Cooperative electron-phonon interaction in molecular chains

Sudhakar Yarlagadda

Past Collaborators: Sanjoy Datta and Arnab Das

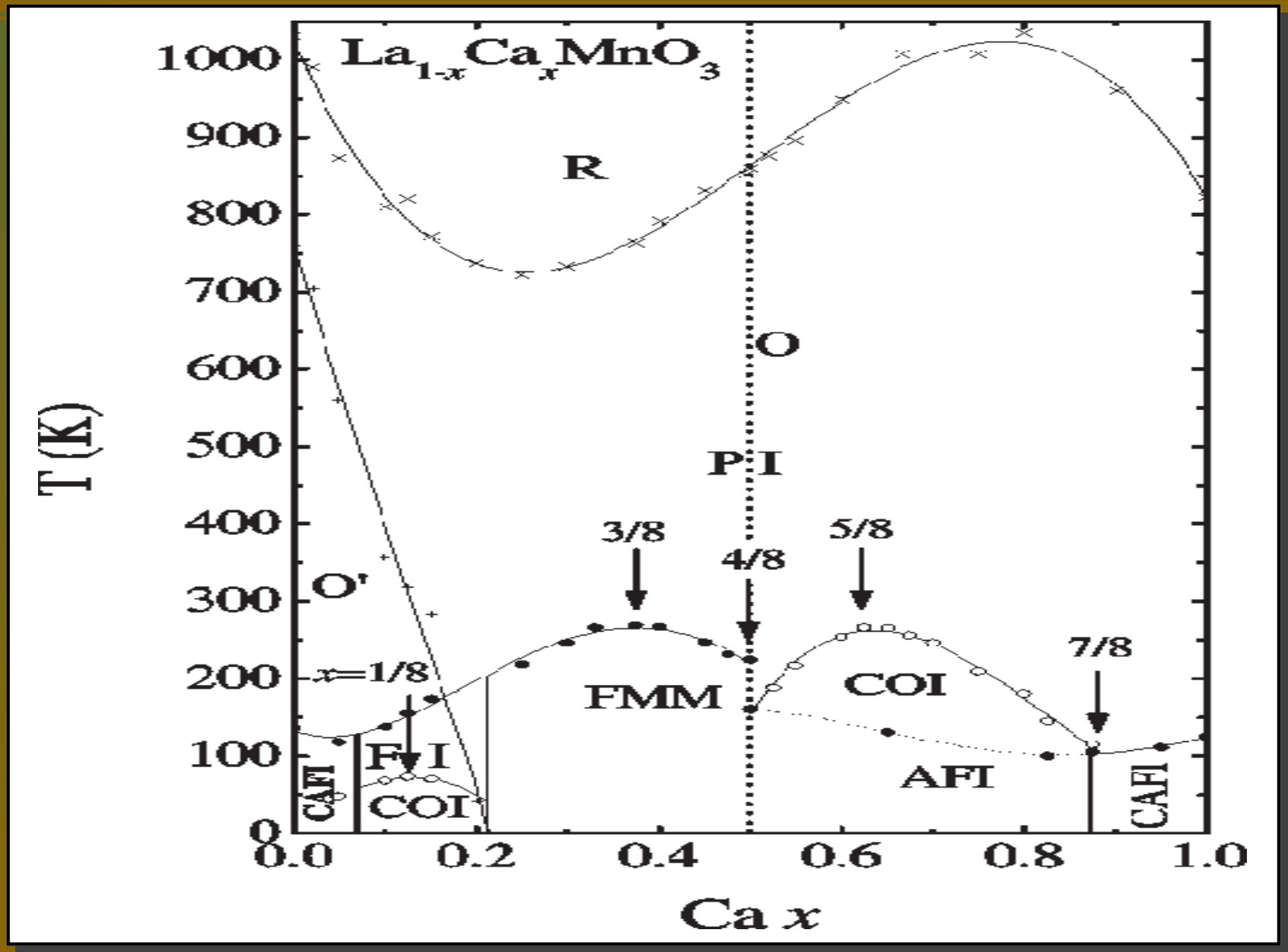
Discussion: P.B. Littlewood, S. Kos, D. E. Khmelnitskii

Cavendish Lab and Saha Institute of Nuclear Physics

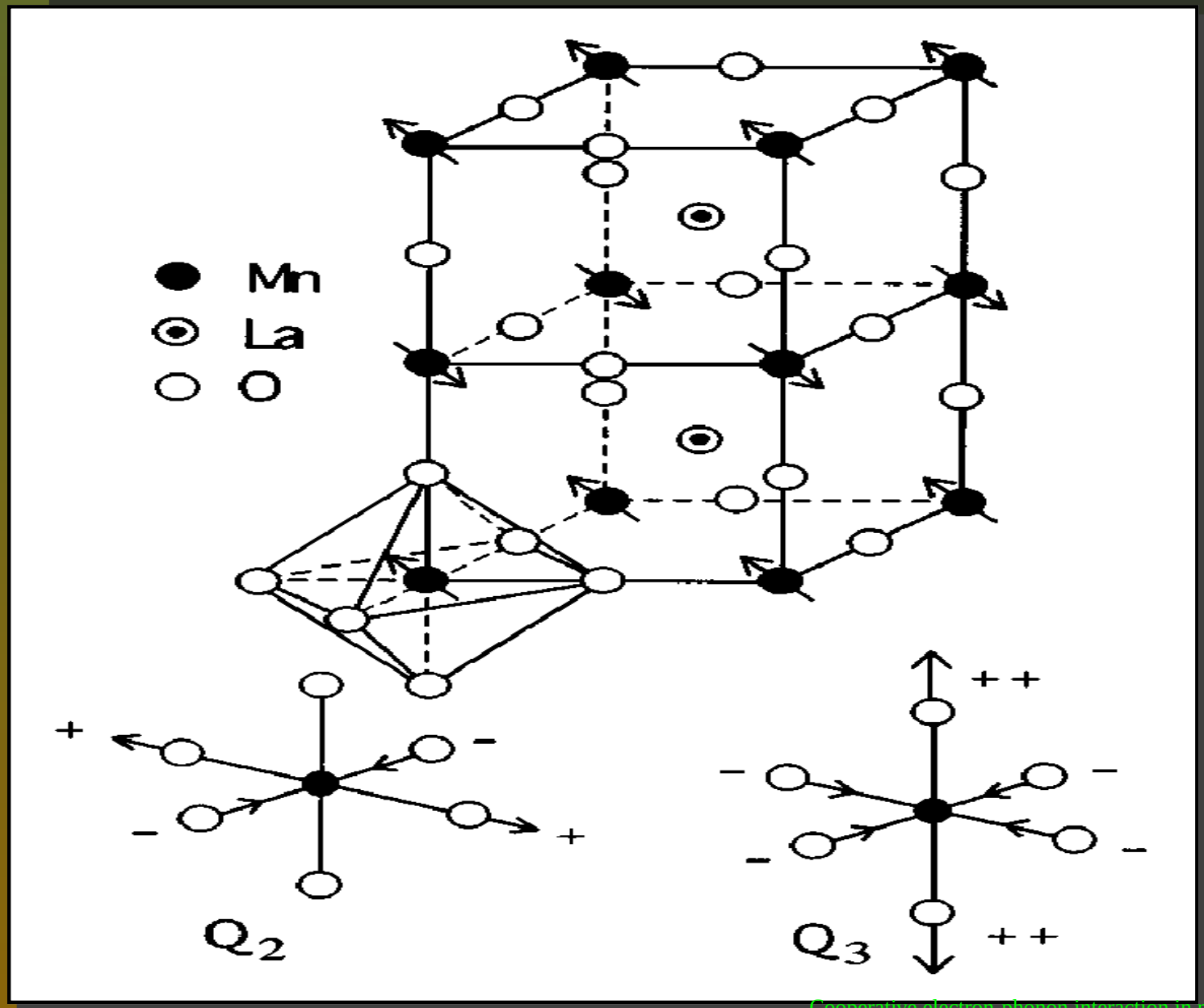
Introduction:

- Transition metal oxides (TMO) with one carrier in e_g orbitals (E.g., Mn^{3+}, Cu^{2+}, Ni^{3+}) undergo cooperative Jahn-Teller (JT) distortion. Leads to interplay between charge, spin, and orbital degrees and results in exotic phases.
- Coupling between e_g electron and neighboring oxygen is $pd\sigma$ type and produces $\approx 10\%$ JT distortions as shown by EXAFS, pulsed neutron diffraction, resonant X-ray scattering.
- In TMO, effective Hamiltonians derived for all interactions except cooperative JT (E.g., Double exchange for Hund's coupling, Gutzwiller & DMFT for Hubbard interaction, superexchange for localized spins).

