

Path Integral Formulation for Quantized Fermion and Boson Fluids

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An isomorphism between fully quantized fermion and boson fluids and classical polymer mixtures is used as a point of departure to initiate an analytic treatment of quantum fluids.

KEY WORDS: Path integral; quantum statistical mechanics; Fermi fluids; Bose fluids, polymer mixtures.

1. INTRODUCTION

Among the many accomplishments of Oliver Penrose, his work on quantum fluids stands out.⁽¹⁾ It seems especially appropriate, therefore, to submit to this festschrift volume a contribution on quantized systems.

In the late 1950s and early 1960s there was a great proliferation of perturbative treatments of the statistical mechanics of quantum fluids that culminated in a number of formally exact expansion procedures for treating the thermodynamics and structure of fluids of interacting particles (see, e.g., ref. 2). These permitted the correction of ideal-gas results through the use of expansions in fugacity, but for technical reasons the resummations necessary to obtain the pressure of a quantum fluid directly in terms of the number density proved much more cumbersome than in the case of classical fluids. One of the most powerful and elegant starting points for such results was Feynman's path-integral formulation of quantum mechanics,⁽³⁾ which was used in particular in the path-integral approach of Montroll and Ward,⁽⁴⁾ who introduced polymerlike elements they called torons to describe quantized bosons or fermions.

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Twenty years later, further progress was made through the exploitation of the observation that the path-integral approach enables one to think of quantum problems as limiting cases of certain classical statistical mechanical problems, since a path integral can be regarded as a limit of approximating sums that can be thought of as classical configuration integrals.⁽⁵⁻⁷⁾ Barker⁽⁵⁾ pointed out the way this observation can be used to extend classical Monte Carlo simulation methods to quantized systems, and Høye and Stell,⁽⁷⁾ Thompson *et al.*,⁽⁸⁾ and others^(9,10) showed how it could be used to treat the quantized internal degrees of freedom of fluid particles, such as those responsible for polarizability, using analytic liquid-state methods already developed for classical fluids. A more far-reaching observation in this connection was made by Chandler and Wolynes,⁽⁶⁾ who noted a very general isomorphism between interacting fermion and boson systems and a classical system of interacting polymers, described in a continuum infinite-monomer limit.

This article has two main purposes. The first is essentially pedagogic—we call attention to the relationship between the Montroll–Ward and Chandler–Wolynes results, which makes it possible to unify conceptually the considerable development of the 1960s based on the Montroll–Ward toron formalism and the substantial body of more recent work based on the polymer picture.

The second aim of this paper is to initiate an analytic study based on the polymer picture that goes beyond existing results. The polymer picture is the starting point for a significant fraction⁽¹³⁾ of the extensive modern literature on path-integral simulations of quantum systems. However, analytic path-integral studies using the polymer picture have been largely restricted to lattice-model studies,⁽¹⁴⁾ to certain few-particle problems,⁽¹⁵⁾ or to investigations in which only the internal degrees of freedom in fluid systems have been treated quantum mechanically.⁽⁷⁻¹²⁾ In each of these analytic studies, the full problem of quantum indistinguishability and statistics has been avoided. On the other hand, the fully quantized models considered in the much earlier studies using the Montroll–Ward formalism, such as the quantum plasma⁽¹⁶⁾ and the Bose gas of interacting particles⁽¹⁷⁾ have for the most part not been reinvestigated using analytic methods that fully exploit the potential power of the isomorphism between quantum and classical systems. These methods hinge on the availability of the recipes of classical statistical mechanics developed since the 1950s that yield through functional differentiation and topological reduction expressions for the logarithm of the partition function and its associated n -point distribution and correlation functions in terms of number density, as well as a variety of classical thermodynamic perturbation theories.⁽¹⁸⁾ Here we shall obtain some fundamental reference-system results for free fermions and bosons in

a form appropriate to their use as ingredients in a dense-fluid perturbation theory, which we shall continue to develop elsewhere. We also include a brief development for charged bosons or fermions that yields the Debye shielding for such systems as well as some remarks concerning fully quantized particles on a lattice.

In Section 2 we demonstrate the isomorphism between a fully quantized system of bosons or fermions and a classical polymer system. Our demonstration is that of Chandler and Wolynes, but organized a bit differently. In Section 3 we go on to establish some reference-system results using the polymer picture, as well as the charged-particle and lattice-system results. Some of the reference-system and charged-particle results are equivalent to results already obtained or implicit in the earlier literature, but they are expressed somewhat differently by us and obtained by us in a considerably more economical fashion that we believe illustrates the power of the polymer picture.

In 1957, Montrol and Ward⁽⁴⁾ wrote, "In view of the difficulties encountered in the computation of classical cluster-integrals, we cannot expect to breeze through the explicit calculation of their quantum-mechanical counterparts." Our results do not alter the continued validity of this observation, but by using the isomorphism with classical polymers we easily eliminate the fugacity in favor of the density as an independent variable, which immediately facilitates the application of liquid-state perturbation theories.

In this connection, the use of γ expansions^(18,19) and the related self-consistent γ ordering^(18,20) that leads to the mean-spherical approximation (MSA) as a low-order result^(18,21) seem especially promising. Such ordering in the context of the MSA has already proved extremely fruitful in the partially-quantized polarizable fluid case.⁽⁷⁻¹²⁾ The isomorphism between fully quantized systems and polymer models can be readily extended to lattice systems,⁽⁹⁾ to which γ -ordering remains applicable. Tight-binding and Hubbard models are such systems that lend themselves to our approach, as we discuss in Section 3.

