Abstract

We use a formalism developed in recent years to describe a reaction diffusion problem through a field theoretic representation starting from the master equation. This is accomplished using methods developed originally in Quantum Field Theory, specifically the coherent state representation of many particles. Such a field theoretic description can then be subject to Renormalization Group (RG) calculations in order to systematically understand the role of fluctuations and identify critical dimensions and parameters. The starting aim was to derive a field theoretic Hamiltonian and subsequently perform RG calculations to understand the role of fluctuations in lower dimensions. Having fallen short of our goal because of time limitations, we stop short at formulating the Hamiltonian.

Field theoretic representation of a diffusion limited positive feedback reaction

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May 7, 2010

Chemical reactions that are limited by diffusion of reacting species exhibit anomalous kinetic behavior in lower dimensions strongly diverging from mean field predicitions because of fluctuations [6]. Progress has been made in recent years in the systematic analysis of these fluctuations in reaction diffusion systems far from equilibrium using methods developed in Quantum Field Theory [3, ?]. In particular, renormalization group (RG) techniques have been applied to identify critical dimensions and signatures of dynamic phase transitions in such systems.

The basic idea of the procedure is as follows. Inhomogenous reacting systems can be described exactly by the continuous time Master Equation [2] by approximating the space as a d-dimensional lattice. The state of the system is described is described by the occupation numbers of the reactant molecules at each site of the lattice. If multiple reactant molecules are allowed to reside on a particular lattice site, the master equation can be converted to a time-dependent Schrödinger equation of bosons through the procedures of 'second-quantization' [4] well known in many-particle quantum systems[1]. This is accomplished by the use of creation and annihilation operators [5] corresponding to the reaction species at each lattice site. The Schrödinger equation is then converted to a path integral formulation by passing into the coherent state representation [4, 3]. The time dependent 'action' in the path integral now plays the role of the field theoretic Hamiltonian and may be used to compute averages values of observables.

We derive the equations for reaction system $A + B \rightarrow 2A$ on a d-dimensional lattice assuming multiple occupancy per site. We follow the procedure of Lee and Cardy [3], who considered the reaction $A + B \rightarrow \Phi$.

1 Master Equation

Master equations describing the temporal evolution of the probability distribution across the states of a system can be cast as follows,

[1] As an aside, we note that modifications to this procedure have been made to treat systems with hard core repulsions [7, 1]

$$\frac{dP(\mathcal{C};t)}{dt} = \sum_{\mathcal{C}'} \mathrm{W}_{\mathcal{C}'\to\mathcal{C}} P(\mathcal{C}';t) - \sum_{\mathcal{C}'} \mathrm{W}_{\mathcal{C}\to\mathcal{C}'} P(\mathcal{C};t) \tag{1}$$

where $\mathcal{C}$, $\mathcal{C}'$ denote configurations of the system and $\mathrm{W}_{\mathcal{C}\to\mathcal{C}'}$ denotes the transition rate for the process $\mathcal{C} \to \mathcal{C}'$. For diffusing and reacting molecules on a lattice, any configuration is described by the integer site occupation numbers denoted as $\{n_i\}= \{n_i^A,\, n_i^B\}$ for brevity. $i = 1, 2 \ldots, N$ where N is the total number of lattice sites. The master equation can be decomposed into its diffusing (D) and reacting (R) parts as follows:

$$\frac{dP(\{n_i\};t)}{dt} = \sum_i \left[\frac{\partial P(n_i;t)}{\partial t}|_D + \frac{\partial P(n_i;t)}{\partial t}|_R\right] \tag{2}$$

Here

$$\begin{aligned}\frac{\partial P(n_i;t)}{\partial t}|_D = \frac{D_A}{l_0^2} \sum_{\{e\}} \left[(n_e^A+1)P(\{\ldots,\, n_i^A-1,\, n_e^A+1,\ldots\},\, \{n_i^B\};t) - n_i^A P(\{n_i\};t)\right] + \\ + \frac{D_B}{l_0^2} \sum_{\{e\}} \left[(n_e^B+1)P(\{n_i^A\},\, \{\ldots,\, n_i^B-1,\, n_e^B+1,\ldots\};t) - n_i^B P(\{n_i\};t)\right]\end{aligned} \tag{3}$$

Here, $\{e\}$ denotes the nearest neighbors to site i on the lattice. For the reactions,

$$\begin{aligned}\frac{\partial P(n_i;t)}{\partial t}|_R = \frac{\lambda}{l_0^d} \left[(n_i^A-1)(n_i^B+1)P(\{\ldots,\, n_i^A-1,\ldots\},\, \{\ldots,\, n_i^B+1,\ldots\};t)\right] - \\ - \frac{\lambda}{l_0^d} \left[(n_i^A)(n_i^B)P(\{n_i\};t)\right]\end{aligned} \tag{4}$$

The initial condition for the system is not of high consequence when only stationary state properties are to be considered; we assume that the initial distribution is uncorrelated and Poissonian.