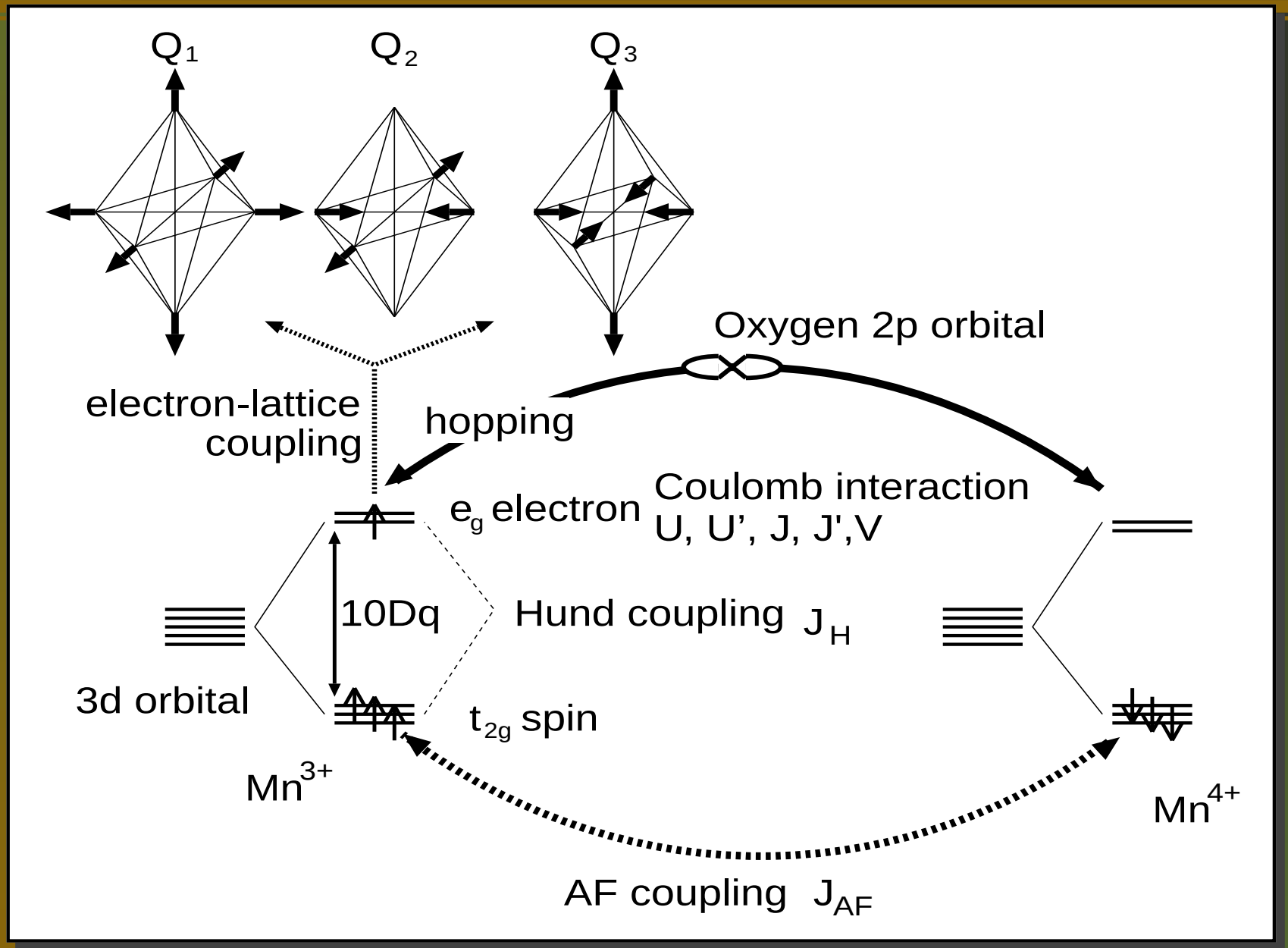
Phase Diagram (Cheong *et al.*):



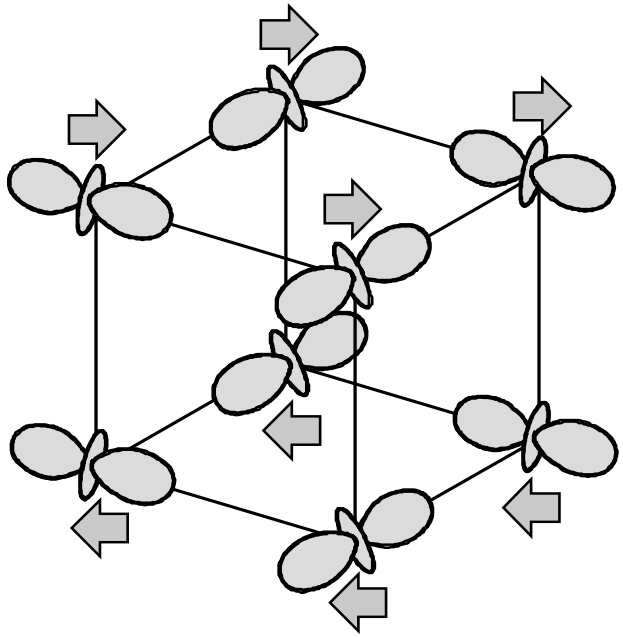
$LaMnO_3$ Structure:



