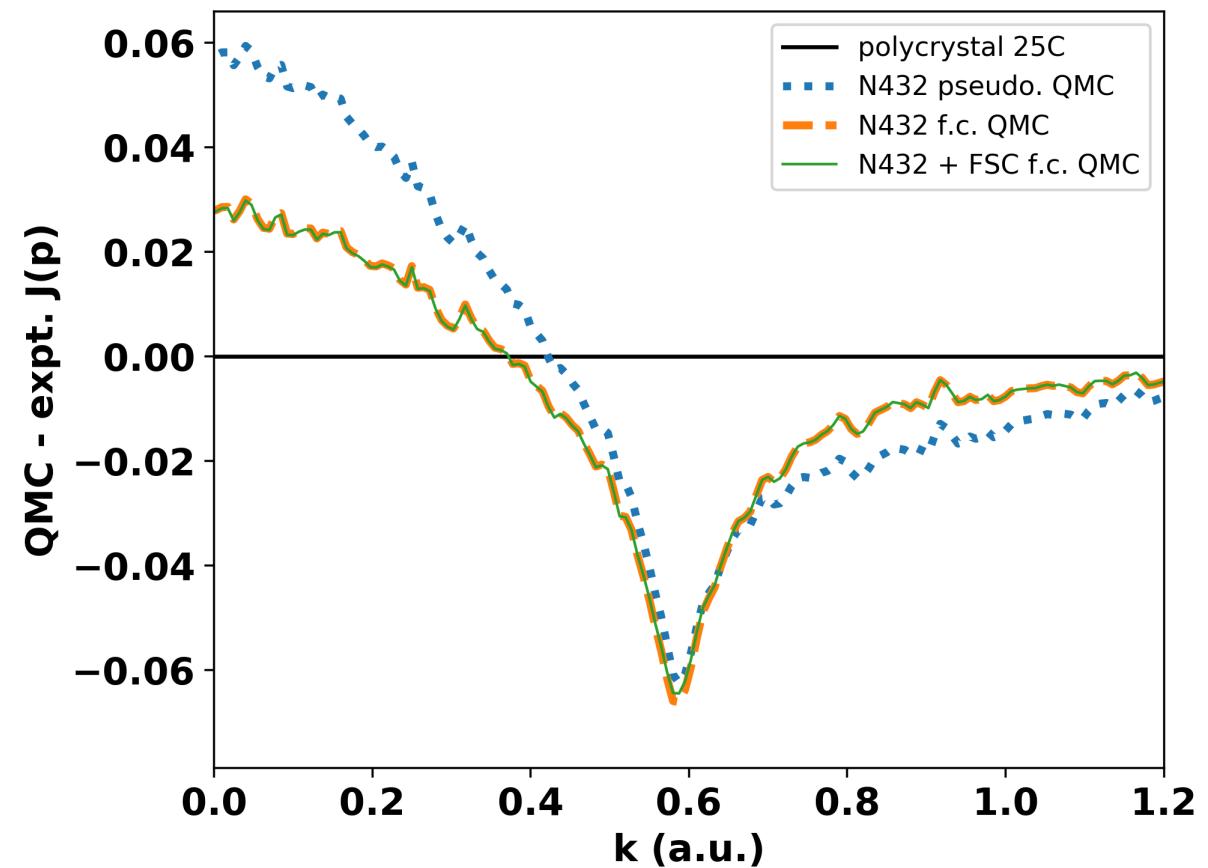
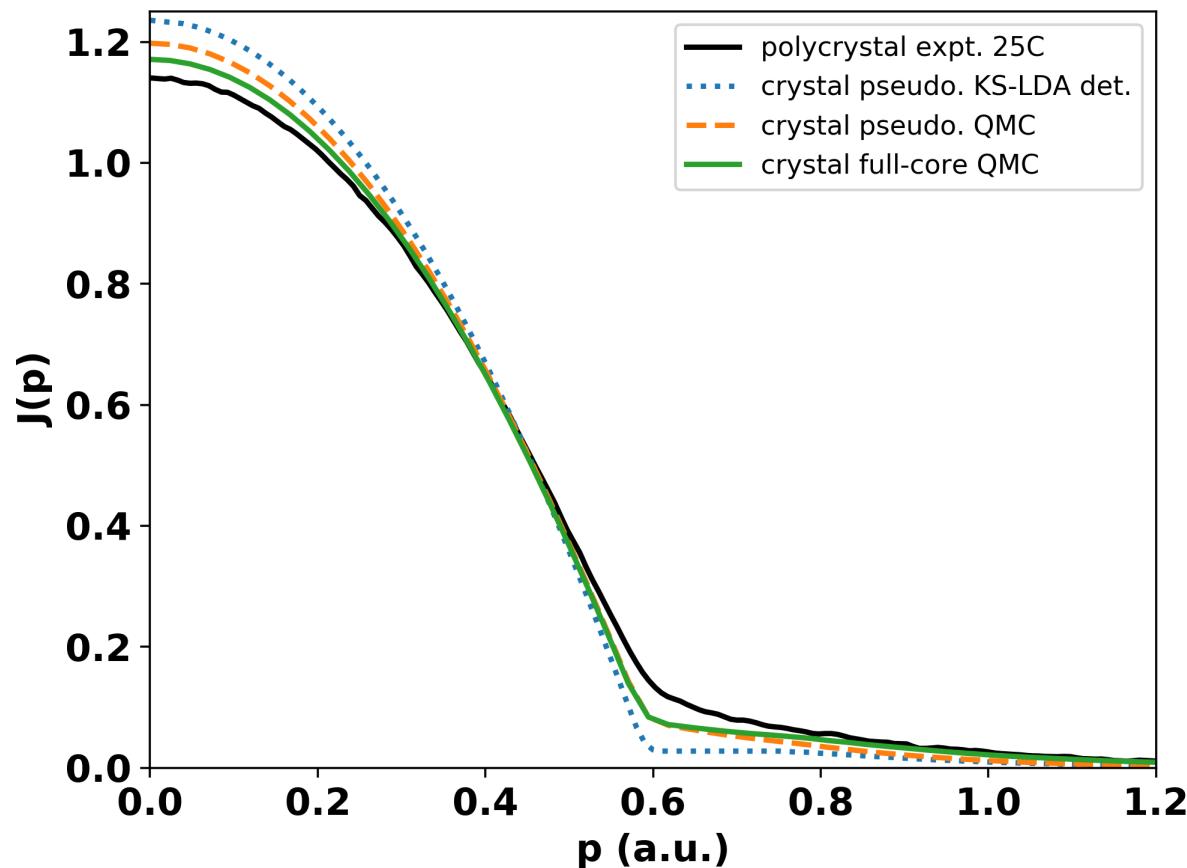
Liquid configurations