$$P(\{n_i^A,\, n_i^B\};0) = e^{-(N^A(0)+N^B(0))} \prod_i \frac{\bar{n_0^A}^{n_i^A}\, \bar{n_0^B}^{n_i^B}}{n_i^A! n_i^B!} \tag{5}$$

2 Master Equation to Field Theory

The state of the system is entirely described by occupation numbers $\{n_i^A,\, n_i^B\}$ at the sites $i = 1, 2, \ldots, N$ and therefore may be represented as a $2N$ dimensional state ket in the second quantization representation of bosons, $|\{n_i^A,\, n_i^B\}\rangle$. Two sets of annihilation and creation operators are introduced at each site on the lattice- $\hat{a}_i, \hat{a}_i^\dagger$ for A particles and $\hat{b}_i$, $\hat{b}_i^\dagger$ for B particles at site i. They satisfy the usual commutation relations,

$$[\hat{a}_i,\, \hat{a}_j^\dagger] \,=\, \delta_{ij} \quad , \quad [\hat{b}_i,\, \hat{b}_j^\dagger] \,=\, \delta_{ij} \tag{6}$$

All other commutators are zero. The null ket is defined for all i as,

$$\hat{a}_i|0\rangle \,=\, 0 \quad , \quad \hat{b}_i|0\rangle \,=\, 0 \tag{7}$$

A state eigenket in second quantized representation can, therefore, be written as $|\{n_i^A,\, n_i^B\}\rangle = \prod_i (\hat{a}_i^\dagger)^{n_i^A}(\hat{b}_i^\dagger)^{n_i^B}|0\rangle$. The effect of creation or annihilation operators on the above state is to raise or lower the site occupation number by 1 respectively,

$$\begin{aligned} \hat{a}_i^\dagger|\{\ldots,\, n_i^A,\, \ldots\},\, \{n_i^B\}\rangle &= |\{\ldots,\, n_i^A+1,\, \ldots\},\, \{n_i^B\}\rangle \\ \hat{a}_i|\{\ldots,\, n_i^A,\, \ldots\},\, \{n_i^B\}\rangle &= n_i^A|\{\ldots,\, n_i^A-1,\, \ldots\},\, \{n_i^B\}\rangle \end{aligned} \tag{8}$$

Consistency of 8 requires,

$$\langle\{{n'}_i^A\},\, \{{n'}_i^B\}|\{\, n_i^A\},\, \{n_i^B\}\rangle = \left(\prod_i \delta_{{n'}_i^A,n_i^A}\delta_{{n'}_i^B,n_i^B}\right)\prod_i n_i^A!n_i^B! \tag{9}$$

In terms of these operators the state of the system can be defined as a time dependent state vector as,

$$|\Phi(t)\rangle = \sum_{\{n_i^A,\, n_i^B\}} P(\{n_i^A,\, n_i^B;t\})|\{n_i^A,\, n_i^B\}\rangle \tag{10}$$

The master equation can now be transformed into a time-dependent Schrödinger equation,

$$\frac{\partial}{\partial t}|\Phi(t)\rangle = -\mathrm{H}|\Phi(t)\rangle \tag{11}$$

H is the normal ordered Hamiltonian,

$$\begin{aligned} \mathrm{H}[\{\hat{a}_i^\dagger,\, \hat{a}_i\},\, \{\hat{b}_i^\dagger,\, \hat{b}_i\}] &= \sum_{i=1}^{N}\mathrm{H}_i \\ &= -\sum_{i=1}^{N}\left(\sum_{<j>}\left[\frac{D_A}{l_0^2}\hat{a}_i^\dagger(\hat{a}_j-\hat{a}_i) + \frac{D_B}{l_0^2}\hat{b}_i^\dagger(\hat{b}_j-\hat{b}_i)\right]\right) - \\ &\quad - \frac{\lambda}{l_0^d}\sum_{i=1}^{N}\left(\hat{a}_i^\dagger(\hat{a}_i^\dagger-\hat{b}_i^\dagger)\hat{a}_i\hat{b}_i\right) \end{aligned} \tag{12}$$

The formal solution of equation 11 can be written as,

$$|\Phi(t)\rangle = e^{-\mathrm{H}t}|\Phi(0)\rangle \tag{13}$$

In such a formalism, the time-dependent expectation values of observables A can be expressed as $\langle A(t)\rangle = \sum_{\{n_i^A,\, n_i^B\}} A(\{n_i^A,\, n_i^B\})P(\{n_i^A,\, n_i^B; t\})$. Such quantities may be calculated from $|\Phi(t)\rangle$ by introducing the projection state,

$$\langle P| = \langle 0|\prod_i e^{\hat{a}_i+\hat{b}_i} \tag{14}$$

The expectation value for observable A is now expressed as,

$$\langle A(t)\rangle = \langle P|\mathrm{A}e^{-\mathrm{H}t}|\Phi(0)\rangle \tag{15}$$

The operator analog for $A(\{n_i^A,\, n_i^B\})$ can be derived by Taylor expanding the latter with respect to $\{n_i^A,\, n_i^B\}$ and substituting $n_i^A \rightarrow \hat{a}_i^\dagger \hat{a}_i$ and $n_i^B \rightarrow \hat{b}_i^\dagger \hat{b}_i$. One notes that $\langle P|$ is a right eigen-vector of any of the annihilation operators $\hat{a}_i$ or $\hat{b}_i$ with eigenvalue unity. This property implies that $\langle P|\mathrm{A}(\{\hat{a}_i^\dagger,\, \hat{a}_i\},\, \{\hat{b}_i^\dagger,\, \hat{b}_i\}) = \langle P|\mathrm{A}(\{1,\, \hat{a}_i\},\, \{1,\, \hat{b}_i\})$ if the operator A is normal-ordered.

