

# Statistical–mechanical models with separable many-body interactions: especially partition functions and thermodynamic consequences

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**Abstract** We start from a classical statistical–mechanical theory for the internal energy in terms of three- and four-body correlation functions  $g_3$  and  $g_4$  for homogeneous atomic liquids like argon, with assumed central pair interactions  $\phi(r_{ij})$ . The importance of constructing the partition function (pf) as spatial integrals over  $g_3$ ,  $g_4$  and  $\phi$  is stressed, together with some basic thermodynamic consequences of such a pf. A second classical example taken for two-body interactions is the so-called one-component plasma in two dimensions, for a particular coupling strength treated by Alastuey and Jancovici (J Phys (France) 42:1, 1981) and by Fantoni and Tellez (J Stat Phys 133:449, 2008). Again thermodynamic consequences provide a particular focus. Then quantum–mechanical assemblies are treated, again with separable many-body interactions. The example chosen is that of an  $N$ -body inhomogeneous extended system generated by a one-body potential energy  $V(\mathbf{r})$ . The focus here is on the diagonal element of the canonical density matrix: the so-called Slater sum  $S(\mathbf{r}, \beta)$ , related to the pf by  $\text{pf}(\beta) = \int S(\mathbf{r}, \beta) d\vec{r}$ ,  $\beta = (k_B T)^{-1}$ . The Slater sum  $S(\mathbf{r}, \beta)$  can be related exactly, via a partial differential equation, to the one-body potential  $V(\mathbf{r})$ , for specific choices of  $V$  which are cited. The work of Green (J Chem Phys 18:1123, 1950), is referred to for a generalization, but now perturbative, to two-body forces. Finally, to avoid perturbation series, the work concludes with some proposals to allow the

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treatment of extended assemblies in which regions of long-range ordered magnetism exist in the phase diagram. One of us (Z.D.Z.) has recently proposed a putative pf for a three-dimensional (3D) Ising model, based on two, as yet unproved, conjectures and has pointed out some important thermodynamic consequences of this pf. It would obviously be of considerable interest if such a pf, together with conjectures, could be rigorously proved.

**Keywords** Statistical–mechanical models · Many-body interactions · Partition functions · Thermodynamic consequences

## 1 Introduction

The purpose of this article is to discuss four statistical–mechanical models set out in Sects. 2, 3, 4 and 5 below. In the first two models, which are, in principle, governed by the BBGKY statistical–mechanical hierarchy [1], the main focus will be on higher-order particle correlation functions, eg three- and four-particle forms  $g_3$  and  $g_4$ . The relation of these functions to thermodynamically accessible quantities will be emphasized. Then in Sect. 4, the quantal canonical density matrix [2] and its diagonal element, the so-called Slater sum [3], will be the focus, for the case of an initially uniform electron assembly which is made inhomogeneous by the introduction of a one-body potential  $V(\mathbf{r})$ . Section 5, plus the Appendix are concerned with Ising models, with particular emphasis on the partition function and the critical exponents for the three-dimensional case [4].

With this brief introduction, we turn to the statistical–mechanical modeling of a classical monatomic liquid typified by argon. Here, it is certainly a useful approximation to represent the many-body force field, which ultimately of course must be calculated from the quantum–mechanical Schrödinger equation, as a sum of two-body central terms, characterized by a density-independent pair potential  $\phi(r_{ij})$  acting between atoms at separation  $r_{ij}$ .

## 2 Statistical–mechanical model of a homogeneous classical liquid (eg argon) with assumed central pair force

The statistical mechanics of a classical liquid such as argon, which we know to be describable with good accuracy by such a central pair potential  $\phi(r_{ij})$ , is subsumed into the BBGKY hierarchy [1]. Writing the pair correlation function  $g(r)$  in terms of the potential of mean force  $U(r)$ , one has [5]

$$g(r) = \exp\left(-\frac{U(r)}{k_B T}\right). \quad (2.1)$$

Then for a homogeneous classical liquid, the first member of the BBGKY hierarchy, the so-called force equation reads [5]

$$-\nabla_1 U(r_{12}) = -\nabla_1 \phi(r_{12}) - \rho \int \frac{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(r_{12})} \nabla_1 (\phi(r_{13})) d\mathbf{r}_3 \quad (2.2)$$

where  $\rho$  denotes the atomic number density.

As stressed for example in the early work of Johnson and March [6], which was brought to full fruition in the computer simulation studies of Reatto et al. [7], Eqs. 2.1 and 2.2 can be used to extract  $\phi(r)$  from a ‘measured’ pair distribution function  $g(r)$ , which is accessible for argon say by neutron scattering [8].

### 2.1 Internal energy $E$ characterized by higher-order particle correlation functions

In terms of the experimentally accessible [8] pair function  $g(r)$ , the internal energy  $E$  can be generated via the pair potential  $\phi(r)$  introduced above using the volume-derivative relation

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\rho^2}{2} \int \frac{\partial}{\partial \rho} [\rho g(r)] \phi(r) d\mathbf{r} \quad (2.3)$$

But the density dependence of the pair function  $g(r)$  is related to the important three-particle correlation function  $g_3$  entering the lowest-order hierarchical Eq. 2.2 for the present homogeneous liquid example in the pair-force statistical–mechanical model emphasized here. Specifically, an equation due to Schofield [9] then allows Eq. 2.3 to be re-expressed as

$$\left(\frac{\partial E}{\partial V}\right)_T = -\frac{\rho^2}{2S(0)} \left[ \int g(r) \phi(r) d\mathbf{r} + \rho \int \{g_3(\mathbf{r}, \mathbf{S}) - g(r)g(s)\} \phi(r) d\mathbf{r} d\mathbf{S} \right] \quad (2.4)$$

Here, the quantity  $S(0)$  denotes the long-wavelength limit of the liquid structure factor  $S(q)$ . In turn, this is linked to the pair function  $g(r)$  by Fourier transform, as

$$S(q) = 1 + \rho \int [g(r) - 1] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \quad (2.5)$$

Fluctuation theory connects  $S(0)$  with thermodynamically accessible quantities as [5]

$$S(0) = -\rho k_B T \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T. \quad (2.6)$$

2.2 Specific heat difference  $C_P - C_V$  related to the three-particle correlation function  $g_3$

Prompted by the early study of Bratby, Gaskell and March (BGM) [10], we next use Eq. 2.4, plus established thermodynamic relations, to relate the specific heat difference  $C_P - C_V$  to the three-particle correlation function  $g_3$ . This latter quantity is of quite central importance in the present statistical–mechanical model of a liquid such as argon, due to the BBGKY hierarchical member (2.2).