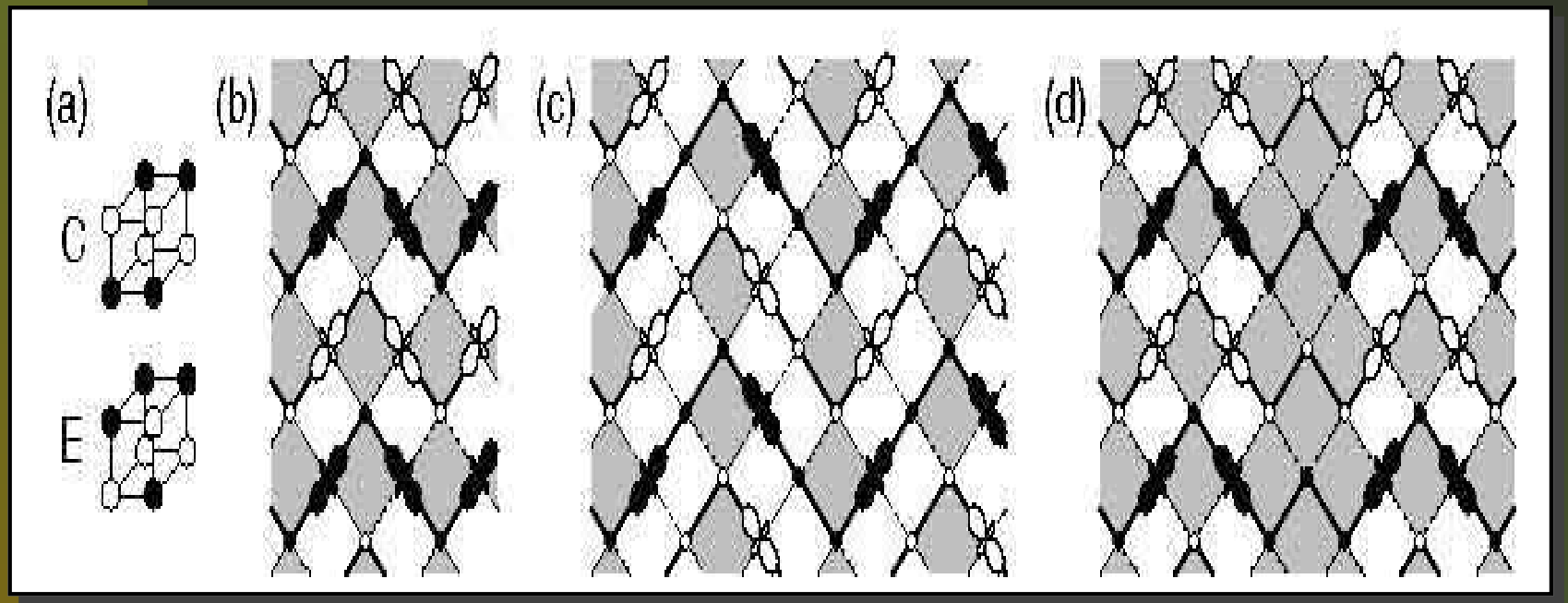
Jahn-Teller physics:



Orbital order in $LaMnO_3$:



(b) $x = 0.5$**;** **(c) & (d)** $x = 2/3$



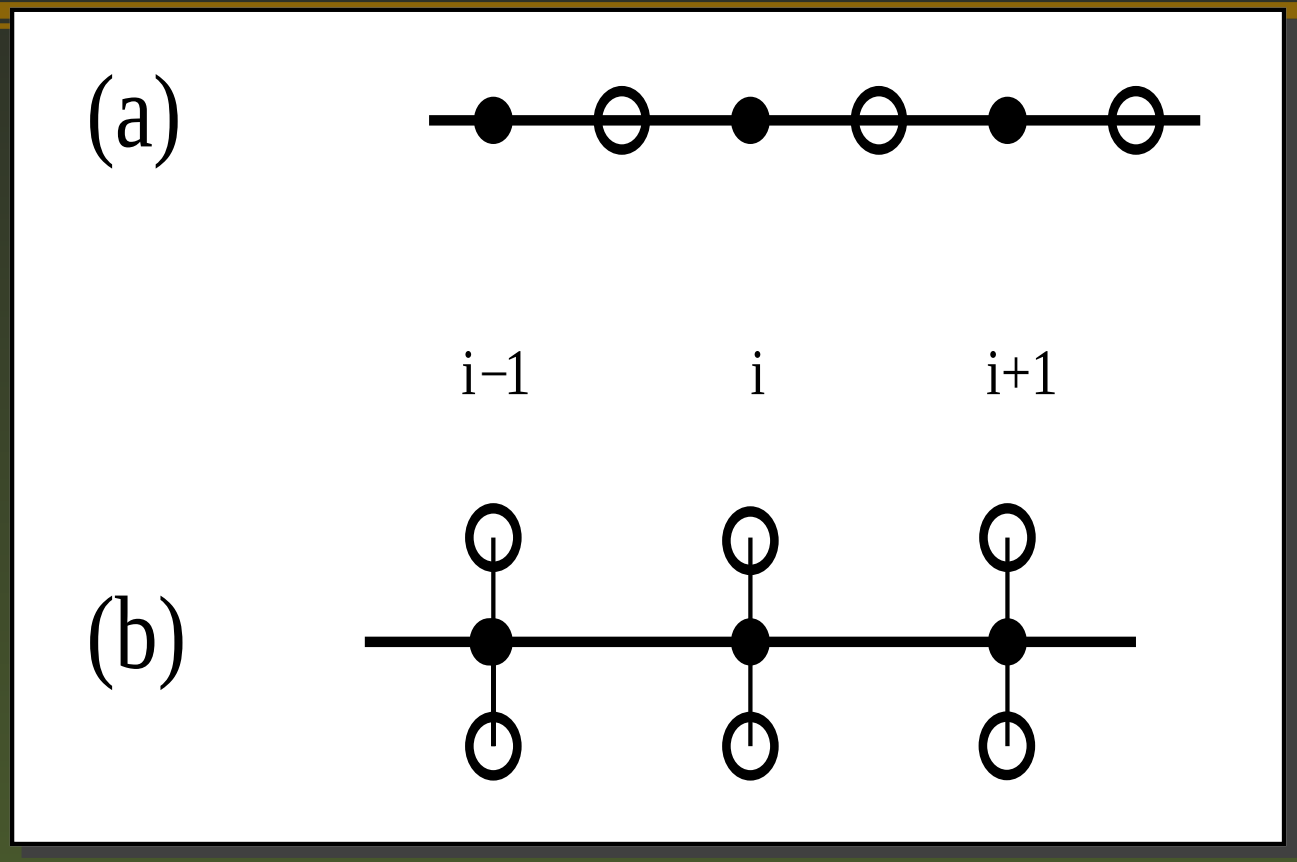
$La_{1-x}Ca_xMnO_3$

Our work overview:

- Controlled analytic treatment of many-polaron effects Holstein model has been reported only recently.
Sanjoy Datta, Arnab Das, and Sudhakar Yarlagadda, Phys. Rev. B, **71** 235118 (2005).
S. Datta and S. Yarlagadda, Phys. Rev. B, **75** 035124 (2007).

- Cooperative interaction leads to non-local distortion which changes nature of long range order.

- Cooperative strong electron-phonon interaction changes dominant hopping from nearest-neighbor to next-to-nearest-neighbor. Strong interaction gives *conducting commensurate* CDW with period independent of density.
S. Yarlagadda arXiv:0712.0366



Molecular chains with d_{z^2} orbital hopping sites (filled circles) and oxygen sites (empty circles) in (a) our cooperative electron-phonon interaction model and (b) Holstein model.

HAMILTONIAN: $H = H_t + H_{ep} + H_l$, where

(1) $$H_t = -t \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}),$$

(2) $$H_l = \omega_0 \sum_j a_j^\dagger a_j,$$

and for Holstein model electron-phonon interaction

(3) $$H_{ep} = -\sqrt{2} g \omega_0 \sum_j n_j (a_i^\dagger + a_i),$$

and for *our model*

(4) $$H_{ep} = -g \omega_0 \sum_j (n_j - n_{j+1})(a_i^\dagger + a_i),$$

Modify Lang-Firsov transformation $\tilde{H} = e^S H e^{-S}$, with $S = g\sum_j (a_j - a_j^\dagger)(n_j - n_{j+1})$.

Then, one obtains $\tilde{H} = H_0 + H_1$, where

$$H_0 = \omega_0 \sum_j a_j^\dagger a_j - 2\omega_0 g^2 \sum_j n_j + \omega_0 g^2 \sum_j n_j n_{j+1}$$

$$-te^{-3g^2} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}), \quad (5)$$

$$H_1 = \sum_j H_j = -te^{-3g^2} \sum_j (c_j^\dagger c_{j+1} \{\mathcal{T}_+^{j\dagger} \mathcal{T}_-^j - 1\} + \text{H.c.}),$$

with $\mathcal{T}_\pm^j = \exp[\pm g(2a_j - a_{j-1} - a_{j+1})]$.

