Particle Path Correlations in a Phonon Bath

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The path integral formalism is applied to derive the full partition function of a generalized Su-Schrieffer-Heeger Hamiltonian describing a particle motion in a bath of oscillators. The electronic correlations are computed versus temperature for some choices of oscillators energies. We study the perturbing effect of a time averaged particle path on the phonon subsystem deriving the relevant temperature dependent cumulant corrections to the harmonic partition function and free energy. The method has been applied to compute the total heat capacity up to room temperature: a low temperature upturn in the heat capacity over temperature ratio points to a glassy like behavior ascribable to a time dependent electronic hopping with variable range in the linear chain.

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1. INTRODUCTION

Determining the polaron properties is a relevant problem in many body theory [1,2]. The electron motion through the crystal is generally accompanied by a lattice deformation whose size and entity depend both on the strength of the electron-phonon coupling and on the value of the adiabaticity parameter peculiar of the system [3–18]. In general, the lattice deformation does not follow instantaneously the electron dragging it and the retardation effect becomes a key ingredient of this many body problem. The Holstein [19] and the Su-Schrieffer-Heeger (SSH) [20] Hamiltonian models are fundamental tools in polaron physics. While the former has been mainly used to describe electron coupling to local optical phonons, both acoustic [21] and optical branches are present in the dimerized lattice of the latter. However, acoustic phonons in the SSH model are not essentially affected by the e-ph coupling whereas optical phonons are strongly softened due to single electron polarization [22].

In this paper we address the general problem of the interplay between an electron and the optical phonon subsystem (a set of independent oscillators providing the bath for the particle) in a generalized SSH model, studying i) the temperature dependent electronic correlations induced by the dissipative phonon bath and ii) the thermodynamical behavior of the latter in the presence of a perturbating particle motion. The path integral method [23], being valid for any value of the e-ph coupling, seems particularly suitable to our task. Moreover, it naturally introduces the time (as an inverse temperature) into the formalism thus allowing us to derive the thermal particle correlation functions and the cumulant expansion for the phonon free energy. In Section 2, we present the model and discuss the particle correlations in the oscillators bath. The phonon free energy is calculated in Section 3 while in Section 4 we apply the model to compute the total heat capacity of the system both in weak and strong e-ph coupling regimes. Some conclusions are drawn in Section 5.

2. THE MODEL

The 1D SSH interacting Hamiltonian reads:

\[ H = \sum_r J_{r,r+1} (f_r^\dagger f_{r+1} + f_{r+1}^\dagger f_r) \]

\[ J_{r,r+1} = -\frac{1}{2} \left[J + \alpha(u_r - u_{r+1})\right] \]  

(0.1)

where \( J \) is the hopping integral for an undistorted chain, \( \alpha \) is the electron-phonon coupling, \( u_r \) is the dimerization coordinate relative to the displacement of the atomic group on the \( r \)– lattice site along the molecular axis, \( f_r^\dagger \) and \( f_r \) create and destroy electrons on the \( r \)– group. The free Hamiltonian is given by a set of classical independent oscillators. By introducing \( x(\tau) \) and \( y(\tau') \) as the electron coordinates at the \( r \) and \( r+1 \) lattice sites, respectively and mapping \( u_r \rightarrow u(\tau) \) and \( u_{r+1} \rightarrow u(\tau') \) we transform the real space Hamiltonian of eq.(1) into the time dependent Hamiltonian:
\[ H(\tau, \tau') = J_{\tau, \tau'} \left( f^\dagger(x(\tau)) f(y(\tau')) + f^\dagger(y(\tau')) f(x(\tau)) \right) \]

\[ J_{\tau, \tau'} = -\frac{1}{2} [J + \alpha(u(\tau) - u(\tau'))] \]  

(0.2)

The SSH Hamiltonian has a twofold degenerate ground state which undergoes a Peierls instability. In real space the soliton connects the two degenerate phases with different senses of dimerizations and a localized electronic state is associated with each soliton. Both electron hopping to band states (thermal excitation) and electron hopping between solitons are allowed.