BGM start from the relation [11]

$$C_P - C_V = -\frac{T}{N} \left( \frac{\partial P}{\partial T} \right)_V^2 \left( \frac{\partial V}{\partial P} \right)_T. \tag{2.7}$$

This is readily re-written in the form

$$C_P - C_V = \frac{1}{\rho^2 k_B} \left( \frac{\partial P}{\partial T} \right)_V^2 \left[ -\rho k_B T \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \right]. \tag{2.8}$$

But from Zemansky [11], we have also

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P. \tag{2.9}$$

Using Eq. 2.9 to remove  $\left( \frac{\partial P}{\partial T} \right)_V^2$  from Eq. 2.8 then yields

$$C_P - C_V = S(0) \left[ \frac{P}{\rho k_B T} + \frac{1}{\rho k_B T} \left( \frac{\partial E}{\partial V} \right)_T \right]^2 k_B. \tag{2.10}$$

Next we employ Eq. 2.4 involving  $g_3$  to remove  $(\partial E/\partial V)_T$  from Eq. 2.10 to find

$$\begin{aligned} \frac{C_P - C_V}{k_B S(0)} &= \left\{ 1 - \frac{2\pi\rho}{3k_B T} \int g(r)r^3 \frac{\partial\phi}{\partial r} dr - \frac{\rho}{2k_B T S(0)} \right. \\ &\quad \left. \times \left[ \int g(r)\phi(r)dr + \rho \int \{g_3(\mathbf{r}, \mathbf{S}) - g(r)g(s)\} \phi(r)d\mathbf{r}d\mathbf{S} \right] \right\}^2 \end{aligned} \tag{2.11}$$

where the virial result for the pressure  $P$  [5] has also been employed.

It is of interest at this point to note that early work of Schofield [9] employing fluctuation theory allowed  $C_V$  to be expressed in terms of  $g_3$  and the four-particle

correlation function  $g_4$  in such a pair-force statistical–mechanical model as

$$\begin{aligned}
 C_V = & \frac{3}{2}k_B + \frac{1}{k_B T^2} \left[ \frac{1}{2}\rho \int g(r)\phi^2(r)dr + \rho^2 \int g_3(\mathbf{r}, \mathbf{S})\phi(r)\phi(s)drd\mathbf{S} \right. \\
 & \left. + \frac{1}{4}\rho^3 \int \{g_4(\mathbf{r}, \mathbf{S}, \mathbf{t}) - g(r)g(|\mathbf{t} - \mathbf{S}|)\} \phi(r)\phi(|\mathbf{t} - \mathbf{S}|) drd\mathbf{S}dt \right] \\
 & - \frac{[\rho \int g(r)\phi(r)dr + \frac{1}{2}\rho^2 \int \{g_3(\mathbf{r}, \mathbf{S}) - g(\mathbf{r})\} \phi(\mathbf{r})drd\mathbf{S}]^2}{S(0)} \quad (2.12)
 \end{aligned}$$

The interested reader is referred to the work of Bratby et al. [10] on simple insulating liquids like argon. Their numerical studies make it quite clear that to recover experimental results for both  $C_P - C_V$  and  $C_V$  alone involve truly major cancellations between much larger individual terms in Eq. 2.11 for  $C_P - C_V$  and in Eq. 2.12 for  $C_V$  alone. This makes it apparent that these two central equations are very sensitive to any approximations made in writing  $g_3$  and  $g_4$ , given  $\phi(r)$ . Fortunately, the computer simulation studies of Reatto et al. [7] have solved the hierarchical Eq. 2.2 without the need for any such approximation to  $g_3$  in the exact model equations presented here.

### 2.3 Changes required in simple liquid metals such as Na and Be, due to density dependence of pair potentials

The statistical–mechanical model above is appropriate to argon, with the assumption that the central pair potential  $\phi(r)$  is density independent. We wish to conclude this section, as well as to introduce the next section, by referring briefly to simple liquid metals such as Na and Be. These metals have been studied using electron theory by Perrot and March [12, 13]. In Ref. [12], the pair potential  $\phi(r, \rho)$  thus obtained for Na for a given density  $\rho$  is displayed in Fig. 2 where it is compared with that extracted for the same density by Reatto et al. [7], using the hierarchical Eq. 2.2, with input of the experimentally determined  $g(r)$ , plus the use of computer simulation to avoid approximations to the three-body correlation function  $g_3$ . All the main features of the density-dependent  $\phi(r, \rho)$  obtained for Na using the statistical–mechanical model discussed above are reproduced by electron theory for the particular density  $\rho$  for which the pair function  $g(r)$  is known. That the density dependence of  $\phi(r)$  was important in metals like Na and Be was stressed in the early work of Worster and March [14].

It is of interest here also to return to Be, for which Perrot and March [13] have calculated  $\phi(r, \rho)$  for a particular density  $\rho$ , again using electron theory. In Fig. 5 of Ref. [13], for this chosen density, the pair potential  $\phi(r, \rho)$  is shown to be crucially different from  $\phi(r)$  in the insulating liquid argon. For the liquid metal Be, electron theory predicts a large repulsive ‘hump’ following the first minimum in  $\phi(r, \rho)$ , the height of the hump being even larger than the depth of the first minimum. It will be of considerable interest for the future to use this prediction of the pair potential in Be to derive the pair function  $g(r)$  plus the three-body function  $g_3$  from the statistical–mechanical model characterized by Eq. 2.2, employing of course the computer

techniques set out by Reatto et al. [7] to avoid approximating  $g_3$  in terms of  $g(r)$ , using say the superposition approximation of Kirkwood [15].