3 Passing into coherent state representation

Standard procedures developed in Quantum Field theory enable us to convert the Schrödinger picture in equation 11 into a path integral representation. The basis for the representation are the coherent states, which are eigenstates corresponding to the annhilation operators $\hat{a}_i$ and $\hat{b}_i$. These coherent states may be represented by $|a_i\rangle$ and $|b_i\rangle$. Each of these are normalized states of the respective annihilation operators with complex eigenvalues, a_i and b_i respectively such that,

$$|a_i\rangle = e^{a_i\hat{a}_i^\dagger - |a_i|^2/2}|0\rangle \quad |b_i\rangle = e^{b_i\hat{b}_i^\dagger - |b_i|^2/2}|0\rangle \tag{16}$$

It is important to note that the coherent states are a complete basis for the Fock space of the bosonic system. The expectation value in 15 can be written down as a coherent-state path integral,

$$\langle A(t)\rangle = \frac{\int \prod_i d\hat{\psi}_i d\psi_i d\hat{\phi}_i d\phi_i A(\{\psi_i,\, \phi_i\}) e^{-S[\hat{\psi}_i,\, \psi_i,\, \hat{\phi}_i,\, \phi_i; t]}}{\int \prod_i d\hat{\psi}_i d\psi_i d\hat{\phi}_i d\phi_i e^{-S[\hat{\psi}_i,\, \psi_i,\, \hat{\phi}_i,\, \phi_i; t]}} \tag{17}$$

with the effective action,

$$S[\hat{\psi}_i,\, \psi_i,\, \hat{\phi}_i,\, \phi_i; t] = \sum_i \left(\int_0^t dt \left[\hat{\psi}_i(t)\partial_t \psi_i(t) + \hat{\phi}_i(t)\partial_t \phi_i(t) + H_i(\hat{\psi}_i(t),\, \psi_i(t),\, \hat{\phi}_i(t),\, \phi_i(t)) \right] \right) - \\ - \sum_i \left(\psi_i(t) + \phi_i(t) + \bar{n_0^A} \hat{\psi}_i(0) + \bar{n_0^B} \hat{\phi}_i(0) \right) \tag{18}$$

Following steps, indicated in ref [], we take the formal continuum limit,

$$\begin{aligned} &\sum_i \to l_0^{-d} \int d^d x, \quad \psi_i(t) \to l_0^d \psi(\mathbf{x}, t), \quad \hat{\psi}_i(t) \to \hat{\psi}(\mathbf{x}, t), \\ &\phi_i(t) \to l_0^d \phi(\mathbf{x}, t), \quad \hat{\phi}_i(t) \to \hat{\phi}(\mathbf{x}, t), \quad \bar{n^A}_0 \to l_0^d n_0^A, \quad \bar{n^B}_0 \to l_0^d n_0^B, \\ &\sum_{\{e\}} [\psi_e(t) - \psi_i(t)] \to l_0^{d+2} \nabla^2 \psi(\mathbf{x}, t), \sum_{\{e\}} [\phi_e(t) - \phi_i(t)] \to l_0^{d+2} \nabla^2 \phi(\mathbf{x}, t) \end{aligned} \tag{19}$$

This results in the effective action

$$\begin{aligned} S[\hat{\psi},\, \psi,\, \hat{\phi},\, \phi; t] = \int d^d\mathbf{x} \Bigg[\int_0^t & \Big\{ \hat{\psi}(\mathbf{x}, t) \left(\partial_t - D_A \nabla^2\right) \psi(\mathbf{x}, t) + \hat{\phi}(\mathbf{x}, t) \left(\partial_t - D_A \nabla^2\right) \phi(\mathbf{x}, t) - \\ & - \lambda_0 \hat{\psi}(\mathbf{x}, t) \left(\hat{\psi}(\mathbf{x}, t) - \hat{\phi}(\mathbf{x}, t) \right) \psi(\mathbf{x}, t) \phi(\mathbf{x}, t \Big\} \\ & - \psi_i(t) - \phi_i(t) - \bar{n_0^A} \hat{\psi}_i(0) - \bar{n_0^B} \hat{\phi}_i(0) \Bigg] \end{aligned} \tag{20}$$

$S[\hat{\psi},\, \psi,\, \hat{\phi},\, \phi; t]$ is analogous to a field theoretic Hamiltonian.

References

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