Mapping the Hamiltonian onto the time scale we set up the finite \( T \) formalism in which thermally activated electron hops become time dependent and the retarded nature of the interactions is accounted for. \( H(\tau, \tau') \) is more general than the real space SSH Hamiltonian since hopping processes are not constrained to first neighbors sites along the chain. A variable range hopping introduces some local disorder in the system [24], therefore the present approach may apply to polymers in which hopping conduction mechanisms prevail. We point out that in real systems, the Peierls gap can be smeared by temperature or doping induced disordering effects [25]. Eq.(2) displays the semiclassical nature of the model as quantum mechanical degrees of freedom interact with the classical variables \( u(\tau) \). Setting \( \tau' = 0 \), \( u(0) \equiv y(0) \equiv 0 \), averaging the electron operators over the ground state and pinning the chemical potential to the zero energy level, we write the average energy per lattice site:

\[ < H(\tau) > \over N = V(x(\tau)) + u(\tau)j(\tau) \]

\[ V(x(\tau)) = -Ja \int_0^{\pi/a} dk \cos[kx(\tau)] \cosh(\epsilon_k \tau/\hbar)n_F(\epsilon_k) \]

\[ j(\tau) = -a \int_0^{\pi/a} dk \cos[kx(\tau)] \cosh(\epsilon_k \tau/\hbar)n_F(\epsilon_k) \]  

(0.3)

where \( N = L/a \), with \( L \) the chain length and \( a \) the lattice constant. \( n_F \) is the Fermi function and \( \epsilon_k = -J \cos(k) \) is the electron dispersion relation. \( V(x(\tau)) \) is an effective term accounting for the \( \tau \) dependent electronic hopping while \( j(\tau) \) is the external source current for the oscillator path \( u(\tau) \). Averaging the electrons over the ground state we neglect the fermion-fermion correlations [26] which lead to effective polaron-polaron interactions in non perturbative analysis of the model. This approximation however is not expected to affect substantially our thermodynamical calculations. Being the energy in eq.(2) linear in the displacements we can write the general path integral [27] at any temperature as:

\[ < x(\beta)|x(0) >= \prod_i \int D\tilde{u}_i(\tau) \int Dx(\tau) \cdot \exp \left[ -\frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \sum_i \frac{M_i}{2} \left( \dot{u}_i^2(\tau) + \omega_i^2 u_i^2(\tau) \right) \right] \cdot \exp \left[ -\frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \left( \frac{m}{2} \dot{x}^2(\tau) + V(x(\tau)) - \sum_i u_i(\tau) j(\tau) \right) \right] \]  

(0.4)

where we have taken a large number of oscillators \( (u_i(\tau), i = 1..\tilde{N}) \) as the bath for the quantum mechanical particle whose coordinate is \( x(\tau) \). \( \beta \) is the inverse temperature, \( m \) is the electron mass and \( \omega_i \) are the oscillators frequencies. The oscillator masses are considered as independent of \( i \), \( M_i \equiv M \) and hereafter we set \( M = 10^4 m \). After integrating out the oscillators coordinates over the paths \( D\tilde{u}_i(\tau) \), imposing a closure condition \( \left( x(\beta) = x(0) \right) \) on the particle paths and replacing \( \tau \to \tau/\hbar \), we obtain the full partition function in the functional form

\[ Z(j(\tau)) = Z_{ph} \int Dx(\tau) \exp \left[ -\frac{m}{2} \dot{x}^2(\tau) - V(x(\tau)) - A(j(\tau)) \right] \]

\[ Z_{ph} = \prod_{i=1}^{\tilde{N}} \frac{1}{2 \sinh(\hbar \omega_i \beta/2)} \]
\[ A(j(\tau)) = -\frac{\hbar^2}{4M} \sum_{i=1}^{N} \frac{1}{\hbar \omega_i \sinh(\hbar \omega_i / 2)} \int_0^\beta d\tau_1 j(\tau_1) \int_0^\beta d\tau_2 \cosh(\omega_i(\tau_1 - \tau_2 - \beta / 2)) j(\tau_2), \]  

(0.5)

The thermodynamics of the interacting system can be derived from eqs.(5) as a function of \( J, \alpha \) and oscillators bath. An application is shown in Section 4 where the total heat capacity is computed versus temperature. In terms of the generating functional \( Z(j(\tau)) \) the two particle correlation function is defined as

\[ G^{(2)}(\tau_1, \tau_2) = \hbar^2 \left[ Z^{-1}(j) \frac{\delta^2}{\delta j(\tau_1) \delta j(\tau_2)} Z(j) \right]_{j=0} \]  