Second Order Perturbation for $te^{-3g^2} << \omega_0$:

$$-H^{(2)}\frac{\omega_0}{t^2 e^{-6g^2}} =$$

$$\sum_j \{[n_j(1-n_{j+1})+(1-n_j)n_{j+1}]$$

$$[F_3(4,1,1)+2F_2(4,1)+F_1(4)+2F_1(1)+F_2(1,1)]$$

$$+[c^\dagger_{j-1}(1-2n_j)c_{j+1}+\text{H.c.}][2F_1(2)+F_2(2,2)]$$

$$+2[c^\dagger_{j-2}c_{j-1}c^\dagger_{j+1}c_j+\text{H.c.}]F_1(1)$$

$$+2[c^\dagger_{j-1}c_{j-2}c^\dagger_{j+1}c_j+\text{H.c.}]F_1(-1)\Big\}, \quad (6)$$

where

$F_n(\alpha_1,...,\alpha_n) \equiv \sum_{m_1=1}^{\infty}...\sum_{m_n=1}^{\infty}\frac{(\alpha_1 g^2)^{m_1}...(\alpha_n g^2)^{m_n}}{m_1!...m_n!(m_1+...+m_n)}$.

When $g^2 >> 1$, $F_n \approx \exp(g^2\sum_{i=1}^n \alpha_i)/(g^2\sum_{i=1}^n \alpha_i)$ for $\sum_{i=1}^n \alpha_i \geq 1$.

For $g^2 >> 1$,

$$H_{eff}^{Coop} = -\left[2g^2\omega_0 + \frac{t^2}{3g^2\omega_0}\right]\sum_j n_j(1-n_{j+1})$$

$$-te^{-3g^2}\sum_j (c_j^\dagger c_{j+1} + \text{H.c.})$$

$$-\frac{t^2e^{-2g^2}}{4g^2\omega_0}[c_{j-1}^\dagger(1-2n_j)c_{j+1} + \text{H.c.}]. \quad (7)$$

$$H_{eff}^{\text{Holstein}} = -2g^2\omega_0\sum_j n_j - \frac{t^2}{2g^2\omega_0}\sum_j n_j(1-n_{j+1})$$

$$-te^{-2g^2}\sum_j (c_j^\dagger c_{j+1} + \text{H.c.})$$

$$-\frac{t^2e^{-2g^2}}{2g^2\omega_0}\sum_j [c_{j-1}^\dagger(1-2n_j)c_{j+1} + \text{H.c.}]. \quad (8)$$

At $g^2 >> 1$:
(i) For Holstein case, NN hopping $>>$ NNN hopping.
(ii) *For Cooperative case, NNN hopping dominates!*

Physical expl. for Holstein model:

• Although results are for $te^{-2g^2} << \omega_0$ & $g^2 >> 1$, we explain for restrictive adiabatic ($t >> \omega_0$) & small polaronic regime ($g^2\omega_0 >> t$).

• Coeff. $\frac{t^2}{2g^2\omega_0}$ of $\sum_j n_j(1-n_{j+1})$ results from adiabatic hopping from j to $j+1$ and back. II order perturbation gives t^2/(energy change).

• Coeff. $\frac{t^2e^{-2g^2}}{2g^2\omega_0}$ of $\sum_j(c^\dagger_{j-1}(1-2n_j)c_{j+1}+\text{H.c.})$ results when *intermediate* j does not distort/relax and gives $t\exp[-2g^2]\times\frac{t}{2g^2\omega_0}$ where $t\exp[-2g^2]$ is due to distortions at sites $j-1$ and $j+1$.

Small Parameter

Higher order terms in perturbation dominated by electron hops between j and $j+1$. Dominant kth order term for even k:

$$\omega_0 \left[\frac{t}{g\omega_0}\right]^k \sum_j n_j(1-n_{j+1}), \tag{9}$$

for odd k:

$$te^{-\gamma g^2} \left[\frac{t}{g\omega_0}\right]^{k-1} \sum_j (c_j^\dagger c_{j+1} + \text{H.c.}), \tag{10}$$

where γ = 2 (3) for non-cooperative (cooperative) case. Each term should $<$ ω_0 implies *small parameter* is $t/(g\omega_0)$.

Using Wigner-Jordan transformation $\sigma_i^+ = \Pi_{j<i}(1-2n_j)c_i^\dagger$, we map exactly on to the following NNN anisotropic Heisenberg spin chain:

$$H_{eff}^{spin} = -g^2\omega_0 \sum_j \sigma_j^z - J_1 \sum_j (\sigma_j^+ \sigma_{j+1}^- + \text{H.c.})$$
$$+ J^z \sum_j \sigma_j^z \sigma_{j+1}^z - J_2 \sum_j (\sigma_{j-1}^+ \sigma_{j+1}^- + \text{H.c.}),$$

Although NNN interactions do not produce frustration, cannot be solved by Bethe ansatz. Hence we analyze properties numerically by using modified Lanczos technique [Gagliano *et al.* PRB **34**, 1677 (1986)].

Effective Hamiltonian

$$H^C_{eff} = -T\sum_j (c^\dagger_{j-1}(1-2n_j)c_{j+1} + \text{H.c.})$$

(11)
$$+V\sum_j n_j n_{j+1}.$$

Although $T/V << 1$, due to novelty, we study for a general T/V.

For $T/V << 1$, in rings with even sites (e-rings), only one sub-lattice occupied. Because each new electron added to system has more hopping sites on same sub-lattice as previous electrons.

For $V = 0$, for e-rings, both sub-lattices equally occupied.

Correlation Functions:

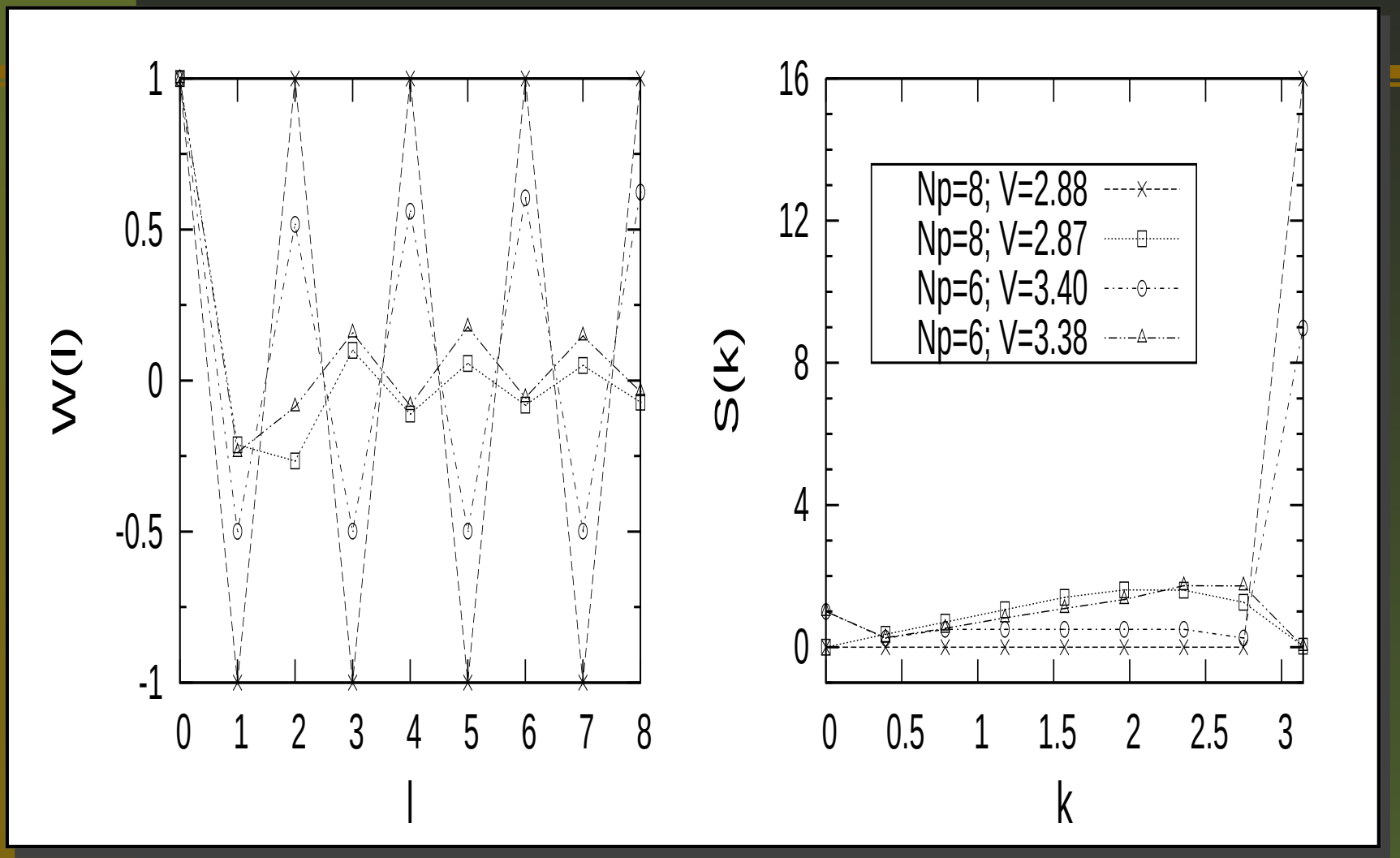
Density-density correlation function:
$w_l = 4/N \sum_j \langle (n_j - 0.5)(n_{j+l} - 0.5) \rangle$.

Static structure factor:
$S(k) = \sum_l \exp(ikl) w_l$.

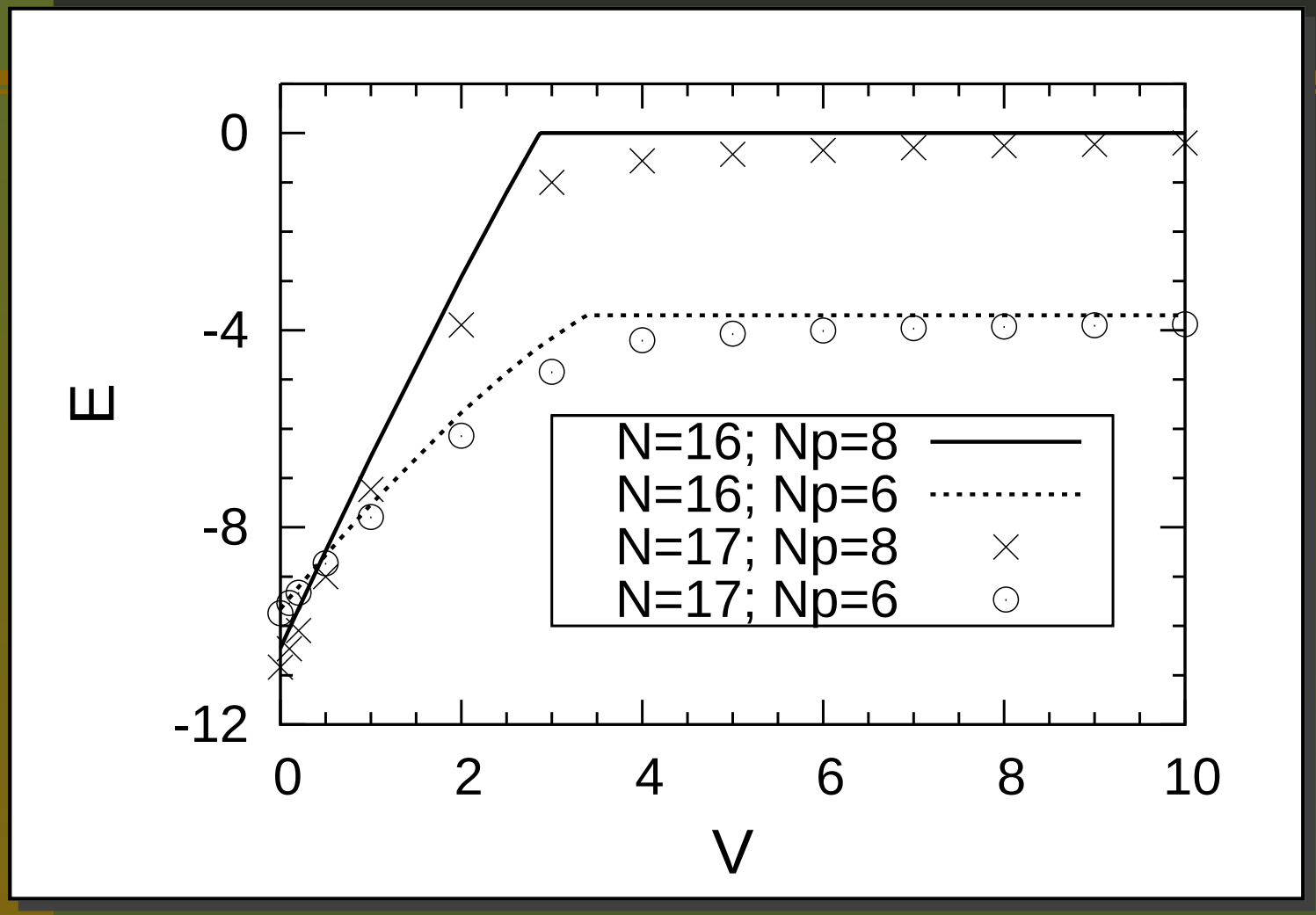
At $V = 0$, for even no. of particles N_p, $S(\pi) = 0$; and for odd N_p, $S(\pi) = 4/N$.

When $V/T >> 1$, we get $S(\pi) = 4N_p^2/N$ and $w_{l\text{odd}} = 1 - 4N_p/N$.