2. THE PATH-INTEGRAL REPRESENTATION AND ITS EQUIVALENCE TO A CLASSICAL POLYMER DESCRIPTION

2.1. Derivation

The partition function of a quantum mechanical system is defined by

$$Z = \text{Tr } e^{-\beta H} = \sum_n \langle \psi_n | e^{-\beta H} | \psi_n \rangle$$

where H is the Hamiltonian operator and ψ_n are the eigenfunctions of the system or some other complete set of eigenfunctions (or eigenstates) that are normalized. As shown, e.g., in ref. 5, this may be rewritten as a path integral. For a single particle this is given by Eq. (16) of ref. 5 as the limit $Z = \lim_{N \rightarrow \infty} Z^{(N)}$, where

$$Z^{(N)} = \int \exp \left\{ - \sum_{p=0}^{N-1} \left[\frac{1}{2} \frac{\sigma}{\eta} (\mathbf{s}_{p+1} - \mathbf{s}_p)^2 + \eta \phi(\mathbf{s}_p) \right] \right\} \prod_{q=0}^{N-1} (A d\mathbf{s}_q) \quad (1a)$$

with

$$\sigma = \frac{M}{(he)^2} \quad \text{and} \quad A = \left(\frac{\sigma}{2\pi\eta} \right)^{3/2} \quad (1b)$$

Here the path of length $\beta = \eta N$ is discretized in steps of length η , and β is held fixed as $N \rightarrow \infty$, so $\eta \rightarrow 0$. (Here $\beta = 1/k_B T$, where T is temperature and k_B is Boltzmann's constant.) The M in (1b) is the mass of the particle, while h is Planck's constant divided by 2π . The e is the charge of the oscillating particle within a molecule resulting in a dipole moment $\mathbf{s}_p = e\mathbf{r}_p$, where the subscript p indicates the position along the path, and \mathbf{r}_p is the position within the molecule. The $\phi(\mathbf{s}_p)$ is the potential within which the particle oscillates. The path integral is restricted by the condition that the endpoints of each path are at the same position such that we have $\mathbf{s}_N = \mathbf{s}_0$. Expression (1) may then be interpreted as the classical partition function of a flexible polymer chain of length $\beta = \eta N$ in a potential $\phi(\mathbf{s}_p)$ such that the chain forms a closed loop or ring.

In the present analysis the position \mathbf{r}_p does not represent an internal coordinate of a molecule creating a polarization \mathbf{s}_p . Instead it is the position of the particle within a container of volume V . Thus it is more natural to use \mathbf{r}_p rather than \mathbf{s}_p as a variable in the present application. This is accomplished in (1) by replacing \mathbf{s}_p with \mathbf{r}_p and letting $e = 1$. The potential $\phi(\mathbf{s}_p)$ will furthermore be set equal to zero, since the particle will no longer be tied to a certain place, except that it must be kept within the volume V , which has macroscopic dimensions. This latter requirement can be met by restricting one of the integrations, e.g., the one with respect to \mathbf{r}_0 , to the volume V while the remaining ones are free. The error introduced by this procedure can be neglected for macroscopic V , since it will occur only for configurations such that \mathbf{r}_p , $p \geq 1$, is close to the surface of the container, and the stiffness and limited length of the polymer will restrict the relative distance $\mathbf{r}_p - \mathbf{r}_0$ to be microscopic.

Now we consider the partition function for an arbitrary number of particles. If these particles do not interact, the partition function is nothing

but the product of single-particle partition functions if we regard the particles as distinguishable, i.e., if the particles are not identical or if we use Boltzmann instead of Bose or Fermi statistics when they are identical. Then the extension to pairwise interacting particles is effected simply by replacing the potential $\phi(s_p)$ in (1) with pair potentials. Thus for N_0 particles such a partition function will be $Z_{N_0} = \lim_{N \rightarrow \infty} Z_{N_0}^{(N)}$, where

$$Z_{N_0}^{(N)} = \int \exp \left\{ - \sum_{p=0}^{N-1} \left[\sum_{1 \leq i \leq N_0} \frac{1}{2} \frac{\sigma}{\eta} (\mathbf{r}_{i,p+1} - \mathbf{r}_{i,p})^2 + \eta \sum_{1 \leq i < j \leq N_0} \phi(\mathbf{r}_{ij,p}) \right] \right\} \prod_{i=1}^{N_0} \prod_{q=0}^{N-1} (A d\mathbf{r}_{i,q}) \quad (2a)$$

and (for three-dimensional systems)

$$\sigma = \frac{M}{\hbar^2}, \quad A = \left(\frac{\sigma}{2\pi\eta} \right)^{3/2} \quad (2b)$$

Here the $\phi(\mathbf{r}_{ij,p})$ is the pair interaction, with $\mathbf{r}_{ij,p} = \mathbf{r}_{i,p} - \mathbf{r}_{j,p}$ the relative distance between particles i and j at position p along the paths formed in the polymers. (The ϕ can also be time-dependent, such as a radiating electromagnetic field. Then $\mathbf{r}_{ij,p} \rightarrow \mathbf{r}_{ij,pq} = \mathbf{r}_{i,p} - \mathbf{r}_{j,q}$.^(22,23))