Solid configurations

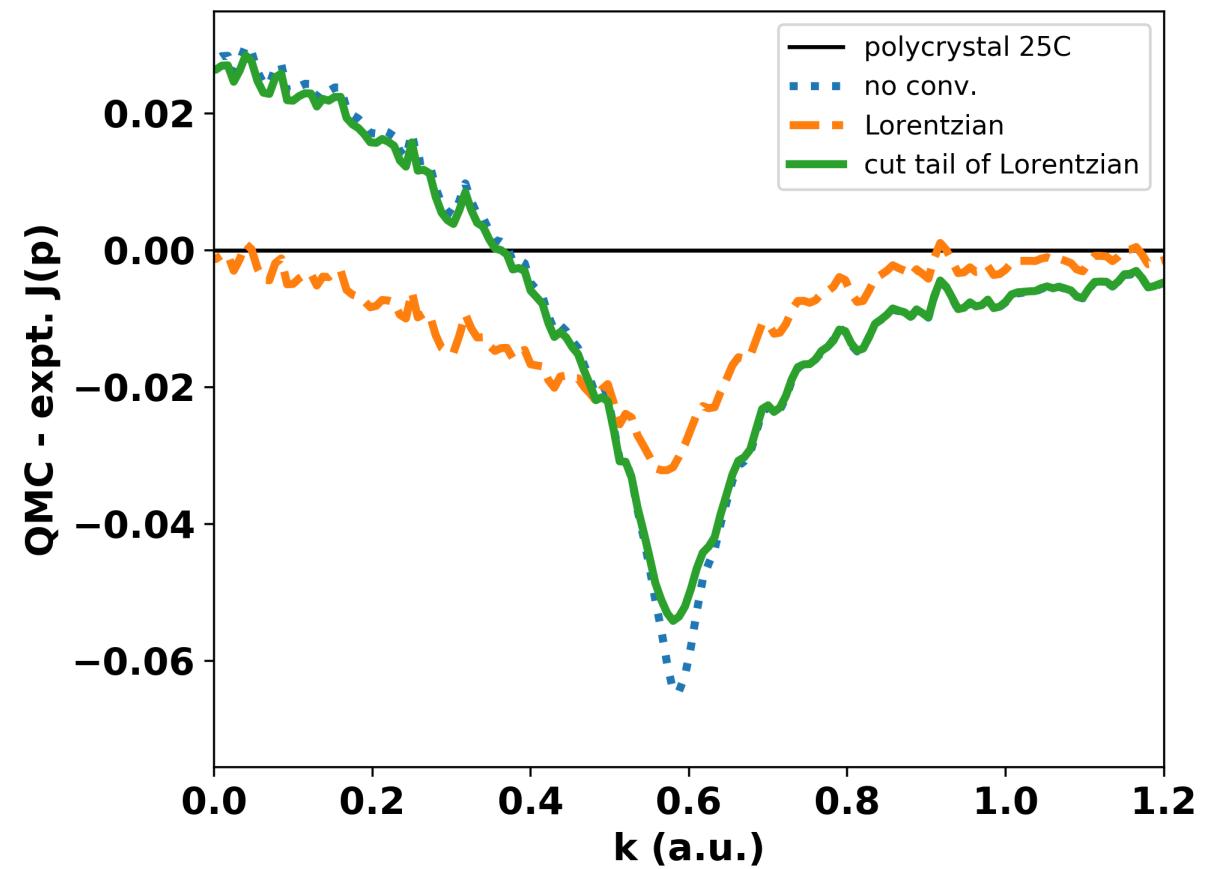