Of course, Na liquid metal is a two-component mixture of  $\text{Na}^+$  ions and valence electrons, and is therefore a ‘Coulomb liquid’ [16]. The simplest such metallic liquid is the one-component plasma (OCP), and the above discussion leads us to treat immediately below such a OCP in two dimensions, using a statistical–mechanical model with a  $\ln(r_{ij})$  interaction. For one coupling strength, the important three-body correlation function  $g_3$  can be found analytically.

### 3 Statistical mechanical model of a two-dimensional (2D) Coulomb one-component plasma for a specific coupling strength, plus an application to 3D liquid metal Na

Jancovici et al. [17, 18] solved the above model some time ago for a particular coupling strength (see below for details). However, the model is of considerable current interest [19] and has intimate connection with the three-body correlation function given some prominence in the previous section. We shall therefore set out below (see also Rashid et al. [20]) some results of this model which are especially relevant in the present context.

The model under discussion in the first part of this section concerns a 2D classical system of one species of charged particles immersed in a neutralizing background and interacting via a 2D Coulomb potential (a realistic quantum–mechanical interaction will then be introduced later for the 3D liquid metal Na). The 1D analogy of the Coulomb case referred to above has been solved exactly, going back at very least to the study of Edwards and Lenard [21].

Quite specifically, in 2D, the interaction potential  $\phi(r)$  used by Jancovici [17] takes the form  $\phi(r) = -e^2 \ln(r/L)$  where  $L$  is a length scale and  $e$  is the charge on each of the  $N$  identical particles. The excess free energy per particle is readily shown for this model to take the form

$$\frac{F_{\text{exc}}}{N} = -\frac{1}{4}e^2 \ln(\pi\rho L^2) + f(T). \quad (3.1)$$

Therefore, it follows that the equation of state is given by

$$P = \left( k_B T - \frac{1}{4}e^2 \right) \rho \quad (3.2)$$

where  $\rho = N/(\pi R^2)$  is the number density [17, 18], with  $R$  the interparticle spacing. As Jancovici et al. demonstrated, further information can be obtained at a particular coupling strength  $\Gamma = e^2/(k_B T)$ , which can be characterized by a special temperature  $T_0$  say given by  $T_0 = e^2/(2k_B)$ , i.e.  $\Gamma = 2$ . At  $T_0$ , Eq. 3.1 becomes precisely

$$\frac{F_{\text{exc}}}{N} = -\frac{1}{4}e^2 \ln(\pi\rho L^2) + e^2 \left[ \frac{1}{2} - \frac{1}{4} \ln(2\pi) \right]. \quad (3.3)$$

The important pair correlation function  $g(r)$  at  $\Gamma = 2$  is then given by

$$g(r) = 1 - \exp(-\pi\rho r^2) \quad (3.4)$$

In the present context, the key result for the three-particle correlation function at this coupling strength is then [17, 18, 20]

$$g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = 1 - \exp(-\pi\rho r_{12}^2) - \exp(-\pi\rho r_{23}^2) - \exp(-\pi\rho r_{31}^2) \\ + 2 \exp\left(-\frac{1}{2}\pi\rho (r_{12}^2 + r_{23}^2 + r_{31}^2)\right) \cos[2\pi\rho A(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)] \quad (3.5)$$

where  $A$  is the area [17] of the triangle formed by the particles (1, 2, 3).

Rashid et al. [20] have used the work in Refs. [17] and [18] to relate  $g_3$  to the density dependence of the pair function (3.4). These workers also constructed the important Ornstein–Zernike direct correlation function [5]  $c(r)$  in the above model at coupling strength  $\Gamma = 2$  (see also Hernando [22, 23]). The so-called collective part [20]  $c_c(r)$ , defined by  $c_c = c - c_P$ , where  $c_P$  is defined, following Kumar et al. [24], by invoking thermodynamic consistency, and now in  $d$  dimensions, as

$$c_P(r) = -\frac{\phi(r)}{k_B T} \frac{1}{2dr^{d-1}} \frac{\partial^2}{\partial\rho\partial r} \left[ \rho^2 r^d g(r) \right] \quad (3.6)$$

is found to only be important at small  $r$ . The potential contribution  $c_P(r)$  is dominant in  $c(r)$  outside an initial core region, for this particular coupling strength  $\Gamma = 2$ .

Solution of the force equation of the BBGKY hierarchy

We turn next to summarize the work of Golden et al. [25]. These authors demonstrate that, provided the assumed pair potential  $\phi(r)$  has a Fourier transform  $\tilde{\phi}(q)$ , then the first member of the BBGKY hierarchy; the force Eq. 2.2 can be expressed as

$$\frac{\tilde{\phi}(q)}{k_B T} = -\frac{\tilde{E}(q)}{S(q)} \quad (3.7)$$

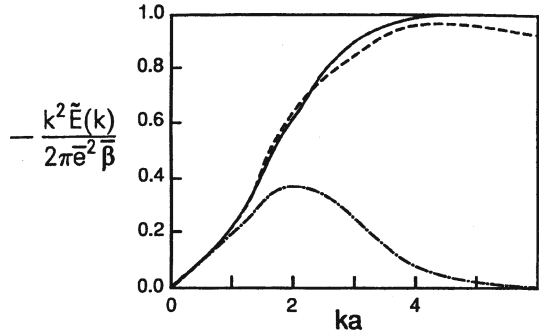
where  $S(q)$  is the liquid structure factor,  $S(q) - 1$  being the Fourier transform (FT) of  $g(r) - 1 \equiv h(r)$ , the total correlation function. It only remains then to define  $\tilde{E}(q)$  in Eq. 3.7 as [25]

$$\tilde{E}(q) = \tilde{h}(q) + \Sigma(q) \quad (3.8)$$

where  $\tilde{h}(q)$  is the FT of the total correlation function  $h(r)$ . The summation  $\Sigma$  in Eq. 3.8 can be written in terms of  $g_3$  and  $\phi$ , where  $g_3$  is usefully separated into the form [25]

$$g_3(r_{12}, r_{32}) = 1 + h(r_{12}) + h(r_{32}) + h(r_{31}) + t(\mathbf{r}_{12}, \mathbf{r}_{32}) \quad (3.9)$$