For identical particles that are treated as bosons or fermions the partition function (2) is not appropriate. Symmetry requirements have to be imposed on the wavefunctions, which will reflect itself in the partition function. The modification appropriate to this situation has been established; see, e.g., the book by Feynman and Hibbs.⁽³⁾ In expression (2) the endpoint of each polymer, representing a particle, is located at its starting point, forming a single polymer loop. However, for identical particles the symmetry requirement implies that all endpoints should be permuted in all possible ways to form a set of path-integral contributions. For bosons, all of these contributions are added to yield the N_0 -particle partition function when divided by $N_0!$, the number of permutations. For fermions, however, these contributions are added when the permutations are even and subtracted when they are odd. So we can write

$$Z_{N_0} = \lim_{N \rightarrow \infty} Z_{N_0}^{(N)} \quad (3a)$$

$$Z_{N_0}^{(N)} = \frac{1}{N_0!} \sum_{\{\mathbf{P}\}} Z_{N_0}^{(N)}(\mathbf{P}) \quad (3b)$$

for the approximating sums to the N_0 -particle partition function. Here the \mathbf{P} denotes the permutation of endpoints over which to sum, and $Z_{N_0}^{(N)}(\mathbf{P})$ is the corresponding result with this permutation performed in the path integral (2). ($\mathbf{P} = \mathbf{I}$ will indicate unpermuted endpoints.) For fermions we let $Z_{N_0}^{(N)}(\mathbf{P})$ include a minus sign when \mathbf{P} is an odd permutation.

We may write down the grand partition function

$$Z_g = \sum_{N_0=0}^{\infty} e^{\beta\mu N_0} Z_{N_0} \quad (4)$$

where Z_{N_0} is given by (3), and μ is the chemical potential. Now we want to investigate whether the Z_g can be interpreted as the grand partition function of some classical system. We have already noticed that expression (2) may be interpreted as the partition function of a classical polymer problem. For identical particles such an interpretation does not seem as obvious any longer due to the permutations required in (3). However, after closer examination we shall find that the grand partition function (4) can indeed be interpreted as that associated with a classical polymer mixture.

In expression (2) the endpoint of the path for a particle is the same as its starting point. Accordingly, the path forms a ring polymer consisting of a single loop of length $\beta = \eta N$. The other particles form similar ring polymers consisting of single closed loops, and (2) is the partition function for a fluid of such single polymer loops.

In expressions (3) and (4), however, the endpoint of the path, representing a quantized particle, may be the same as the starting point of another particle, and the endpoint of that may again be the starting point of a third particle, etc. After q such steps we may come back to the starting point of the first particle with which we started, and the process of linking single polymers of length β into longer ones stops. This new, longer polymer of length $q\beta$ will also form a ring or closed chain, since the starting point and the final endpoint are the same; thus this new ring is a coil consisting of q loops. (If one likes, the process of forming longer coils by permutation may be regarded⁽⁶⁾ as a chemical reaction where the basic single loops are dissociated from each other and then associated together into coils of various length with an associated chemical equilibrium for the number of these species.) Thus we get a fluid mixture consisting of coils of various length. A natural question is whether this fluid mixture can be regarded as a classical mixture problem for which the methods of classical statistical mechanics are applicable. If so, we can reformulate (4) into a classical mixture problem for polymers.

Consider one of the terms in the sum (3). It represents an approximating sum to the partition function for N_0 particles. Due to permutation

of endpoints of paths it will further represent a mixture of polymer coils of various sizes. Let N_q be the number of coils consisting of q loops (i.e., chain length $q\beta$). Then obviously

$$N_0 = \sum_{q=0}^{\infty} q N_q \quad (5)$$

Any of the coils with q loops will have the same properties and can thus be regarded as identical polymers, i.e., they represent one kind of species in the polymer mixture. Thus any permutation \mathbf{P} that yields the same number N_q ($q = 1, 2, 3, \dots$) will produce the same contribution $Z_{N_0}^{(N)}(\mathbf{P})$. All such \mathbf{P} 's can be added together to yield the sum of such contributions. Thus if there are $P(\{N_q\})$ such permutations, we can write

$$P(\{N_q\}) Z_{N_0}(\mathbf{P}) = Z(\{N_q\}) \quad (6)$$

To compute $P(\{N_q\})$, consider a permutation that yields the particle numbers or numbers of various coils N_q . The N_0 loops can be distributed among the various coils in

$$\frac{N_0!}{\prod_q (q!)^{N_q}}$$

ways. However, coils consisting of the same number of loops q can be exchanged without creating a new permutation. This reduces the number of different distributions to

$$\frac{N_0!}{\prod_q N_q! (q!)^{N_q}}$$

For each such different distribution the single loops may be exchanged within each coil creating a number of $(q-1)!$ different permutations for each. (The number will not be $q!$, since a cyclic change of q loops in a closed chain does not give a new permutation.) Thus the number of permutations yielding the particle number N_q is

$$P(\{N_q\}) = \frac{N_0!}{\prod_q N_q! (q!)^{N_q}} \prod_p [(p-1)!]^{N_p} = \frac{N_0!}{\prod_q q^{N_q} N_q!} \quad (7)$$

The basic permutation of exchanging two polymer or path endpoints will either split a coil into two smaller ones (when the endpoints are within one coil) or it will create a combined coil out of two coils (when the endpoints are in separate coils). Accordingly, permutations that preserve coils must be even. Thus we find that permutations of endpoints that give the same

particle number N_q must either be all even or they are all odd, since preservation of these numbers requires an even number of permutations. Thus even for fermions all contributions will add up with the same sign (either + or -).