(0.6)

Then, using eqs.(5) and the fact that the source action \( A(j(\tau)) \) is quadratic in the current, we can study the effect of the phonon bath on the electronic correlations at any temperature. Setting \( \tau_2 = 0 \), we plot in Figures 1 the square root of \( G^{(2)}(\tau) \equiv x(x)x(0) > (\tau \in [0, \beta]) \) for three choices of oscillator baths: 1) a low phonon spectrum made of ten oscillators \( \hbar \omega_1 = 2meV, ..., \hbar \omega_{10} = 20meV \) (spaced by \( 2meV \), ii) an intermediate phonon spectrum with \( \hbar \omega_1 = 22meV, ..., \hbar \omega_{10} = 40meV \) and iii) an high phonon spectrum with \( \hbar \omega_1 = 42meV, ..., \hbar \omega_{10} = 60meV \). \( N \) and oscillator energies are purely arbitrary. The periodic condition \( G^{(2)}(\tau) = G^{(2)}(\beta - \tau) \) holds as a general property of the particle-phonon correlation function which, up to a prefactor, coincides with the sum of the oscillators Green functions and therefore it does not depend on the width of the electron band. At low temperatures (Fig.1(a)), small oscillator energies favor larger electronic correlations which however get the maximum value of 0.26 \( A \) at \( \tau \to 0 \). Increasing the temperature at \( T = 100K \) (Fig.1(b)) leads to a substantial enhancement of \( \sqrt{G^{(2)}(\tau)} \) which becomes of order 1\( A \) in the case of a low energy phonons bath. At room temperature (Fig.1(c)) and for the same bath the electrons are correlated over a distance of about 2\( A \) in the whole \( \tau \)-range. Larger phonon spectra tend to lock the electrons thus reducing the particle mobility over the time scale and decreasing the space electronic correlations. Since the upper limit in the \( \tau \) range of Figs. 1(a)-1(c) is necessarily \( T \) dependent we plot in Fig.2, for an intermediate phonon bath, \( \sqrt{G^{(2)}(\tau)} \) versus a common \( \tau \)-axis to emphasize the temperature effect on the particle correlations. Only the room temperature correlation function retains periodicity over the selected \( \tau \)-range.

While we focus in the following on the equilibrium thermodynamics of the particle-phonons interacting system, it should be noted that generalization of eq.(4) through the closed-time path formalism [28] would permit to derive dissipative properties due to the phonon bath friction from the two points correlation function. A density matrix study for the similar problem of a particle in a photon bath (in three dimensions) has been carried out by Haba and Kleinert [29].

### 3. PHONON FREE ENERGY

Next we turn to analyse the effect of the particle motion on the phonon subsystem. The set of \( N \) independent oscillators is perturbed by the particle path \( x(\tau) \) which couples to each oscillator through the strength \( \alpha \) (assumed independent of \( i \)) of the SSH Hamiltonian. Then, the partition function of the disturbed oscillators system can be expanded in perturbation series as

\[ Z_{\text{ph}}[x(\tau)] \simeq (1 - < C > + < C^2 > - < C^3 > + \cdot \cdot \cdot )Z_{\text{ph}} \]

\[ < C^k >= Z_{\text{ph}}^{-1} \prod_i \oint D\alpha_i(\tau) \frac{\alpha_i^k}{k!} \int_0^\beta d\tau_1 u_i(\tau_1)x(\tau_1) \cdot \int_0^\beta d\tau_2 u_i(\tau_2)x(\tau_2) \cdot \exp \left[ - \int_0^\beta d\tau \sum_i \frac{M_i}{2} (\dot{u}_i^2(\tau) + \omega_i^2 u_i^2(\tau)) \right] \]  

(0.7)