**Fig. 1** Scaled form of function  $\tilde{E}(q)$  for coupling strength  $\Gamma = 2$  describing three-particle correlations in the two-dimensional one-component plasma model (Redrawn from Golden et al. [25]). *Solid curve* exact result. *Dashed curve* HNC approximation. *Dot-dash curve* random phase approximation



Then with  $\tilde{t}$  denoting the FT of  $t$  in the above Eq. 3.9 one has

$$\Sigma(q) = \frac{1}{V} \sum_k \frac{\mathbf{q} \cdot \mathbf{k}}{q^2} \beta \rho \tilde{\phi}(q) \left\{ \tilde{h}(|\mathbf{q} - \mathbf{k}|) + \rho \tilde{t}(\mathbf{q} - \mathbf{k}, \mathbf{k}) \right\}, \tag{3.10}$$

with  $\beta = (k_B T)^{-1}$ . It is important to reiterate that given the assumptions made about the existence of FTs, Eqs. (3.7), (3.8) and (3.10) represent an exact solution of the BBGKY Eq. 2.2.

Returning briefly to the specific case of the 2D OCP, one can clearly plot the exact form of  $\tilde{E}(q)$  in this model for coupling strength  $\Gamma = 2$  and the result is shown in Fig. 1. The full curve represents the exact form of  $\tilde{E}(q)$  describing three-particle correlations in this model. The dashed curve shows, for comparison the hypernetted chain approximation (denoted by HNC), namely

$$\tilde{E}_{\text{HNC}}(q) = -[S(q) - 1]^2 - \frac{\tilde{U}(q)}{k_B T} S(q). \tag{3.11}$$

where  $\tilde{U}(q)$  is the FT of the potential of mean force  $U(r)$  in Eq. 2.2. While  $\tilde{E}_{\text{HNC}}(q)$  is a great improvement on the so-called random phase approximation (RPA) given by

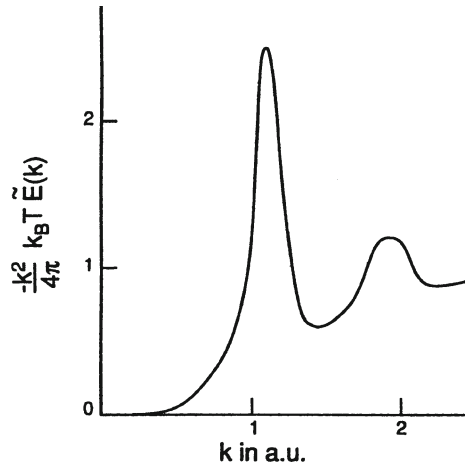
$$\rho \tilde{E}_{\text{RPA}}(q) = \rho \tilde{h}(q) = S(q) - 1, \tag{3.12}$$

which is also plotted in the dot–dash curve of Fig. 1,  $\tilde{E}_{\text{HNC}}(q)$  does not yield the correct limit of  $\tilde{E}(q)$  at large  $q$  for this example of the 2D OCP.

Finally, in this same statistical–mechanical model, based on the initial assumption of a many-body force field as a sum of central pair interactions, one can construct the function  $\tilde{E}(q)$  as a function of  $q$  in atomic units as in Fig. 2 for liquid Na just above the freezing point. The input is the pair potential  $\phi(r)$  obtained from electron theory by Perrot and March [12] plus the experimental liquid structure factor  $S(q)$  from Greenfield, Wellendorf and Wiser [26]. Thereby, the three-particle correlation function  $g_3$  becomes quantitatively accessible, though numerically rather than analytically because of the experimental input of  $S(q)$  into Eq. 3.7.



**Fig. 2** Scaled form of function  $\tilde{E}(q)$  describing three-particle correlations in liquid metal Na near freezing (Redrawn from Golden et al. [25]) Wave number  $k$  is in atomic units



#### 4 Quantal canonical density matrix and Slater sum for non-interacting uniform electron liquid made inhomogeneous by switching on a one-body potential $V(\mathbf{r})$

Since the early studies of March and Murray [27,28] there has been considerable interest in a quantal free Fermion homogeneous assembly perturbed by a one-body potential  $V(\mathbf{r})$ . With a total Hamiltonian which is a sum over  $N$  particles of a one-body form

$$H_r = -\frac{\eta^2}{2m} \nabla_r^2 + V(\mathbf{r}) \quad (4.1)$$

the canonical density matrix  $C(\mathbf{r}, \mathbf{r}', \beta)$ , which is the main tool employed in this section, along with its diagonal element  $S(\mathbf{r}, \beta)$ :

$$S(\mathbf{r}, \beta) = C(\mathbf{r}, \mathbf{r}', \beta)|_{r'=r}, \quad (4.2)$$

the so-called Slater sum, is defined by

$$C(\mathbf{r}, \mathbf{r}', \beta) = \sum_{\text{all } i} \exp(-\beta \epsilon_i) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}'). \quad (4.3)$$

Here  $\psi_i(r)$  and  $\epsilon_i$  are respectively the Schrödinger wave functions and corresponding eigenvalues generated by the one-body Hamiltonian  $H$ . As shown in the early study of Bloch [29], the canonical density matrix  $C(\mathbf{r}, \mathbf{r}', \beta)$  satisfies the partial differential equation

$$H_r C = -\frac{\partial C}{\partial \beta}, \quad (4.4)$$

and obviously the completeness condition satisfied by the wave functions must be used as a ‘boundary condition’, namely

$$C(\mathbf{r}, \mathbf{r}', \beta) \Big|_{\beta=0} = \delta(\mathbf{r} - \mathbf{r}'). \quad (4.5)$$

March and Murray rewrote Eqs. (4.4) and (4.5) in the form of an integral equation:

$$C(\mathbf{r}, \mathbf{r}', \beta) = C_0(\mathbf{r}, \mathbf{r}', \beta) - \int dr_1 \int_0^\beta d\beta_1 C_0(\mathbf{r}, \mathbf{r}_1, \beta - \beta_1) V(r_1) C(\mathbf{r}_1, \mathbf{r}', \beta_1), \quad (4.6)$$

where  $C_0$  is the homogeneous solution of Eq. 4.4, namely

$$C_0(\mathbf{r}, \mathbf{r}', \beta) = \frac{1}{(2\pi\beta)^{3/2}} \exp\left[-\frac{|\mathbf{r} - \mathbf{r}'|^2}{2\beta}\right], \quad (4.7)$$

atomic units  $m = \hbar = e$  being employed here and below.