Expressions (6) and (7) may then be used in the partition function (3), where instead of summing over permutations, one now sums over the particle numbers N_q under the restriction $N_0 = \sum_q q N_q$. When further used in the grand partition function (4) this latter restriction can be taken away, and one can sum freely over the N_q . We find therefore

$$Z_\kappa = \sum_{\{N_p\}} \prod_q \frac{\pm 1}{N_q!} \left(\frac{e^{\beta\mu_q}}{q} \right)^{N_q} Z(\{N_p\}) \quad (8)$$

For bosons the + sign is always used, while for fermions the + sign is used for even permutations and the - sign is used for odd permutations. The rules for the sign in the latter case are easily derived. Creating a coil of two loops requires the permutation of two endpoints (from single loops). Thus each such coil will imply a factor -1. Similarly a coil of three loops will require an even permutation, yielding a factor +1. Continuing in this way, one sees that coils with an even number of loops each involve an odd permutation and each yields a factor -1, while coils with odd numbers of units each involve an even permutation and each yields a factor +1. Thus for fermions we can make the replacement in (8)

$$\pm 1 \rightarrow [(-1)^{q-1}]^{N_q} \quad (9)$$

(while for bosons $\pm 1 \rightarrow 1$).

We now note that (8) has precisely the form of the grand partition function for a mixture of polymer coils where the chemical potential μ_q for a coil of q loops is identified as

$$e^{\beta\mu_q} = \begin{cases} \frac{1}{q} e^{\beta\mu_q} & \text{for bosons} \\ \frac{(-1)^{q-1}}{q} e^{\beta\mu_q} & \text{for fermions} \end{cases} \quad (10)$$

For fermions the $e^{\beta\mu_q}$ is clearly negative when q is even. This will imply negative densities for such coils. For classical partition functions the $e^{\beta\mu_q}$ (and thus the densities) are always considered positive. In this regard our final results are going beyond an isomorphism with realizable classical polymer models. With this caveat, one sees that the $Z(\{N_p\})$ in expression (8) can be identified with the $N \rightarrow \infty$ limit of a classical partition function for polymer coils that interact via a pair interaction. This quantity is noth-

ing but the partition function (2) with the endpoints of paths permuted. [In the notation of (3b) the $Z_{N_0}^{(N)}$ of (2a) is $Z_{N_0}^{(N)}(\mathbf{I})$, where \mathbf{I} is the identity permutation corresponding to unpermuted endpoints.] These permutations have the effect that the single loops are incorporated into longer closed chains or coils. These coils interact via the pair interaction $\phi(\mathbf{r}_{ij, p})$, but it should be noted that there will be multiple loop-loop interactions between two coils since each loop in a coil will interact with every other loop in other coils and in the same coil.

The final result (8), along with (10), is equivalent to the result obtained by Chandler and Wolynes.⁽⁶⁾ However, they do not incorporate the factor $1/q$ into their equations in quite the same language that we have used. Instead it appears via a chemical equilibrium constant for coils consisting of q loops. The result (8), without the explicit observation embodied in Eq. (10), was obtained by Montroll and Ward.⁽⁴⁾

2.2. Equation of State for Ideal Fermions and Bosons

When there are no interactions between particles, i.e., the $\phi(\mathbf{r}_{ij, p})$ in (2) is zero, the grand partition function (8) will be the one for noninteracting polymer coils. Thus the equation of state will be the one for an ideal gas mixture. The pressure p is then given by

$$\beta p = \sum_{q=1}^{\infty} \rho_q \quad (11)$$

where ρ_q is the number density of polymer coils consisting of q loops. The total number density ρ of particles (fermions or bosons) will be

$$\rho = \sum_{q=1}^{\infty} q \rho_q \quad (12)$$

since a coil of q loops represents q particles. So far the ρ_q are unknown. For their determination we turn to the partition function (2). With $\phi(\mathbf{r}_{ij, p}) = 0$ the path integral factorizes into Gaussian path integrals for each polymer. Such integrals can be performed by standard methods which we have no reason to review at this point. The result must be in accordance with the well-known partition function for a quantized particle in a box of volume V , and it is, yielding

$$R_1 = Z_{N_0=1}(I) = \frac{1}{\Lambda^3} V \quad (13)$$

$$\Lambda^2 = 2\pi \frac{\eta}{\sigma} N = 2\pi \frac{\beta \hbar^2}{M} = \frac{\hbar^2}{2\pi M k T}$$

The λ is the well-known de Broglie thermal wavelength for quantized particles. Thus we need the result for a coil consisting of q units. Such coils are obtained by permutations of the endpoints of paths in (2). The path integral for such a coil is then seen to be nothing but the one for a single loop, except that its length is q time as long. Thus we simply replace the β in (13) with βq to obtain for an arbitrary coil

$$R_q = q^{-3/2} R_1 = \frac{1}{q^{3/2} \lambda^3} V \quad (q = 1, 2, 3, \dots) \quad (14)$$

The canonical partition function with particle numbers N_p is thus

$$Z(\{N_p\}) = \prod_q R_q^{N_q} \quad (15)$$

which inserted in (8) yields

$$Z_g = \prod_q \sum_{N_q=0}^{\infty} \frac{(z_q V)^{N_q}}{N_q!} = \exp\left(V \sum_q z_q\right) \quad (16a)$$

where we define the fugacity by

$$z_q = e^{\beta \mu_q} R_q \frac{1}{V} \quad (16b)$$

With (10) and (14) inserted into (16b) we find

$$z_q = \frac{1}{\lambda^3} (\pm 1)^{q-1} \frac{\zeta^q}{q^{5/2}}; \quad \zeta = e^{\beta \mu} \quad (17)$$

The pressure p is then

$$\beta p = \frac{1}{V} \ln Z_g = \sum_q z_q \quad (18)$$

The number densities are

$$\rho_q = \frac{1}{V} \langle N_q \rangle = \frac{1}{V} \frac{\partial \ln Z_g}{\partial (\beta \mu_q)} = z_q \frac{\partial (\beta p)}{\partial z_q} = z_q \quad (19)$$

The total number density is

$$\rho = \frac{1}{V} \frac{\partial \ln Z_g}{\partial \beta \mu} = \frac{1}{V} \sum_q q \langle N_q \rangle = \sum_q q z_q \quad (20)$$

Equations (18)–(20) are the same as Eqs. (11) and (12). Use of Eq. (17) will then fully specify the equation of state by which $\rho_q = z_q$ is explicitly

determined in terms of $\zeta = e^{\beta\mu}$. The result we have obtained here as an ideal-gas polymer mixture is recognized as the well-known exact equation of state for an ideal boson or fermion gas.