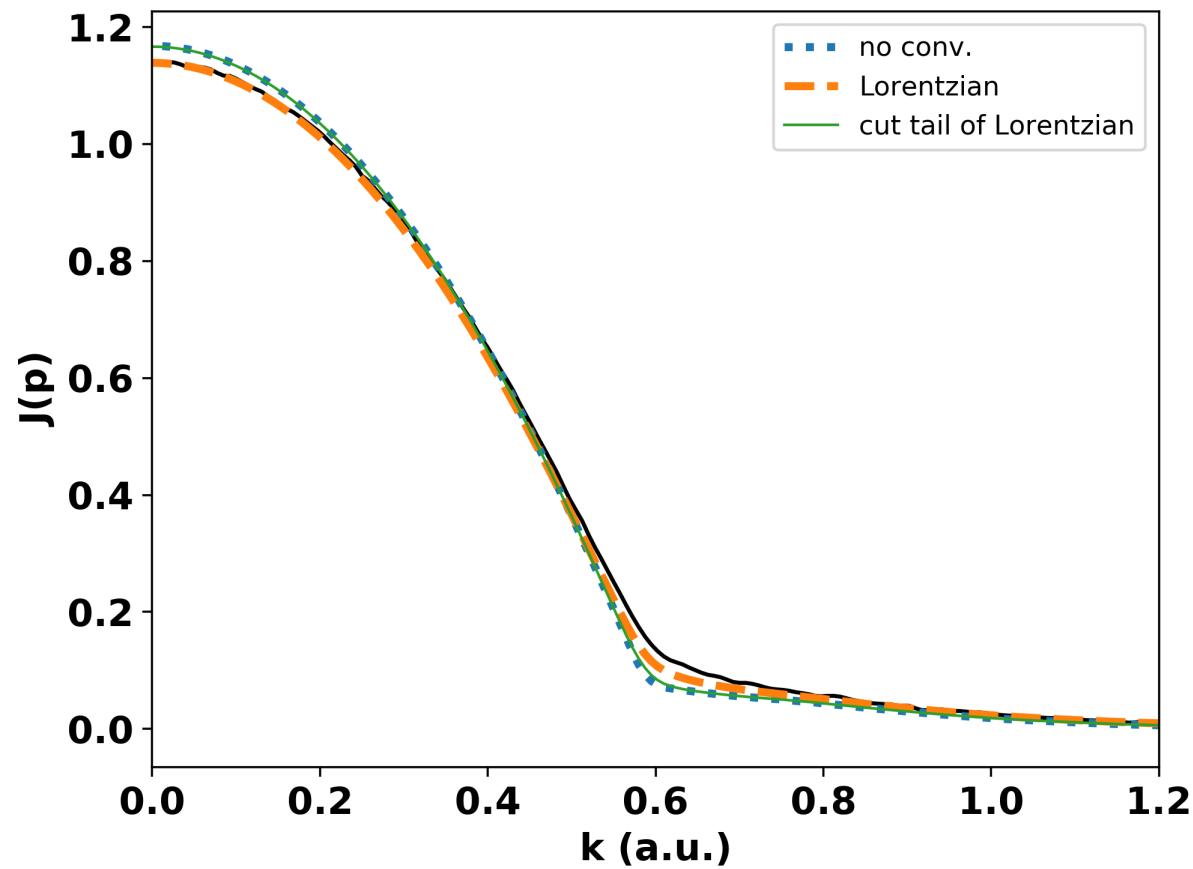