While March and Murray showed that by insertion of  $C = C_0$  in the integral term in Eq. 4.6 in lowest order the infinite series in Eq. 4.9 below could be established, we shall also focus below on specific solutions for chosen  $V(\mathbf{r})$ , namely the Coulomb potential  $-Ze^2/r$  and the case of harmonic confinement, the latter being of considerable interest currently in connection with experiments on cold confined Fermion gases [30].

What will be one important focal point below will be to show that for some cases, one can bypass the solution for  $C(\mathbf{r}, \mathbf{r}', \beta)$  and work directly with the Slater sum  $S(\mathbf{r}, \beta)$  in Eq. 4.2, which evidently then yields the partition function, denoted by  $Z(\beta)$  below, as

$$Z(\beta) = \int S(\mathbf{r}, \beta) d\mathbf{r}. \quad (4.8)$$

But before that, let us summarize briefly below the important iterative solution to all orders in  $V(\mathbf{r})$  of the integral Eq. 4.6, the lowest order result being the free electron form  $C_0$  in Eq. 4.7. The result is readily written as an infinite series:

$$C(\mathbf{r}, \mathbf{r}_0, \beta) = \sum_{j=0}^{\infty} C_j(\mathbf{r}, \mathbf{r}_0, \beta) \quad (4.9)$$

where  $C_j(\mathbf{r}, \mathbf{r}_0, \beta)$  can be generated quite explicitly in the form

$$C_j(\mathbf{r}, \mathbf{r}_0, \beta) = (2\pi\beta)^{-3} \int \prod_{l=1}^j \left\{ -d\mathbf{r}_l \frac{V(\mathbf{r}_l)}{2\pi} \right\} \left( \sum_{l=1}^{j+1} s_l \right) \times \exp \left\{ -\frac{1}{2\beta} \left( \sum_{l=1}^{j+1} s_l \right)^2 \right\} / \prod_{l=1}^{j+1} s_l \quad (4.10)$$

and  $s_l = |\mathbf{r}_l - \mathbf{r}_{l-1}|$ ,  $\mathbf{r}_{j+1} = \mathbf{r}_1$ .

As an immediate example of Eqs. (4.9) and (4.10) we note that they can be summed for the harmonic potential  $V = \frac{1}{2}kr^2 \equiv \frac{1}{2}m\omega^2 r^2$ ,  $\beta = (k_B T)^{-1}$  to get in particular the Slater sum  $S(\mathbf{r}, \beta) \equiv C(\mathbf{r}, \mathbf{r}', \beta)|_{\mathbf{r}'=\mathbf{r}}$  as [3]

$$S(r, \beta) = \left( \frac{m}{2\pi\hbar} \right)^{3/2} \left[ \frac{\omega}{\sinh \hbar\omega\beta} \right]^{3/2} \exp \left( -\frac{m}{\hbar} \omega r^2 \tanh \left( \frac{1}{2} \hbar\omega\beta \right) \right). \quad (4.11)$$

Below we shall give particular attention to the form of differential equation one can expect  $S(\mathbf{r}, \beta)$  to satisfy, taking Eq. 4.11 as starting point.

#### 4.1 Form of differential equation expected for the Slater sum $S(\mathbf{r}, \beta)$

In the early work of March and Murray [28] it was shown, via in fact the radial Schrödinger equation for central field problems, that in one dimension, with  $S \equiv S(x, \beta)$ , there is a quite general partial differential equation for an arbitrary form of potential  $V(x)$ . This reads [31]

$$\frac{\hbar^2}{8m} S'''(x, \beta) - \frac{\partial^2}{\partial\beta\partial x} S(x, \beta) - V(x)S'(x, \beta) - \frac{1}{2}V'(x)S(x, \beta) = 0 \quad (4.12)$$

For the central field result (4.11) with harmonic confinement, the partial differential equation satisfied by  $S(r, \beta)$  is readily verified, after some modest manipulation, to be

$$\frac{\hbar^2}{8m} \frac{\partial}{\partial r} \left( \nabla^2 S \right) - \left[ \frac{\partial}{\partial\beta} + V(r) \right] \frac{\partial S}{\partial r} - \frac{1}{2} \frac{\partial V}{\partial r} S = 0 \quad (4.13)$$

where  $V = \frac{1}{2}m\omega^2 r^2$ . Unfortunately, Eq. 4.13 is specific to harmonic confinement, the corresponding result for the bare Coulomb potential  $-Ze^2/r$  being known from the independent studies of Cooper [32] and Pflanzner et al. [33] to have the form

$$\begin{aligned} \frac{r^2}{4Z} \frac{\partial^3}{\partial r^3} S(r, \beta) + \frac{r}{Z} \frac{\partial^2}{\partial r^2} S(r, \beta) + \frac{1}{2Z} \frac{\partial}{\partial r} S(r, \beta) + 2r \frac{\partial}{\partial r} S(r, \beta) + S(r, \beta) \\ = \frac{2r^2}{Z} \frac{\partial^2}{\partial r \partial \beta} S(r, \beta) \end{aligned} \quad (4.14)$$

Unfortunately, to date, no known solution of Eq. 4.14 exists, to the knowledge of the present authors, of comparable elegance to the Slater sum (4.11) for harmonic confinement. There is, however, available for the Coulomb potential the important, albeit somewhat complicated, infinite series form derived by Blinder [34], and displayed in Eq. 3.1 of that reference. However, Whittaker, Laguerre and Hermite functions are all involved in Blinder’s infinite series, which has not, as yet, found significant practical applications. It is therefore important that Eq. 4.14 be studied further, for compact solutions analogous to Eq. 4.11 for the harmonic cases.

#### 4.2 Some limiting results for the Slater sum in $d$ dimensions

To conclude this section, we effect some generalizations of the above results for the Slater sum to general dimensionality  $d$ .