In our considerations here we have not treated degeneracy due to spin. However, if there are no spin interactions, such degeneracy can be easily accounted for. Particles in different spin states may be regarded as being different, so that exchange effects do not take place. In the way things are done here, this means that different particles do not enter the same polymer coil, and in the noninteracting case this means that they give independent contributions to the equation of state.

3. FURTHER RESULTS

3.1. Debye Shielding in Quantum Systems

For a classical fluid the Debye inverse shielding length κ for the Coulomb interaction between charges is

$$\kappa^2 = 4\pi\beta\rho Q^2 \quad (21)$$

where Q is the charge. For a multicomponent system this generalizes to

$$\kappa^2 = 4\pi\beta \sum_i \rho_i Q_i^2 \quad (22)$$

Using (22) for quantized fermion or boson systems, we find

$$\kappa^2 = 4\pi\beta e^2 \sum_q \rho_q q^2 \quad (23)$$

since the charge of a polymer coil will be qe when it consists of q units when e is the charge of a single particle. Utilizing (17), (19), and (20), one sees that ($\rho = \sum_q \rho_q q$)

$$\kappa^2 = 4\pi\beta e^2 \zeta \frac{\partial \rho}{\partial \zeta} = 4\pi\beta e^2 \left[\frac{\partial(\beta\mu)}{\partial \rho} \right]^{-1} = 4\pi\beta \rho e^2 \left[\frac{\partial(\beta\rho)}{\partial \rho} \right]^{-1} \quad (24)$$

This result is precisely what one will obtain by more standard methods invoking linearized Debye-Hückel theory, utilizing the equation of state for ideal fermions (or bosons). (Fermions are usually considered at $T=0$.)

3.2. Distribution Function for Single Free Particles

We want to evaluate the spatial correlation or probability distribution for two positions separated by a distance λ (or $\beta - \lambda$) along a single

polymer loop. To do so we start with the integrand of Eq. (1a) and utilize the fact that integrals will be Gaussian. Taken together with earlier results for the polarizable fluid, this will simplify the calculation. Since the resulting probability distribution must be Gaussian, it will be sufficient to know the average $\langle r^2 \rangle = \langle (\mathbf{r}_q - \mathbf{r}_p)^2 \rangle$ [$\lambda = \eta(q - p)$, $\mathbf{r}_p = \mathbf{s}_p/e$]. As in the case of the polarizable fluid,⁽⁷⁾ Fourier-transform variables can be usefully introduced

$$\mathbf{a}_K = \frac{1}{\sqrt{N}} \sum_{p=1}^N e^{iKnp} \mathbf{s}_p \quad (25)$$

from which the average

$$\langle \mathbf{a}_K \mathbf{a}_{-K} \rangle = 3 \frac{1}{\sigma^2(K^2 + (\hbar\omega_0)^2)} \quad (26)$$

follows.

By Fourier inversion the $\langle (\mathbf{s}_q - \mathbf{s}_p)^2 \rangle$ can be found. Its value will depend upon β . However, in the present case we will simplify to $\beta \rightarrow \infty$. This is because we will specialize to the case of $\omega_0 \rightarrow 0$ in which only relative separations will be relevant. Then the sought probability will be proportional to the probability for separation $\mathbf{r} = \mathbf{r}_q - \mathbf{r}_p$ after imaginary time λ , multiplied by the probability of return to the start after imaginary time $\beta - \lambda$. With (2b) inserted we get [$\lambda = \eta(q - p)$, $\beta \rightarrow \infty$]

$$\langle \mathbf{s}_q \mathbf{s}_p \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mathbf{a}_K \mathbf{a}_{-K} \rangle e^{-ik\lambda} dk = \frac{3}{2\sigma} \frac{e^{\hbar\omega_0\lambda}}{\hbar\omega_0} \quad (27)$$

Taking the limit $\omega_0 \rightarrow 0$, with $\mathbf{r}_p = \mathbf{s}_p/e$, one obtains

$$\langle r^2 \rangle = \langle (\mathbf{r}_q - \mathbf{r}_p)^2 \rangle = 3 \frac{1}{2\sigma} \lambda \quad (28)$$

where σ is now redefined to $\sigma = M/\hbar^2$ as in Eq. (2b). The corresponding probability distribution will be

$$F_\lambda(r) = \left(\frac{\sigma}{2\pi\lambda} \right)^{3/2} \exp \left(- \frac{\sigma r^2}{2\lambda} \right) \quad (29)$$

The sought probability distribution will be

$$P_\lambda(r) = \frac{F_\lambda(r) F_{\beta-\lambda}(r)}{F_\beta(0)} = \left(\frac{\sigma}{2\pi\lambda(1-\lambda/\beta)} \right)^{3/2} \exp \left\{ - \frac{\sigma r^2}{2\lambda(1-\lambda/\beta)} \right\} \quad (30)$$

Its spatial Fourier transform will be

$$\bar{P}_\lambda(k) = \exp \left\{ -\frac{1}{2\sigma} \lambda \left(1 - \frac{\lambda}{\beta} \right) k^2 \right\} \quad (31)$$