In general, the total phonon partition function in presence of an ensemble of particle paths \( [x(\tau)] \) would be given by: \( Z_{\text{ph}}^T = \oint Dx(\tau)Z_{\text{ph}}[x(\tau)] \). Here we take a single particle path, approximating it by the averaged (dimensionless) value \( < x(\tau) >= \frac{1}{T} \int_0^\beta dx(\tau) = x_0 \). Then, the odd k-terms in the series expansion vanish. Since the oscillators are decoupled (and anharmonic effects mediated by the particle path are here neglected) we can study the behavior of the cumulant terms \( < C^k > \) by selecting a single oscillator having energy \( \omega \) and displacement \( u(\tau) \). Hence, after expanding the oscillator path in \( N_F \) Fourier components

\[ u(\tau) = u_n + \sum_{n=1}^{N_F} 2 \left( R u_n \cos(\omega_n \tau) - \Im u_n \sin(\omega_n \tau) \right) \]  

(0.8)
with \( \omega_n = 2n\pi/\beta \) and taking the measure of integration

\[
\oint D\mu(\tau) \equiv \left( \frac{1}{2} \right)^{2N_F} \frac{2\pi \cdot 2N_F\pi}{\sqrt{2\lambda(M^{2N_F+1})}} \int_{-\infty}^{\infty} du_0 \prod_{n=1}^{N_F} \int_{-\infty}^{\infty} d\mu_n \int_{-\infty}^{\infty} d\lambda_n (0.9)
\]

with \( \lambda_M = \sqrt{\pi \hbar^2 / \beta M} \), we obtain for the \( k = th \) cumulant the following expression

\[
< C_k >_{N_F} = Z_{ph}^{-1} \frac{\alpha \omega_0}{k!} \frac{\beta \lambda_M^k (k-1)!}{\pi \omega \omega^k} \cdot \frac{(2\pi)^2}{(2\pi)^2 + (\omega)^2} \cdots \frac{(2N_F\pi)^2}{(2N_F\pi)^2 + (\omega)^2} (0.10)
\]

Since the cumulants should not depend on the number of Fourier components in the particle path expansion, eq.(10) provides a criterion to set the minimum \( N_F \) (at any temperature and for any oscillator) through the condition \( 2N_F\pi \gg \omega \). The thermodynamic properties of the perturbed oscillator can be computed observing that the cumulant corrections to the free energy are given by:

\[
F_{cum} = -\frac{1}{\beta} \ln [1 + < C^2 > + < C^4 > + < C^6 > + \ldots] (0.11)
\]

In Fig.3(a), the three lowest order cumulants are plotted for a weak \( e-ph \) coupling and an high frequency oscillator. At very low temperatures, the cumulants attain the largest values which are substantially independent of the \( k \)-order. By increasing \( T \) all cumulants decrease, \( < C^2 > \) yields the dominant contribution and the perturbation expansion converges rapidly. As shown in Fig.3(b), the free energy corrections are not relevant due to the weak \( \alpha \) coupling. Note that \( F^{(k)}_{cum} \) includes \( F_{ph} \) plus the perturbation given by eq.(11) to the \( k \)-order. The \( k = 4 \) correction is not appreciable with respect to \( F^{(2)}_{cum} \).

In Figures 4 we take a sizeable \( e-ph \) coupling (whose order of magnitude applies to a polymer as polyacetylene), a factor ten larger than in Figs.3: at low \( T \), high order cumulants have to be included in the series expansion but the temperature range (in which their contribution is relevant) shrinks by increasing \( k \). An high number of Fourier components is required in order to get numerical convergence (i.e., \( N_F \sim 18000 \)) at \( T = 1K \) signalling that the particle dynamics strongly interferes with the oscillator at low \( T \). For any \( \alpha \) and any \( T \), one determines the \( k \)-order which makes the cumulant series convergent. For instance, being at \( T \sim 150K \): \( < C^8 > \sim < C^6 > \sim < C^4 > \), the series can be truncated for \( k = 6 \) at \( T > 150K \). Instead, at \( T \sim 90K \), \( < C^{10} > \sim < C^8 > \sim < C^6 > \) so that the \( k = 8 \) term suffices in the series expansion at larger temperatures. Note however that high order cumulant terms should be handled with care in computation of physical quantities since they may provide some significant contributions to the free energy, mainly at growing temperatures. As it is shown in Fig.4(b), the largest correction to the free energy is due to the \( k = 2 \) term which strongly reduces the harmonic value in the whole temperature range whereas the \( k = 4 \) and \( k = 6 \) contributions are also relevant although of decreasing importance. The \( k = 8 \) correction, still appreciable in the range \( 50K \leq T \leq 200K \), tends to vanish above room temperature. By enhancing the temperature, cumulants and free energy become numerically stable taking a smaller \( N_F \): at \( T = 300K \), \( N_F \sim 60 \).