Returning to the definition of the quantal canonical density matrix  $C(\mathbf{r}, \mathbf{r}', \beta)$  in Eq. 4.3, let us note that adding a constant potential  $V$  shifts the eigenvalues  $\epsilon_i$  by this constant, but does not change the eigenfunctions. Thus, in the limit of slowly varying potential  $V(x)$  we can evidently write, using Eq. 4.7 with  $\mathbf{r}' = \mathbf{r}$ , but now modified to one dimension:

$$S(x, \beta) = \frac{1}{(2\pi\beta)^{1/2}} \exp(-\beta V(x)), \tag{4.15}$$

Forming the derivatives appearing in the exact one-dimensional Eq. 4.12 shows that Eq. 4.15 is a solution provided  $S'''(x, \beta)$  is neglected. In fact, Eq. 4.15 is of Thomas-Fermi-like form, and yields the ground-state density  $n(x)$  as [35]

$$n(x) = \text{constant}[\mu - V(x)]^{1/2}, \tag{4.16}$$

since  $n(x)$  is, in fact the inverse Laplace transform of  $S(x, \beta)/\beta$  with respect to  $\beta$ .

As Lehmann and March [36] noted, the analogue of Eq. 4.15 for slowly varying potential in  $d$  dimensions reads

$$S(\mathbf{r}, \beta) = \frac{1}{(2\pi\beta)^{d/2}} \exp(-\beta V(\mathbf{r})), \tag{4.17}$$

Taking the case of  $d$ -dimensional harmonic confinement, the three-dimensional result (4.11), first in fact obtained in three dimensions in the studies of electrons in a constant magnetic field by Sondheimer and Wilson [37], has the  $d$ -dimensional generalization [38]

$$S(r, \beta) = \left(\frac{m\omega}{2\pi\hbar}\right)^{d/2} \left[\frac{1}{\sinh^{d/2}(\beta\hbar\omega)}\right] \times \exp\left[-\frac{m\omega r^2}{\hbar} \tanh\left(\frac{\beta\hbar\omega}{2}\right)\right] \tag{4.18}$$

This can be shown to satisfy the partial differential equation

$$\frac{\hbar^2}{8m} \frac{\partial}{\partial r} [\nabla^2 S] - \left[ \frac{\partial}{\partial \beta} + V(r) \right] \frac{\partial S}{\partial r} - \frac{(d-2)}{2} \frac{\partial V}{\partial r} S = 0 \quad (4.19)$$

where  $V(r)$  now denotes  $\frac{1}{2}m\omega^2 r^2$ . Eq. 4.19 gives back Eq. 4.13 in the special case when  $d = 3$ .

In subsect. 4.3, we record two further limiting cases, for which the Slater sum can be calculated analytically.

#### 4.3 Two further limiting cases in which the quantal canonical density matrix can be calculated from the statistical–mechanical model under discussion

The first example below is motivated by the evidence that if solid  $C_{60}$  is doped with an alkali metal, say  $K$ , the donated electrons are rather localized near the surface of the ‘almost spherical’  $C_{60}$  molecule [39]. This prompted the work by Holas and March [40] on the quantal canonical density matrix for free electrons moving in a spherical surface. The input into Eq. 4.3 for  $C(\mathbf{r}, \mathbf{r}', \beta)$  was therefore the energy levels and corresponding eigenfunctions for electrons confined to move on the surface of a sphere but are otherwise free. The result, which must satisfy the Bloch Eq. 4.4, is given for sphere radius  $R$ , by, with  $S = |\mathbf{r} - \mathbf{r}'|$ :

$$\begin{aligned} C(\mathbf{r}, \mathbf{r}', \beta) &\equiv C(S, \beta) \\ &= (4\pi R^2)^{-1} \sum_{l=0}^{\infty} \exp[-\beta E_R l(l+1)] (2l+1) P_l \left( 1 - 2 \left\{ \frac{S}{2R} \right\}^2 \right) \end{aligned} \quad (4.20)$$

This then is the exact quantal canonical density matrix for free electrons moving on a spherical surface (compare fullerene) of radius  $R$ , where  $E_R$  is the characteristic energy unit given by

$$E_R = \frac{\hbar^2}{2mR^2}. \quad (4.21)$$

The final example in this section connects with the reference to the study of Sondheimer and Wilson [37] in a magnetic field. Generalizing this work, Amovilli and March [41] have obtained results for the Slater sum representing the  $H_2^+$  molecular ion in an intense magnetic field, such as exists say, at the surface of some neutron stars but in  $H_2^+$  applied along the internuclear axis. In the limit as the magnetic field strength  $B$  tends to infinity,  $H_2^+$  in such a field is characterized by a specific one-dimensional Hamiltonian [42].

The major result of Amovilli and March [41] is to obtain an exact analytic form of the canonical density matrix  $C(x, x', \beta)$  for this one-dimensional Hamiltonian, in

their equation (11). The Slater sum  $S(x, \beta)$  is also given analytically in their equation (28). This is in the form of an infinite series in which the general term is known.

### 5 Conjectured exact solution of the 3D Ising model

The Ising model can be applied to understand a group of ‘universal’ critical phenomena at/near the critical point of a second-order (continuous) phase transition in various systems such as magnets, order-disorder alloys, liquid helium, liquids, glassy substances, etc. The difficulties in solving explicitly the 3D Ising model are topologic, which originate from the crossover of the nonplanar bonds (ie high-order terms in the transfer matrix). Recently, one of us (Z.D.Z.) proposed two conjectures [4], ie an additional rotation in the fourth curled-up dimension and three weight factors on the eigenvectors, to serve as a boundary condition to overcome the topologic difficulties of the 3D Ising model. The partition function, and thermodynamic consequences such as the specific heat, the spontaneous magnetization and the true range  $\kappa_x$  of the correlation, and the correlation functions of the 3D simple orthorhombic Ising model were obtained, based on the two conjectures. The critical temperature of the simple orthorhombic Ising lattices was determined by the relation of  $K_1 K^* = K_1 K_2 + K_1 K_3 + K_2 K_3$ , where  $K_i = \beta J_i (i = 1, 2, 3)$  and  $K^*$  is defined by  $e^{-2K_1} \equiv \tanh K^*$ . The golden ratio  $x_c = e^{-2K_c} = \frac{\sqrt{5}-1}{2}$  (or silver ratio  $x_c = \sqrt{2}-1$ ) is the largest solution for the critical temperature of the 3D (or 2D) Ising systems, which corresponds to the most symmetric simple cubic (or square) lattice. The critical exponents for the 3D Ising model were putatively determined to be  $\alpha = 0, \beta = 3/8, \gamma = 5/4, \delta = 13/3, \eta = 1/8$  and  $\nu = 2/3$ , satisfying the scaling laws. The conjectured exact solutions were judged by several criterions, and compared with those of approximation methods and experimental findings.