For use in hypervertices in the graphical representation of graphs in our γ -ordered procedures in Section 3.4 and in other connections the Fourier transform with respect to λ is needed, too. However, the result cannot be integrated analytically, but we can go back to Eq. (30) and regard the product $F_\lambda \cdot F_{\beta-\lambda}$ as a Fourier transform of a convolution in \mathbf{k} -space. Thus

$$\bar{P}_\lambda(k) = \left(\frac{\beta}{2\pi\sigma} \right)^{3/2} \int \bar{F}_\lambda(k') \bar{F}_{\beta-\lambda}(|\mathbf{k} - \mathbf{k}'|) d\mathbf{k}' \quad (32)$$

where

$$\bar{F}_\lambda(k) = \exp \left(-\frac{1}{2\sigma} \lambda k^2 \right) \quad (33)$$

A Fourier transform with respect to imaginary time λ can now be performed,

$$\begin{aligned} \hat{P}_K(k) &= \int_0^\beta \bar{P}_\lambda(k) e^{iK\lambda} d\lambda \\ &= \left(\frac{\beta}{2\pi\sigma} \right)^{3/2} \int \frac{\exp[-(1/2\sigma)\beta k'^2] - \exp[-(1/2\sigma)\beta(\mathbf{k} - \mathbf{k}')^2]}{iK - (1/2\sigma)[k'^2 - (\mathbf{k} - \mathbf{k}')^2]} d\mathbf{k}' \end{aligned} \quad (34)$$

With $\sigma = M/\hbar^2$ one notes that the exponentials are nothing but the Maxwell distributions for classical particles. Thus we can introduce moments $\mathbf{p} = \hbar \mathbf{k}'$ (or velocities $\mathbf{v} = \mathbf{p}/M$) and the Maxwell distribution

$$f_0 = f_0(p) = \left(\frac{\beta}{2\pi M} \right)^{3/2} \exp \left(-\frac{\beta}{2M} p^2 \right) \quad (35)$$

Along with the interchange $\mathbf{k}' \rightleftharpoons \mathbf{k} - \mathbf{k}'$, this then leads to

$$\begin{aligned} \hat{P}_K(k) &= \int \left(\frac{1}{iK + \Delta} - \frac{1}{iK - \Delta} \right) f_0 d\mathbf{p} \\ &= - \int \frac{2\Delta}{K^2 + \Delta^2} f_0 d\mathbf{p} \end{aligned} \quad (36)$$

where $K = 2\pi n/\beta$ with $n = \text{integer}$ and

$$\Delta = E(|\hbar \mathbf{k} - \mathbf{p}|) - E(p) \quad (37a)$$

with energies

$$E(p) = \frac{1}{2M} p^2 \quad (37b)$$

3.3. Distribution Function for Free Fermions and Bosons

The distribution function for a pair of points along a single polymer loop can be extended to polymer coils in a straightforward way. Again we base our derivations upon Eq. (29) for $F_\lambda(f)$. For a coil consisting of n loops the total length of the polymer will be $n\beta$. Due to periodicity, imaginary time λ is obtained for distances

$$\lambda_p = \lambda + p\beta, \quad p = 0, 1, \dots, n-1 \quad (38)$$

along the polymer. The distance remaining before returning to the start is then

$$n\beta - \lambda_p = \beta - \lambda + q\beta, \quad q = n-1-p \quad (39)$$

Using (30) and (32), we find that the probability distribution for two points separated by imaginary time λ in a polymer of length $n\beta$ is thus

$$\tilde{P}_\lambda^{(n)}(k) = \sum_{p=0}^{n-1} \left(\frac{n\beta}{2\pi\sigma} \right)^{3/2} \int \tilde{F}_\lambda(k') \tilde{F}_{\beta-\lambda}(k'') X^p Y^q d\mathbf{k}' \quad (40)$$

where

$$X = \tilde{F}_\beta(k') \quad \text{and} \quad Y = \tilde{F}_\beta(k''), \quad \mathbf{k}'' = \mathbf{k} - \mathbf{k}' \quad (41)$$

with $F_\lambda(k)$ given by (33).

The pair distribution function we require is now obtained by weighted summation over the various coils. The weighing factor for coils of n loops is $n\rho_n$; the factor n represents the n choices among loops for point 1. [The n choices for point 2 are included in the summation over p in Eq. (40).] For free particles the ρ_n is determined by Eqs. (17) and (19) as

$$\rho_n = \frac{1}{A^3} (\pm 1)^{n-1} \frac{\zeta^n}{n^{5/2}} \quad (42)$$

with $\mathcal{A}^2 = 2\pi\beta/\sigma$. Thus with (40) inserted, the pair distribution functions we seek becomes

$$\begin{aligned}\tilde{S}(\lambda, k) &= \sum_{n=1}^{\infty} n\rho_n \tilde{P}_{\lambda}^{(n)}(k) \\ &= \frac{1}{(2\pi)^3} \zeta \int \frac{\tilde{F}_{\lambda}(k')}{1 \mp \zeta X} \frac{\tilde{F}_{\beta-\lambda}(k'')}{1 \mp \zeta Y} d\mathbf{k}'\end{aligned}\quad (43)$$

with k'' , X , and Y as defined by Eqs. (41). Here the upper sign refers to bosons, while the lower one refers to fermions. A Fourier transformation in imaginary time can now be performed precisely as done in Eqs. (34)–(36), since X and Y do not contain λ . We find

$$\hat{S}(K, k) = \frac{\zeta}{(2\pi\hbar)^3} \int \left(\frac{1}{iK + \mathcal{A}} - \frac{1}{iK - \mathcal{A}} \right) \frac{X}{(1 \mp \zeta X)(1 \mp \zeta Y)} d\mathbf{k}' \quad (44)$$

when form (36) is generalized.