4. HEAT CAPACITY

By mapping the electronic hopping motion onto the time scale, we have introduced a continuum version of the interacting SSH Hamiltonian. Unlike previous [24] approaches however, our path integral method is not constrained to the weak \( e-ph \) coupling regime and it can be applied to any range of physical parameters. To compute eqs.(5) one has to select the class of particle paths which mainly contribute to the partition function and fix the physical quantities characterizing the system: the bare hopping integral \( J \), the oscillator frequencies \( \omega_i \) and the effective coupling \( \chi = \alpha^2 \hbar^2 / M \) (in units meV).\(^2\)

We take here a narrow band system (\( J = 100meV \)) to be consistent with previous investigations [30] and with the caveat that electron-electron correlations may become relevant in narrow bands. The total heat capacity has been first (Fig.5) computed up to room temperature assuming the low phonon spectrum of Fig.1. The lowest energy oscillator yields the largest contribution to the phonon partition function mainly in the low temperature regime while the \( \omega_1 \) oscillator essentially sets the phonon energy scale which determines the size of the \( e-ph \) coupling. A larger number \( N \) of oscillators in the aforesaid range would not significantly modify the calculation.

In the discrete SSH model, the value \( \tilde{\alpha} \equiv 4\alpha^2 / (\pi \kappa)J \sim 1 \), marks the crossover between weak and strong \( e-ph \) coupling, with \( \kappa \) being the effective spring constant. In the continuum and semiclassical model of eq.(5) the effective
coupling is the above defined $\chi$. Although in principle, discrete and continuum models may feature non coincident crossover parameters, we assume that the relation between $\alpha$ and $J$ obtained by the discrete model crossover condition still holds in our model. Hence, at the crossover we get: $\chi_c \sim \pi \hbar^2 \omega_{10}^2 / 64$. This means that, in Fig.5, the crossover is set at $\chi_c \sim 2000 \text{meV}^3$. The total heat capacity over temperature ratio shows a peculiar low temperature upturn (also in the weak $\chi$ regime) which can be mainly ascribed to the sizable effective hopping integral term $V(x(\tau))$. The $e$-$ph$ coupling however determines the shape of the low $T$ anomaly. The small phonon contribution to the heat capacity is also reported on to point out that the Dulong Petit value is achieved at $T \geq 200K$.

The effect of the oscillators on the heat capacity is pointed out in Fig.6 where we take the intermediate phonon bath with energies: $\hbar \omega_1 = 22 \text{meV}$,..., $\hbar \omega_{10} = 40 \text{meV}$. Accordingly the crossover is set at $\chi_c \sim 8000 \text{meV}^3$ and three plots out of five lie in the strong $e$-$ph$ coupling regime. The heat capacity grows fast versus temperature at strong couplings due to the source action contribution whereas the presence of the low $T$ upturn in the total heat capacity over $T$ ratio is confirmed. Note that, due to the enhanced oscillators energies, the phonon heat capacity saturates at $T \sim 400K$.

Integrating eq.(5), we select, at any temperature, the ensamble of particle paths over which the hopping potential $V(x(\tau))$ is evaluated. This ensamble is therefore $T$ dependent. However, given a single set of path parameters one can monitor the $V(x(\tau))$ behavior versus $T$. It turns out that the hopping decreases by lowering $T$ but its value remains appreciable also at low temperatures ($\leq 20K$). Since the $d\tau$ integration range is larger at lower temperatures, the overall hopping potential contribution to the total action is relevant also at low $T$. Precisely this property causes the anomalous upturn in the heat capacity linear coefficient. Summing over a large number of paths is essential to recover the correct thermodynamical behavior of the heat capacity in the zero temperature limit.