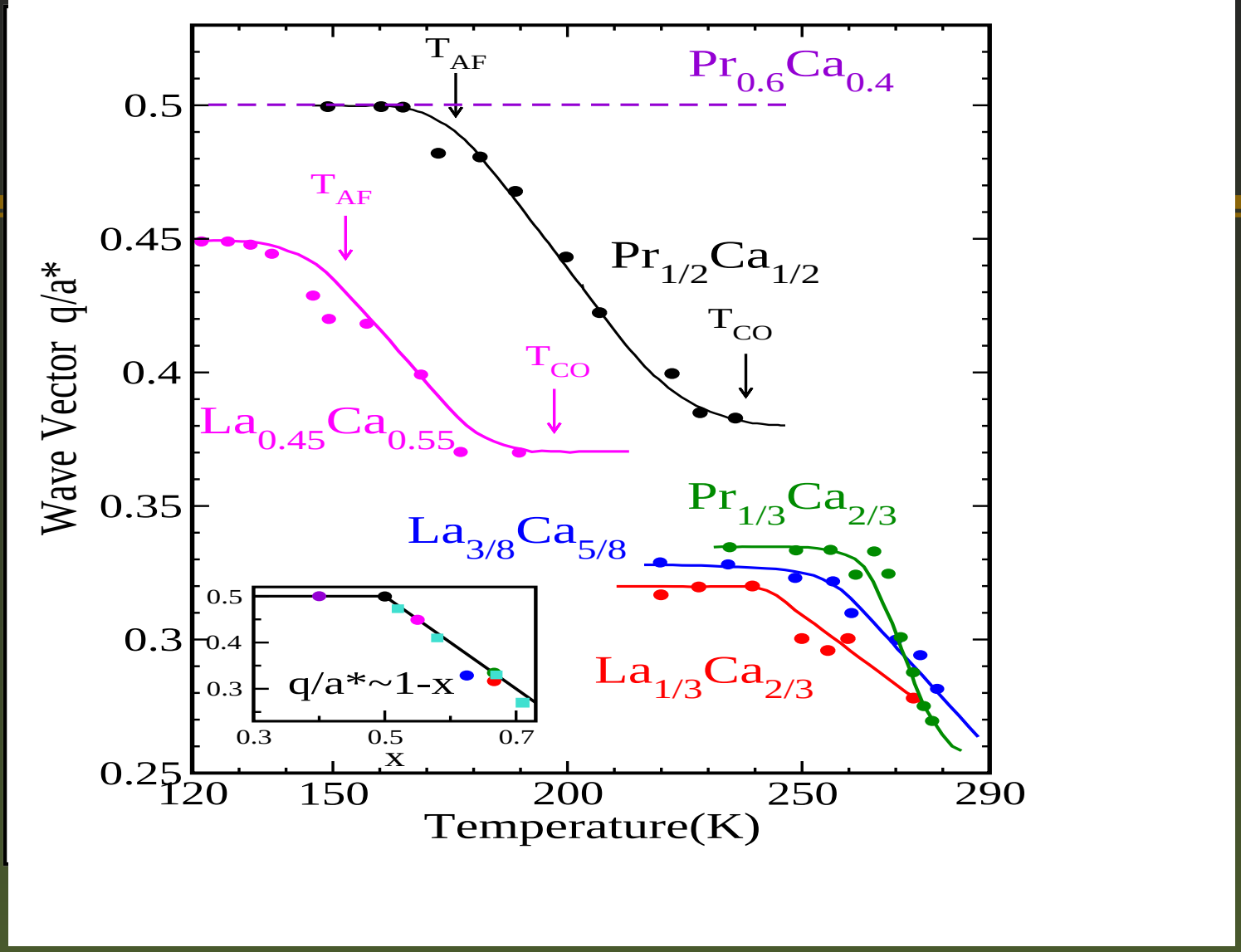
At $(V/T)_{crit}$, $S(\pi)$ jumps from 0 to about $4N_p^2/N$ and $w_{l\text{odd}} \approx 1 - 4N_p/N$.



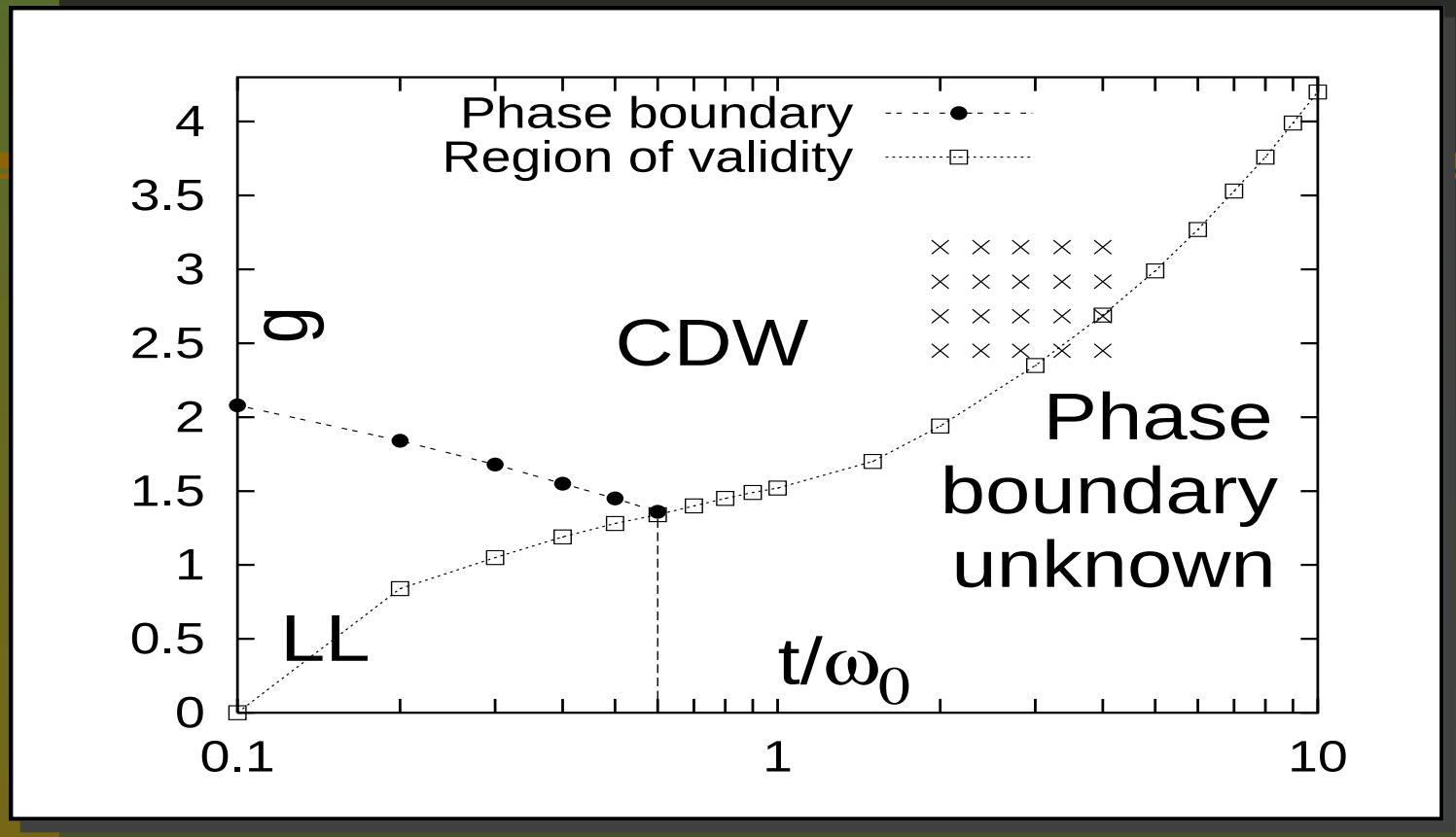
Plot of the density-density correlation function $W(l)$ and structure factor $S(k)$ for a 16-site ring with N_p electrons, interaction strength V, and hopping $T = 1$.