The distribution function $\hat{S}(K, k)$ fully describes static and dynamical correlations for free bosons and fermions at equilibrium, i.e., the dynamics of single particles and pairs of particles within coils due to exchange effects. Thus $\hat{S}(K, k)$ is also the Fourier-transformed response function of the system when a small force is applied. In this case the K is given by $K = -i\hbar\omega$, where ω is frequency, i.e., K is imaginary frequency. This identification was demonstrated by Høye and Brevik.⁽²²⁾ The $\hat{S}(K, k)$ will also be the hypervertex to lowest order in γ -ordering in the graphical representation of our γ -ordered expansions, replacing the transformed reference-system pair correlation function used in the classical case. Compared to the classical case an added feature will be that density distributions for the polymer coils will be affected by perturbing interactions. However, to lowest order in γ this effect can be neglected.

Since $\hat{S}(K, k)$ describes the dynamics of the system, we note that the kinetic theory for systems close to equilibrium as well as the purely static properties of equilibrium systems can be obtained from it.

3.4. The Chain Bond and Excess Free Energy

To form a chain bond, the perturbing pair interaction in Eq. (2a) is needed. To evaluate it, one must perform convolutions in real space and imaginary time. Due to translational invariance, Fourier transform methods can be utilized. This is precisely as in the classical case except that here the fourth dimension (cyclic of length β) of imaginary time is included. For the quantum (polymer) problem the $\hat{S}(K, k)$ of expression (44) is then

nothing but the hypervortex (as long as the density distribution is unperturbed). The Fourier-transformed pair interaction $\tilde{\psi}(k)$ will be precisely as in the classical case. Here $\psi(r_{ij}) = \phi(r_{ij}, \rho)$, when comparing with Eq. (2a). Note that with instantaneous interaction the $\tilde{\psi}(k)$ does not vary with K . With time-dependent interactions the K dependence will enter such that⁽²²⁾ $\tilde{\psi}(k) \rightarrow \hat{\psi}(K, k)$. As in the classical case, the chain bond is now easily written down as

$$\tilde{C}(K, k) = \frac{-\tilde{\psi}(k)}{1 - \hat{S}(K, k)(-\tilde{\psi}(k))} \quad (45)$$

with $\hat{S}(K, k)$ determined by Eq. (44). Note that compared with the classical case the factor β is dropped in front of $\tilde{\psi}(k)$. Instead it is incorporated in $\hat{S}(K, k)$ via with the Fourier transform in imaginary time.

The perturbed structure factor to first order in γ -ordering is then given by

$$\hat{\phi}(K, k) = \hat{S} + \hat{S}\tilde{C}\hat{S} = \frac{\hat{S}(K, k)}{1 - \hat{S}(K, k)(-\tilde{\psi}(k))} \quad (46)$$

This function describes the perturbed equilibrium correlations as well as dynamical ones [due to its dependence upon frequency ($K = -i\hbar\omega$)]. As in the classical case, the excess free energy to first order in γ -ordering can be evaluated from the ring graphs. Use of Fourier transform methods in connection with convolutions then generalizes the classical result to

$$I = -\frac{1}{2} \frac{1}{(2\pi)^3} \sum_K \int d\mathbf{k} \ln[1 - \hat{S}(K, k)(-\tilde{\psi}(k))] \quad (47)$$

Note that (47) when expanded also includes the term $\hat{S}\tilde{\psi}$ that represents the direct self-interaction of a polymer with itself. It has the same effect as adding a piece to the chemical potentials. Since the \hat{S} is linear in the polymer densities ρ_g , it will not appear explicitly in the pressure—only indirectly via the chemical potentials. The quantity I is $-\beta F$, where F is excess Helmholtz free energy per unit volume. Thus all thermodynamic quantities can be derived from it. A challenging problem in this connection is to evaluate the change in density distributions due to the perturbations. First of all, for both fermions and bosons the relative concentrations of polymers of different lengths will change. This must be taken into account because it will influence reference-system quantities like the pressure (11) to first order in γ , but we anticipate that this can be done approximately in a straightforward way. More challenging will be the evaluation of the change in polymer configurations for single polymers or polymer coils. For

polarizable particles this latter problem could be solved exactly in the MSA since the resulting distribution of configurations were Gaussian, too. This will not be the case here, so some approximation has to be made (an approximation of Gaussian type but with perturbed parameters is an obvious starting point). The problem is of great intrinsic interest since it describes the correlations (or dynamics) of single particles due to interaction of a particle with itself via the medium. The well-known polaron problem is of this type. For weak perturbations, Høye and Brevik considered this type of problem when investigating the friction force between two oscillators that moved with respect to each other.^(2,3) When regarding the polymer system as a multicomponent mixture, the density distribution of polymer configurations is again determined via the chemical potentials.

3.5. Quantum lattice models

In quantum lattice models (tight-binding, Hubbard) the electrons of a system are located on the sites of a regular lattice. In its quantum mechanical description, the electrons jump from site to site by quantum fluctuations described by a transition rate. Our results for the continuum case extend in a straightforward way to this case. Whether the particles are bosons or fermions, there will be an equivalent classical polymer problem, and in the present case the polymer will be located on lattice points. In imaginary time the free (noninteracting) particles will be described by random walks with jumping rates proportional to the quantum transition rate.