After that, there have been two rounds of exchanges of Comments/Responses/Rejoinders [43–48]. The progresses have been made further, thanks to these exchanges. In Ref. [44], Conjecture 1, regarding the additional rotation, was understood further as performing a transformation for smoothing all the crossings of the knots, while the weight factors in Conjecture 2 were interpreted as a novel topologic phase. The partition function of the 3D simple orthorhombic Ising model, being dealt within a (3 + 1)-dimensional framework with different weight factors on the eigenvectors, can be written as [4,44]:

$$\begin{aligned}
 N^{-1} \ln Z = \ln 2 + \frac{1}{2(2\pi)^4} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \ln \left[ \cosh 2K_1 \cosh 2(K_2 + K_3 + K_4) \right. \\
 \left. - \sinh 2K_1 \cos \omega' - \sinh 2(K_2 + K_3 + K_4) \right. \\
 \left. \times (w_x \cos \omega_x + w_y \cos \omega_y + w_z \cos \omega_z) \right] d\omega' d\omega_x d\omega_y d\omega_z \quad (5.1)
 \end{aligned}$$

with  $K_4 = K_2 K_3 / K_1$ , and the weight  $w_x = 1$ , while the details of the weights  $w_y$  and  $w_z$  were revealed in Appendixes of Ref. [4], to fit well the high-temperature series expansion at/near infinite temperature. However, the weight factors  $w_x, w_y$  and  $w_z$  in

Eq. 4.1 can be replaced by  $|w_x| \cos \phi_x$ ,  $|w_y| \cos \phi_y$  and  $|w_z| \cos \phi_z$ , respectively [44], since only the real part of the phase factors appears in the eigenvalues. This replacement is realized by generalizing the weight factors in the eigenvectors in eqn (33) of Ref. [4] as complex numbers  $|w_x|e^{i\phi_x}$ ,  $|w_y|e^{i\phi_y}$ , and  $|w_z|e^{i\phi_z}$  with phases  $\phi_x$ ,  $\phi_y$ , and  $\phi_z$  [44].

The spontaneous magnetization  $I$  for the 3D simple orthorhombic Ising lattices was obtained as [4]:

$$I = \left\{ \frac{\left[ \left( (1-x_1^2+4x_1x_2x_3x_4-x_2^2x_3^2x_4^2+x_1^2x_2^2x_3^2x_4^2) (1-x_1^2-4x_1x_2x_3x_4-x_2^2x_3^2x_4^2+x_1^2x_2^2x_3^2x_4^2) \right)^{\frac{1}{2}} \right]^{\frac{3}{4}}}{(1-x_1^2)(1-x_2^2x_3^2x_4^2)} \right\} \quad (5.2)$$

where  $x_i = e^{-2K_i}$  ( $i = 1, 2, 3, 4$ ). It was found that the 3D- to 2D-crossover phenomenon differs with the 2D- to 1D-crossover phenomenon and there is a gradual crossover of the exponents from the 3D values to the 2D ones. However, it is understood in Ref. [49] that if one kept changing the parameters  $K_i$  within the 3D zone in Fig. 4 of Ref. [4], which is close to the most symmetric simple cubic lattice, the 3D- to 2D-crossover would no exist. It can be seen more clearly in a figure represented in the  $K_1 - K_2 - K_3$  parametric space [49]. When one decreases the parameters  $K_i$  while keeping  $K_1 = K_2 = K_3 = K$ , one goes along the  $\langle 111 \rangle$  axis from  $(1,1,1)$  to the origin. This case always corresponds the  $(1, 1)$  point (the star in Fig. 4 of Ref. [4]), so the 3D critical behavior is hold until the origin at which the system becomes the 0D (or 1D). This is similar with the 2D- to 1D-crossover phenomenon. Nevertheless, if one changed the parameters  $K_i$  to cross the boundary curves in Fig. 4 of Ref. [4], the 3D- to 2D-crossover would appear.

As pointed out clearly in Refs. [44,47], all the rigorous theorems in Ref. [50–58] for proving the convergence size of the high-temperature expansion series have been proved only for  $\beta \equiv 1/(k_B T) > 0$ , i.e.,  $T < \infty$ . Exactly infinite temperature has been never touched in these theorems, since there is a possibility of the existence of a phase transition at  $\beta = 0$ , according to the condition  $z \equiv \exp(-2\beta H) = 1$  in the Yang-Lee Theorems [59,60]. The difficulties in the theorems are seen as follows [49]: Setting  $\beta = 1$  equalizes to  $T = 1/k_B \neq \infty$ . Thus, the necessary and sufficient condition for using the dimensionless parameters  $K_i = \beta J_i$ , ( $i = 1, 2, 3$ ) and  $h = \beta H$  and setting  $\beta = 1$  is  $\beta \neq 0$ . On the other hand, it is to be expected that the exact solution of the 3D Ising model does not reproduce term by term the well-known low-temperature series that is divergent [4,44,47]. The lack of information of the global behaviour of the 3D Ising system is the root of such divergence in the well-known low-temperature series [47]. The trouble with it may originate from some difficulties in the foundation of statistical mechanics. It was understood [47] that the lack of ergodicity of the 3D Ising model would lead to the time average being different from the ensemble average, which may not contain complete information of the system. Neglecting the difference between the two averages may work well in other models with dimensions  $D \neq 3$ , but cause serious troubles in the 3D Ising system because of its global topologic behaviour and geometrical structure [4,44]. Since the well-known low- and high-temperature

series of the 3D Ising model might not account properly for the time average of the system, they might be invalid at finite temperatures. Therefore, the well-known low- and high-temperature series cannot serve as a standard for judging the putative exact solution of the 3D Ising model. The conjectured solution can be utilized to understand critical phenomena in various systems [61,62], while the conjectures are still open to rigorous proof. It is to be expected that one has to utilize the knowledge of the knot theory [63] to achieve this rigorous proof.