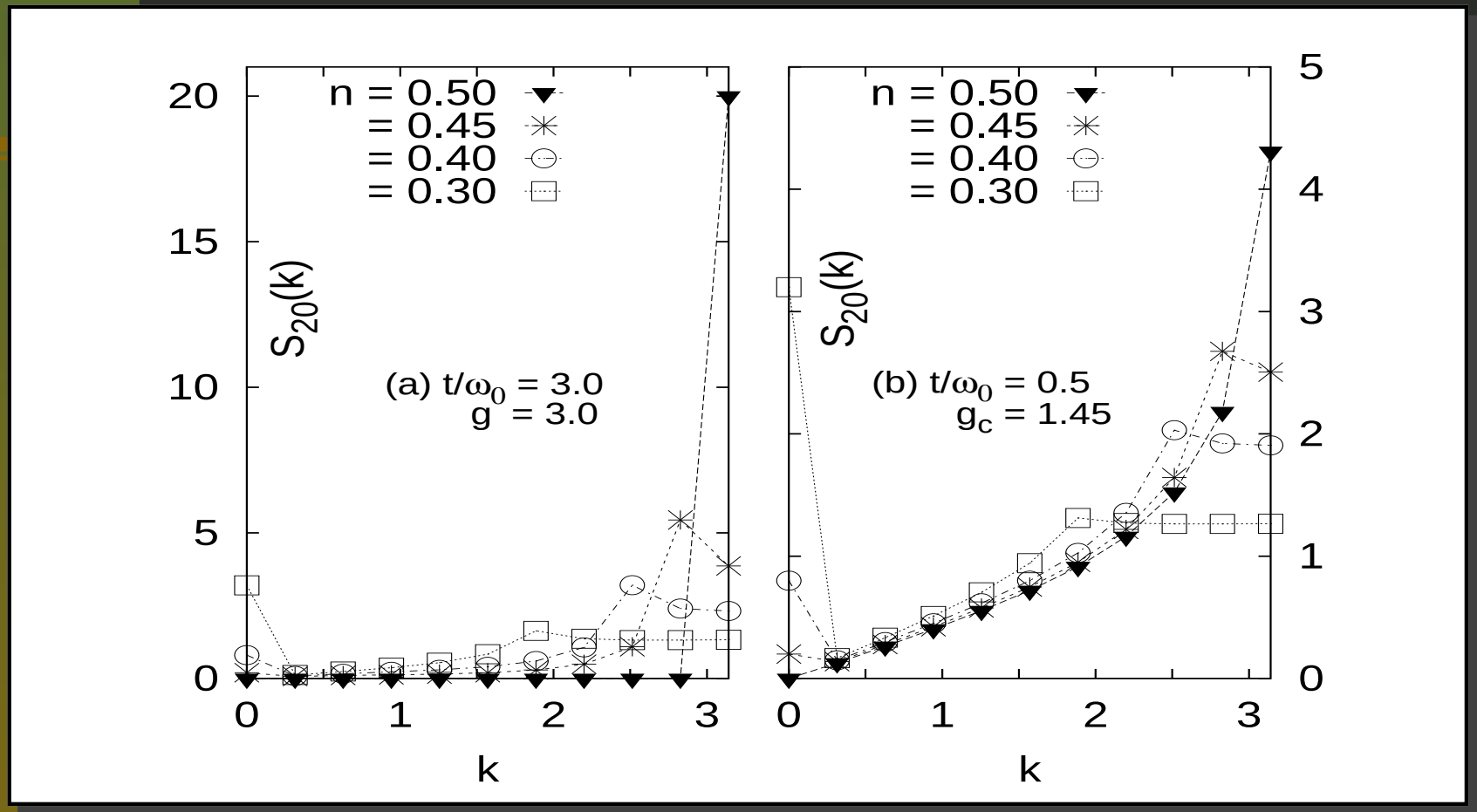
Plots of Energy (E) versus interaction strength (V) for rings with N sites and N_p electrons. For e-rings CDW phase transition occurs at the kink. For N-odd, no 2 sub-lattices and no kink.



Wave vector of the modulation $q/a^\star$ versus temperature for $Pr_{1x}Ca_xMnO_3$ and $La_{1x}Ca_xMnO_3$ at different dopings.(Littlewood *et al.*, Nature **433**, 607 (2005)



Plot of region of validity boundary and LL-CDW phase boundary for g versus t/ω_0 in the effective Holstein Hamiltonian at *half-filling*. The crosses depict realistic regime. In the region to the right of the dashed vertical line and below the region-of-validity curve the phase transition boundary cannot be determined using effective Hamiltonian.



Effective Holstein Hamiltonian Structure factor $S_N(k)$ tells about correlation lengths even in LL phase at all n. The correlation length decreases with increasing width of $S_N(k)$ near its peak at $2\pi n$. Fig. (b) is for LL-CDW transition point at $n = 0.5$, while Fig. (a) depicts situation deep inside CDW phase at $n = 0.5$. At $n = 0.5$, $S_\infty(\pi) \to \infty$ in CDW regime.

Peierls instability

• For $t/\omega_0 > 1$, in the Holstein model, LL to CDW transition condition is obtained exactly to second order in a novel blocked perturbative approach. The small parameter is $g\omega_0/t$. We correct the mean-field criterion for Peierls instability by replacing the static non-interacting susceptibility $\chi_0(2k_F, 0)$ with the dynamic one, to get $1 + 2g^2\omega_0 \mathrm{Re}\chi_0(2k_F, \omega_0) = 0$.
S. Datta and S. Yarlagadda, Phys. Rev. B **75**, 035124 (2007)

Renormalized Phonon Freq.

Heisenberg equation of motion : $\ddot{A} = -[[A, H], H]$

Mean field result : $A = Q_{\vec{p}} = \sqrt{(1/(2M\omega_0))}(a_{\vec{p}} + a^{\dagger}_{-\vec{p}})$

and the approximation $\rho_{-\vec{p}} \propto \chi_0(\vec{p}, 0) Q_{\vec{p}}$ gives

$$\ddot{Q}_{\vec{p}} = -\omega_0[1 + 2g^2\omega_0\chi_0(\vec{p}, 0)]Q_{\vec{p}} = -\omega_R^2 Q_{\vec{p}}$$

In 1D $\chi_0(\vec{p}, 0) \to -\infty$ at $p = 2k_F$.

To derive the true phonon softening, we calculate

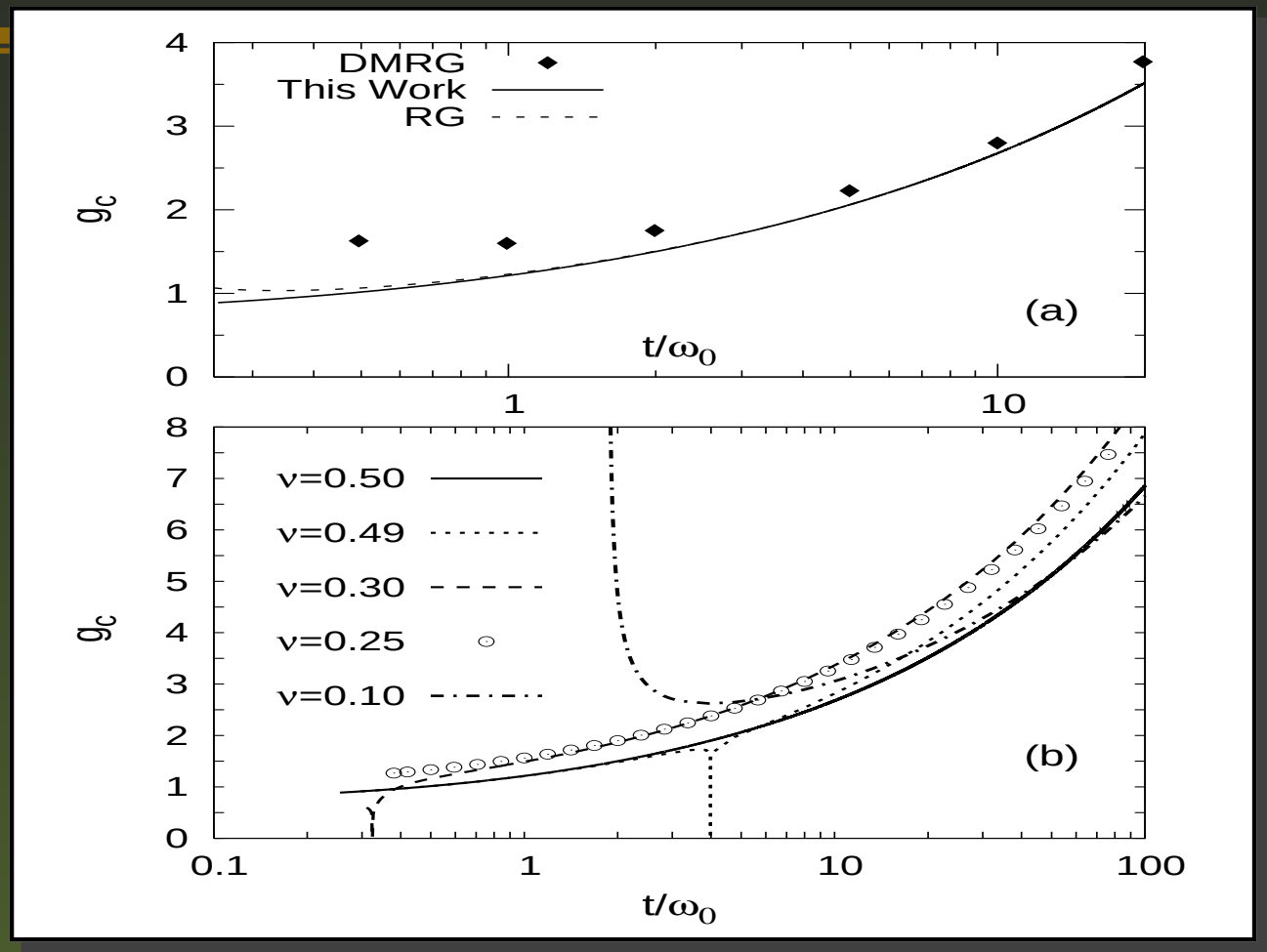
$$\langle\Phi_m|\ddot{A}|\Phi_n\rangle = -(E_{\Phi_m} - E_{\Phi_n})^2\langle\Phi_m|A|\Phi_n\rangle$$