Consider first one dimension for simplicity. For a random walk that starts at the origin, the probability distribution after a small time step η will be described by the Fourier transform

$$\tilde{F}_\eta(k) = 1 - \eta c(1 - \cos k) \quad (48)$$

if jumps are restricted to nearest neighbors. The c is a constant. The random walk will be a Markov process, so by repeated time steps one will have convolutions in r -space. After time λ a number of λ/η such steps have been taken. From the properties of convolutions, the Fourier-transformed probability distribution will thus be

$$\tilde{F}_\lambda(k) = \lim_{\eta \rightarrow 0} [\tilde{F}_\eta(k)]^{\lambda/\eta} = \lim_{\eta \rightarrow 0} [1 - \eta c(1 - \cos k)]^{\lambda/\eta} = \exp[-\lambda E(k)] \quad (49)$$

with $E(k) = c(1 - \cos k)$.

The $E(k)$ will be nothing but the energy spectrum for the free particles. This becomes clear when comparing with Eqs. (33) and (37) ($p \rightarrow \hbar k$) for

the continuum case. Equation (49) is easily extended to three dimensions to obtain

$$\tilde{F}_\lambda(\mathbf{k}) = \exp[-\lambda E(\mathbf{k})] \quad (50)$$

For a simple cubic lattice with jumps only to nearest neighbors, one has, for example,

$$E(\mathbf{k}) = c[1 - \frac{1}{3}(\cos k_x + \cos k_y + \cos k_z)] \quad (51)$$

where the \mathbf{k} is restricted to the Brillouin zone

$$-\pi \leq k_x, k_y, k_z \leq \pi \quad (52)$$

The evaluation of the structure function $\hat{S}(K, k)$ [Eq. (44)] and its application to Eqs. (45)–(47) will now be as in the continuum case. The only change is that integrations over \mathbf{k} will be restricted as given by Eq. (52) and the $\tilde{F}_\lambda(k)$ of Eq. (33) is replaced by expression (50). [This will of course also affect Eqs. (29)–(31).]

Now we want the equation of state for quantized free particles on the lattice. For a single free particle the path integral will be the Markov chain that determines $F_\beta(0)$. The path integral (2b) for the continuum case will be such a Markov chain, too, and for one particle the $F_\beta(0)$ will determine the partition function R_1 . With $F_\lambda(r)$ given by (29), Eq. (13) can be written

$$R_1 = F_\beta(0) \cdot V \quad (53)$$

On a lattice with cells of unit volume this equation will be unchanged. In the lattice case $F_\lambda(0)$ will be a probability instead of probability density, while V becomes the number of unit cells instead of volume, so R_1 stays dimensionless. Likewise Eq. (14) for coils of q loops now can be more generally written

$$R_q = F_{q\beta}(0) \cdot V \quad (54)$$

In terms of its Fourier transform (50) the $F_{q\beta}(0)$ can be written

$$F_{q\beta}(0) = \frac{1}{(2\pi)^3} \int d\mathbf{k} \exp[-q\beta E(\mathbf{k})] \quad (55)$$

With fugacities given by (16b) we then have

$$z_q = e^{\beta\mu q} R_q \frac{1}{V} = (\pm 1)^{q-1} \frac{1}{q} \zeta^q F_{q\beta}(0) \quad (56)$$

So the equations of state, Eqs. (11) and (12), becomes [$\rho_q = z_q$ from Eq. (19)]

$$\beta p = \frac{1}{(a\pi)^3} \int d\mathbf{k} [\mp \ln(1 \mp \zeta X)] \quad (57)$$

$$\rho = \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{\zeta X}{1 \mp \zeta X} \quad (58)$$

where, similar to (41),

$$X = F_\beta(\mathbf{k}) = \exp[-\beta E(\mathbf{k})] \quad (59)$$

Equations (57) and (58) provide the well-known equations of state for free bosons and fermions expressed in terms of integrals over the energy levels.

For the lattice case at high temperatures, i.e., $\beta \rightarrow 0$, this equation of state becomes especially simple. Then the return probabilities $F_{q\beta}(0) \rightarrow 1$, i.e., the random walk has not had time to make one move. Then also X can be replaced by 1, and Eqs. (57) and (58) become

$$\begin{aligned} \beta p &= \mp \ln(1 \mp \zeta) \\ \rho &= \frac{\zeta}{1 \mp \zeta} \end{aligned} \quad (60)$$

Especially for fermions these simple equations are already interesting. Elimination of ζ leads to (+ signs)

$$\beta p = -\ln(1 - \rho) \quad (61)$$

and

$$\beta\mu = \ln \zeta = \ln[\rho/(1 - \rho)]$$

Equation (61) is precisely the equation of state of the classical lattice gas that forbids multiple occupancy, i.e., free fermions act as particles with hard cores.

Above we have considered only the case with one component, while the usual Hubbard model deals with two components corresponding to electrons with spins respectively up and down. With no spin interaction present the two spin states can be regarded as different components of a mixture, i.e., the isomorphism with the classical polymer mixture still holds. Before an interaction is turned on, the up and down spins are independent of each other, and they will add independent (fermion) contributions to the equation of state (11). For the structure function (44) there will now

be two independent (but equal) contributions, as it becomes a matrix where the off-diagonal elements are zero (since the two components are uncorrelated). Likewise the perturbing interaction $\psi(r)$ will become a matrix, and Eqs. (45)–(47) become matrix equations. In Eq. (47) the trace will be taken such that I becomes scalar. In the simplest versions of the Hubbard model up and down spins will only interact when they occupy the same site. Since equal spins cannot occupy the same site anyway, the interaction between the latter can then be dropped. With this the $\psi(r)$ [and $\tilde{\psi}(k)$] will have 0 as its two diagonal elements.

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