## 6 Summary and proposed future directions

In this article, we have emphasized first that two classical statistical–mechanical models are amenable to exact treatment. The first, with a many-body force field which can be realizably modeled in a liquid like argon by central density-independent pair potentials, is then amenable to what is, in principle, an exact solution. However, to work with the lowest member, shown in Eq. 2.2, of the BBGKY hierarchy, it is then essential to bypass approximation of the three-body correlation function  $g_3$  by having recourse to computer simulation methods [7]. However, in the second statistical–mechanical model, progress can be made analytically with  $g_3$  without approximation, for a two-dimensional one-component plasma with  $\ln(r_{ij})$  interparticle interaction.

Attention is next focused on a quantum–mechanical model in which initially uniform non-interacting electrons are rendered inhomogeneous by the switching-on of a one-body potential  $V(\mathbf{r})$ . The quantal canonical density matrix of the resulting Hamiltonian satisfies the so-called Bloch equation. What is the prime focus here however is the diagonal of this canonical density matrix, namely the so-called Slater sum  $S(\mathbf{r}, \beta)$  [3]. This quantity can be generated by perturbation theory to all orders in  $V(\mathbf{r})$  [27]. But to date, the resulted series has only been summed exactly for very specific choices of  $V(\mathbf{r})$ . Hence, attention is devoted here to the question of the differential equation satisfied by  $S(\mathbf{r}, \beta)$  for specific choices of  $V(\mathbf{r})$ . This work has a generalization to quantum–mechanical assemblies of interacting particles given in the early study of Green [64], but so far applications are lacking.

The final statistical–mechanical model chosen here is that corresponding to the 3D generalization of the Ising model. This model but in 2D, was solved exactly in the pioneering work of Onsager [65], and one of us [4] has, by making two, as yet unproved conjectures, proposed a form of partition function set out in Sect. 5 of the present article. This, additionally, led to proposals for the critical exponents of the 3D Ising model, which have been utilized by subsequent workers [61,62].

As to future directions, there is ample opportunity, following particularly the theoretical study of Golden et al. [25], and the experimental work of Johnson et al. [66] to generalize the considerations of Sect. 2 to simple liquid metals like Be and Mg, for which the density-independent pair potential of an insulating liquid like Ar now becomes  $\phi(r, \rho)$ : ie density dependence enters for such liquid metals as an essential feature. Following Refs. [12] and [13], electron theory now provides a tractable route for specific metals to yield  $\phi(r, \rho)$ .

Turning to the quantal Slater sum  $S(\mathbf{r}, \beta)$  focused on in Sect. 4, much progress has proved possible for a Hamiltonian which is of one-body potential form. Appealing



partial differential equations now exist for specific forms of the one-body potential  $V(\mathbf{r})$ , and further work is called for with the aim of replacing the known infinite series in powers of  $V(\mathbf{r})$  by a partial differential equation for  $S(\mathbf{r}, \beta)$  which is characterized solely by  $V(\mathbf{r})$ . Finally, much remains to be achieved on the 3D Ising model. Thus, attempts must be made to understand the basis for the two conjectures on which the presently proposed partition function rests. Also, inequalities for the critical exponents would be invaluable, with which to confront the critical exponents proposed by one of us (Z.D.Z.). As in the statistical–mechanical models discussed in Sect. 2, computer simulation should be invoked whenever it proves possible thereby to establish a well-nigh exact (to chosen numerical accuracy) solution of a specific, chosen model.

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## Appendix

### Collective coordinates in Ising systems

Early work of Bruce [67] was concerned with elucidating the nature of short-range order at criticality as well as exposing the character of the collective excitation spectrum in the critical region. In view of the focus on the 3D Ising model in the main text, it is relevant to summarize the findings of Bruce in this Appendix.

Kadanoff [68] surveys the concept of universality in critical point phenomena. In the vicinity of a second-order (continuous) phase transition, an assembly exhibits properties which can be characterized by a group of ‘universal’ quantities, which are independent of the fine details of the microscopic interactions. For example, the critical exponents discussed in the main text for the 3D Ising model are in this group, as are correlation functions.

Bruce made a start on the identification of the universal aspects of ordering coordinate configurations underlying critical point behavior. The study of Bruce followed Kadanoff [69] in treating the collective critical behavior of the ordering coordinate. Kadanoff described this using a set of block coordinates. Thus the block coordinate  $u_L(\mathbf{x})$  gives the instantaneous value of the local coordinates spatially averaged over a block having linear dimension  $L$  centred on the position  $\mathbf{x}$ . The critical form of such a block coordinate is then usefully characterized by its probability function, denoted by  $P_L(u_L)$ . This probability has been studied in the notable work of Patashinskii [70] and of Jona-Lasinio [71]. Bruce develops a renormalization group (RG) argument [67], following Patashinskii [70], which points to a limiting form  $P^\infty$  of the function  $P_L$ . This quantity  $P^\infty$  now depends only on block size  $L$  through the ratio of  $L$  to the correlation length  $\xi$ , when both  $L$  and  $\xi$  are large compared with a characteristic interatomic spacings. Bruce presents explicit calculations which bear this out [67]. Wilson’s recursion formula [72] was used to determine the form of  $P^*$  for 3D and 2D, but the latter result was substantiated by a calculation based on

exactly established properties of the planar Ising model. We asserted in [73,74] that the critical exponents  $\beta$ ,  $\gamma$  and  $\delta$  given experimentally for CrBr<sub>3</sub> [75,76] agree to excellent accuracy with the conjectured ones for the 3D Ising model [4]. Furthermore, the critical exponent  $\beta = 0.38$ , obtained experimentally for bulk Ni [77], is very close to the Zhang's theoretical value  $\beta = 3/8$  [4]. It is expected that the conjectured exact properties of the 3D Ising models obtained in Ref. 4 will benefit to investigate the probability density functions for collective coordinates in the 3D Ising systems, as Bruce did for the 2D systems [67].

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