Instability occurs when $\omega_{eff}^2 = (E_{\Phi_m} - E_{\Phi_n})^2 \leq 0$ provided $\langle\Phi_m|A|\Phi_n\rangle \neq 0$. Here $|\Phi_m\rangle$'s and E_{Φ_m}'s are eigenvectors and eigenvalues of $H = H_t + H_l + \lambda H_{ep}$

Critical coupling g_c, can be expressed analytically as follows:

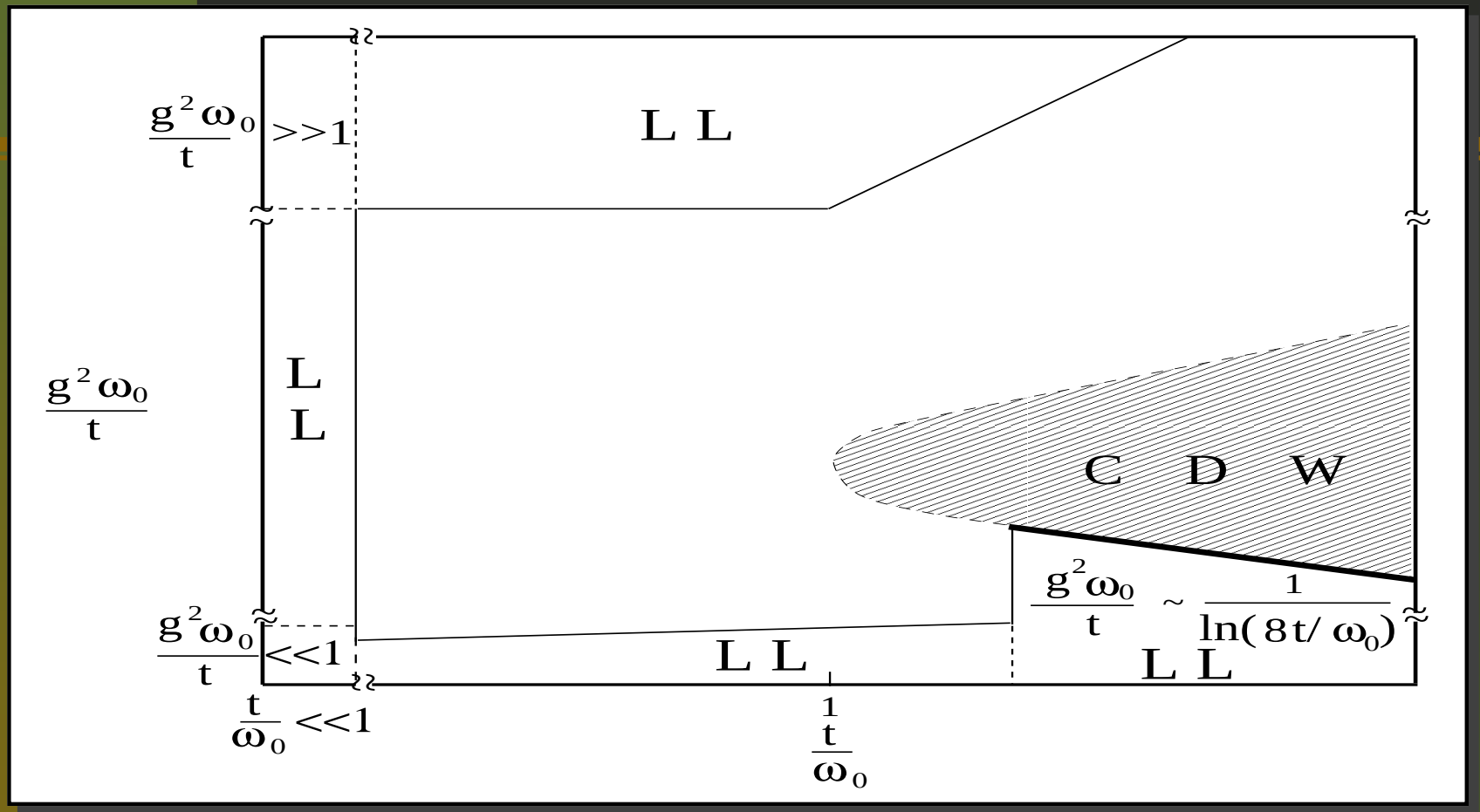
$$\frac{\pi}{g_c^2} = \frac{\gamma}{\sqrt{1-\gamma^2}} \qquad \left\{ \ln \left[\frac{(1-\sqrt{1-\gamma^2})^2 - (\gamma \tan k_F)^2}{(1+\sqrt{1-\gamma^2})^2 - (\gamma \tan k_F)^2} \right] \right.$$
$$\left. -2 \ln \left[\frac{1-\sqrt{1-\gamma^2}}{1+\sqrt{1-\gamma^2}} \right] \right\}$$

where $\gamma \equiv \omega_0/(4t \sin(k_F)) < 1$. At half-filling and for $\gamma^2 << 1$, our expression for g_c reduces to the two-cutoff renormalization result of Caron and Bourbonnais i.e., $\omega_0 = 2ct \exp(-\pi t/g^2\omega_0)$ (with $c \sim 1$), when we take $c = 4$.



TOP: Comparison with the RG and DMRG (Hamer *et al.*) results

BOTTOM: Value of g_c for various fillings



Phase diagram for Holstein model at non-half filling. Regions where CDW and LL phases certainly exist are depicted. The calculated transition from LL to CDW is indicated by a dark line along with its expression .

Summary:

- Cooperative interaction leads to non-local distortion which changes nature of long range order.
- Cooperative strong electron-phonon interaction changes dominant hopping from nearest-neighbor to next-to-nearest-neighbor. Strong interaction gives *conducting commensurate* CDW with period independent of density.
- Away from half-filling in e-rings, Holstein model yields Luttinger liquid at all interactions, whereas our model at strong interactions produces a CDW state.

Thank You