Finite-size correction: peaks at p_F and is small compared to discrepancy



Convolution with Lorentzian can reduce discrepancy

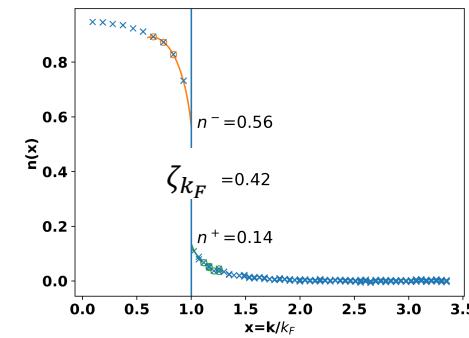
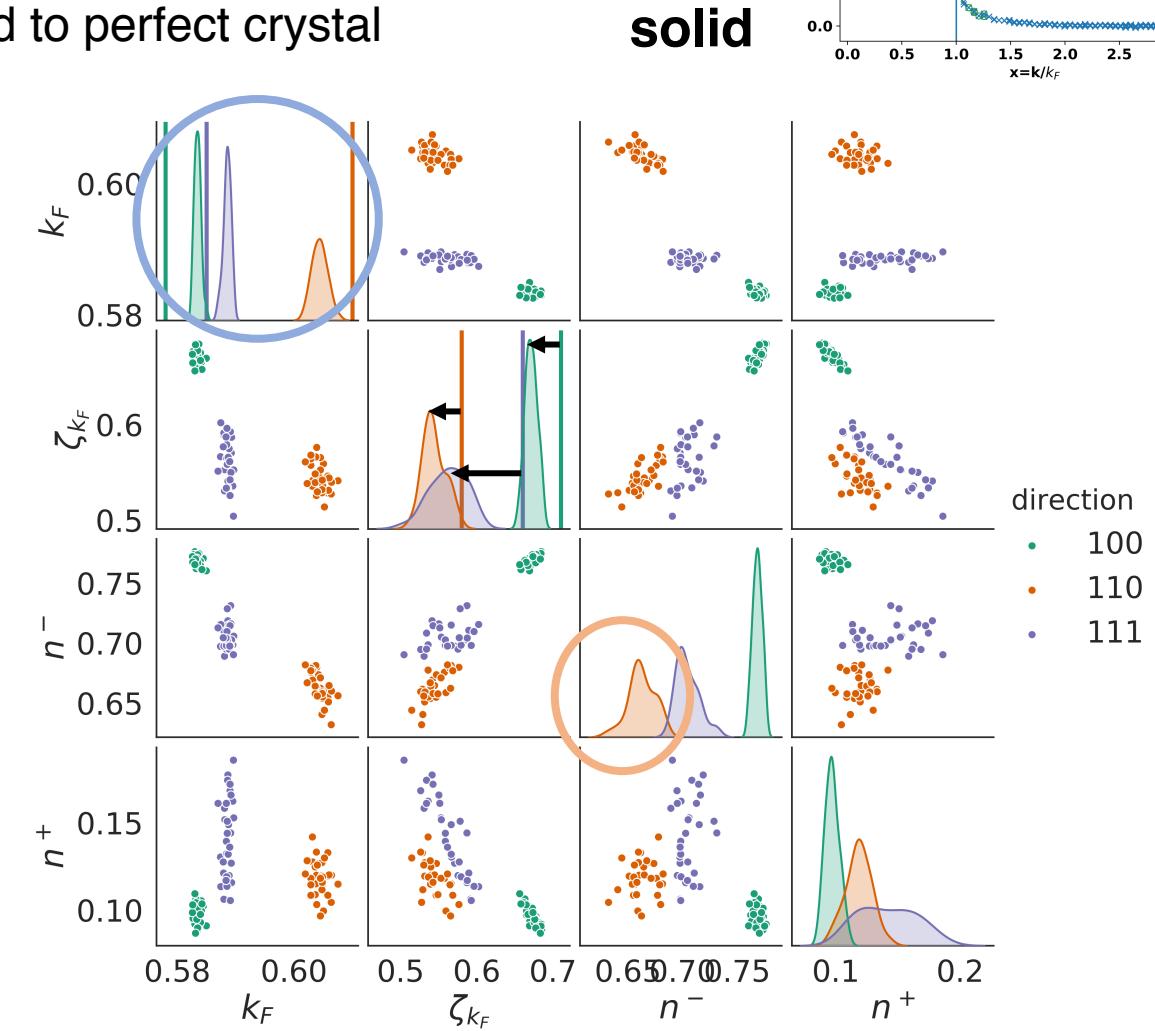
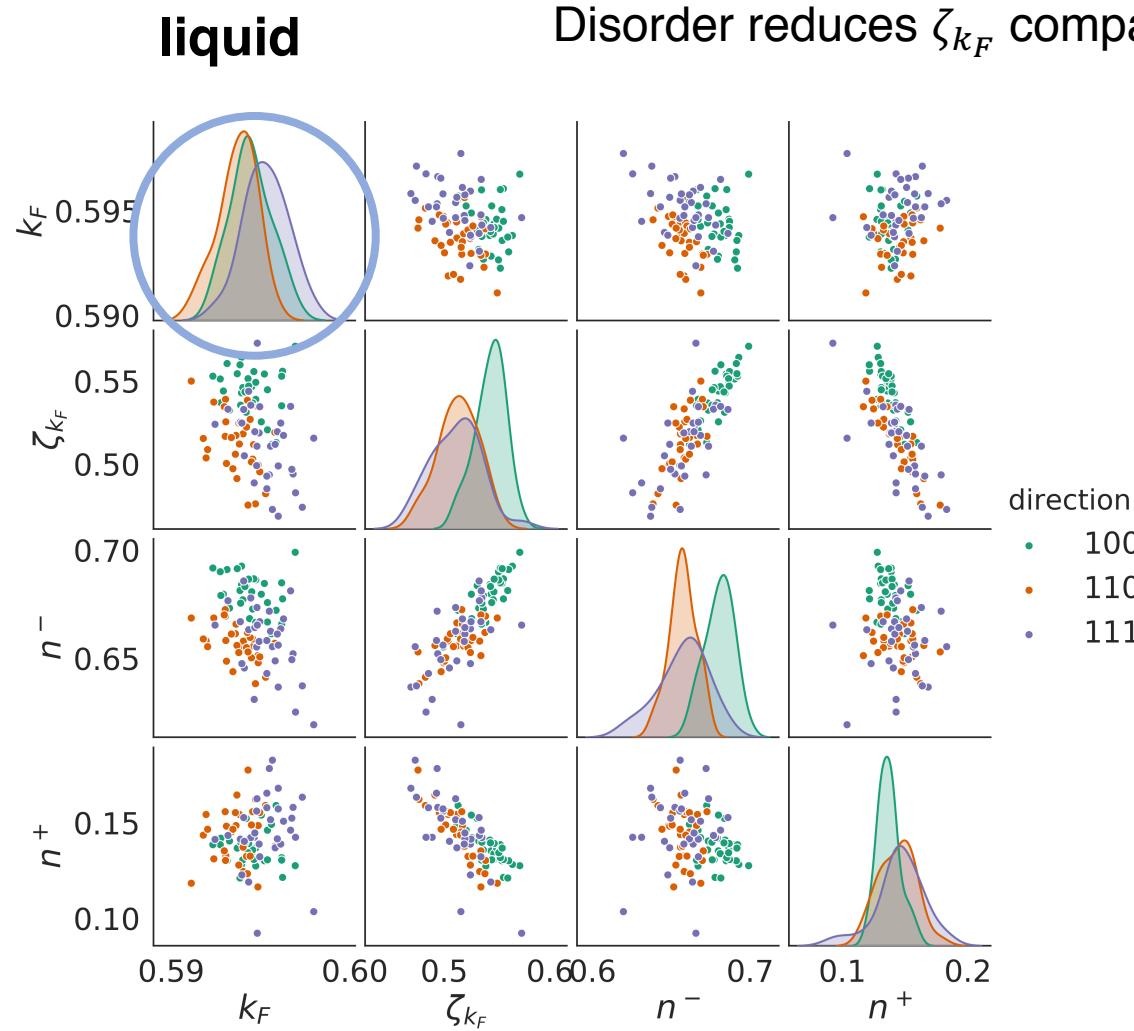
Does spectral function of the electron in the final state have a Lorentzian-like long tail?



Extract Fermi momentum k_F and jump ζ_{k_F} from disorder realizations

Liquid Fermi surface (FS) is isotropic, solid FS is not.

Solid ζ_{k_F} is lowest along [110], and is caused by low n^-



QMC Compton profile of liquid v.s. experiment

Liquid experiment is more robust -
fully isotropic sample no alignment issue

Liquid momentum distribution has no
secondary Fermi surface

Remaining discrepancy is smaller in
the liquid than solid

Still peaks at the Fermi momentum