Further investigation also reveals that the upturn persists both in the extremely narrow ($J \sim 10 \text{meV}$) and in the wide band ($J \sim 1 \text{eV}$) regimes. Our method accounts for a variable range hopping on the $\tau$ scale which corresponds physically to introduce some degree of disorder along the linear chain. This feature makes our model more general than the standard SSH Hamiltonian with only real space nearest neighbor hops. Although I am not aware of any other direct computation of specific heat in the SSH model, hopping type mechanisms have been suggested [31] to explain the striking conducting properties of doped polyacetylene at low temperatures. Since the specific heat directly probes the density of states and integrating over $T$ the specific heat over $T$ ratio one can have access to the experimental entropy, the method here presented may provide a new approach to analyse the transition to a disordered state which indeed exists in polymers [32]. In this regard it is worth remarking that glassy systems [33] infact exhibit a low entropy, the method here presented may provide a new approach to analyse the transition to a disordered state which indeed exists in polymers [34,35].

5. CONCLUSIONS

We have developed a general path integral method to study the interplay between electron motion and oscillators bath in a semiclassical Su-Schrieffer-Heeger model. Using the fact that the time dependent average energy is linear in the oscillator displacement, we have analytically deduced the full partition function as a functional of the $e$-$ph$ source term and computed the two particle correlations induced by the phonon baths at some selected temperatures: at increasing temperatures the electrons are correlated over large distances. Then, we have focussed on the perturbing effect of the electron particle motion on the thermodynamics of a single oscillator. After expanding the time dependent oscillator path in Fourier series, we have derived the $k-$ order cumulant correction (eq.(10)) to the oscillator partition function in the case of a time averaged electron particle path. At decreasing temperatures an increasing number ($N_F$) of Fourier components in the oscillator path is required to compute the cumulant terms with accuracy. $N_F$ is also a growing function of the oscillator energy. The proposed method permits to evaluate, for a given $e$-$ph$ coupling, the cumulant corrections to the harmonic partition function and free energy of each oscillator at any temperature. While higher $k-$ order terms become more relevant at low $T$ and they have to be included in the partition function series expansion, the main corrections to the harmonic free energy are instead ascribable to the lower $k-$order cumulants and their effect is also evident at increasing temperatures. Further refinements on the presented results may be obtained by integrating the oscillator partition function over an ensamble of $\tau$ dependent particle paths. Finally, the path integral method has been applied to compute the heat capacity of the system as a function of the $e$-$ph$ coupling and the oscillators energies. We find a peculiar upturn in the low temperature plots of the heat capacity over temperature ratio indicating that a glassy like behavior can arise in the linear chain as a consequence of a time dependent electronic hopping with variable range.
FIG. 1. Square root of the two-points correlation functions in units Å. A bath of ten phonon oscillators is considered, the largest phonon energy being \( \hbar \omega_{10} = 40 \text{meV} \) (intermediate phonon spectrum) and \( \hbar \omega_{10} = 60 \text{meV} \) (high phonon spectrum). (a) \( T = 1 \text{K} \), (b) \( T = 100 \text{K} \), (c) \( T = 300 \text{K} \).

FIG. 2. Square root of the two-points correlation functions in units Å plotted, at different temperatures, in the range \( \tau < 0.04 \text{meV}^{-1} \). An intermediate phonon spectrum is considered, the largest oscillator energy being \( \hbar \omega_{10} = 40 \text{meV} \).
FIG. 3. (a) Neperian logarithms of the first three cumulants in eq.(10). (b) Phonon free energy and anharmonic corrections due to the first three cumulants. The e-ph coupling $\alpha$ is in units $eV\AA^{-1}$. $\omega$ is the phonon energy.

FIG. 4. As in Fig.3 but with a large e-ph coupling $\alpha$. 
FIG. 5. Total heat capacity over temperature for three values of the effective coupling $\chi$ (in units $meV^3$). A bath of ten phonon oscillators is considered, the largest phonon energy being $\hbar \omega_{10} = 20meV$. The phonon heat capacity is also plotted.

FIG. 6. Total heat capacity over temperature for five values of the effective coupling $\chi$ (in units $meV^3$). The largest oscillator energy of the phonon bath is $\hbar \omega_{10} = 40meV$.

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CUMULANTS

\[ \omega = 1 \text{ eV} \]

\[ \ln(\langle c^6 \rangle) \]

\[ \ln(\langle c^4 \rangle) \]

\[ \ln(\langle c^2 \rangle) \]
