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Indirect Exponential Coupling in the Classical Many-Body Problems*

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The usual coupling procedure consists of multiplying the interparticle potential $U_N(\mathbf{r}^N)$, by a coupling parameter λ and then expanding thermodynamic functions in powers of λ. The Kirkwood variation of this procedure couples only one particle of the system, resulting in an integrodifferential equation for distribution functions, which also can be expanded in powers of the coupling parameter. These expansions converge and are valid only for weakly coupled systems. If the Ursell f bonds are coupled instead of the direct interaction potentials, we can expand certain thermodynamic functions in powers of the exponential coupling parameters; for actual physical systems these expansions are *practically finite* low-order polynomials in the coupling parameters. Integrodifferential equations for distribution functions are derived, and it is seen that distribution functions are given by ratios of two practically finite polynomials in the exponential coupling parameters. The coefficients in these polynomials are *finite* even for strongly singular (e.g., hard sphere) potentials. The method provides a well-defined expansion parameter for the Kirkwood-Salzburg hierarchy and appears related to the f-bond chain summation and nodal expansion methods. Present and possible future applications include: theory of fused salts and electrolytes, theory of ferroelectricity, ion pairing in semiconductors, equation of state of the high-temperature electron gas, and problems of phase transitions. The possibility of applying exponential coupling to quantum-mechanical systems is noted.

THE device of coupling all or part of interparticle interactions by multiplying them by a parameter whose value varies from zero (independent particles) to unity (fully coupled system) is well known in both classical[1] and quantum[2] statistics. This method suffers from the disadvantage that the resulting equations can be solved exactly in the limit of weak coupling only, that is, through terms linear in the coupling parameters. Clearly, such solutions cannot describe a great majority of actual many-body systems, in particular, when the pair interaction potentials become strongly singular at small separations. Furthermore, the convergence of the usual coupling parameter expansions has never been proved and, in fact, appears doubtful. This note outlines another coupling method for the determination of distribution and thermodynamic functions of classical many-body systems. Expansions in powers of the new coupling parameters are applicable even to strongly singular (e.g., hard sphere) potentials; moreover, for realistic physical models, certain thermodynamic functions are given as *low-order polynomials* in the new coupling parameters, while distribution functions are simple ratios of such polynomials. Besides the formal connection with the Kirkwood coupling parameter method,[1] the present development is related to the Kirkwood-Salsburg[3] hierarchy, the Montroll-Mayer chain summation,[4] and the nodal expansion procedure.[5,6] In principle, it appears applicable also to quantum-mechanical systems.

The canonical ensemble configuration partition function Z_N of a system of N particles in a volume V, interacting with a potential

$$U(\mathrm{N})=\sum_{i<j}^{N} U(\mathbf{r}_{ij}),$$

at the reciprocal temperature $\beta=1/kT$, can be written

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[1] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935).

[2] See e.g., M. Goldberger and E. Adams, J. Chem. Phys. **20**, 240 (1952).

[3] J. G. Kirkwood and Z. Salsburg, Discussions Faraday Soc. **15**, 28 (1953).

[4] E. W. Montroll and J. E. Mayer, J. Chem. Phys. **9**, 626 (1941).

[5] E. Meeron, J. Math. Phys. **1**, 192 (1960).

[6] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958). The Percus-Yevick integral equation is the linearized convolution approximation of reference 5.

as an integral of a product of Ursell f bonds:

$$Z_N=\int_V \exp[-\beta U(\mathbf{N})]d\mathbf{r}^N=\int_V \prod_{i<j}^{N}[1+f(ij)]d\mathbf{r}^N \quad (1)$$

with

$$f(ij)=\exp[-\beta U(\mathbf{r}_{ij})]-1.$$

Now, instead of introducing coupling parameters directly into the interaction potential $U(\mathbf{N})$, we multiply each function $f(ij)$ by parameters $0\leq\lambda_i,\ \lambda_j\leq 1$,

$$Z_N(\lambda_1,\cdots,\lambda_N)=Z_N(\boldsymbol{\lambda})=\int_V \prod_{i<j}^{N}[1+\lambda_i\lambda_j f(ij)]d\mathbf{r}^N. \quad (2)$$

When all the λ's are unity we recover the actual fully coupled system; when the coupling parameter λ_i of particle i is zero we have a system of $N-1$ interacting particles and one free particle i. The distribution function $\rho(1,2,\cdots,n;\boldsymbol{\lambda})=\rho(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_n;\boldsymbol{\lambda})$ of particles $1,\cdots,n$ is given by

$$\rho(1,2,\cdots,n;\boldsymbol{\lambda})=\frac{N!}{(N-n)!}\frac{1}{Z_N(\boldsymbol{\lambda})} \times\int_V \prod_{i<j}[1+\lambda_i\lambda_j f(\mathbf{r}_{ij})]d\mathbf{r}^{N-n}. \quad (3)$$

On differentiating both sides of Eq. (3) with respect to λ_1 we have

$$\frac{\partial}{\partial\lambda_1}\ln\rho(1,2,\cdots,n;\boldsymbol{\lambda})=\sum_{i=2}^{n}\frac{\lambda_i f(1i)}{1+\lambda_1\lambda_i f(1i)}+\frac{1}{N-n}\sum_{j=n+1}^{N}\int_V \frac{\lambda_j f(1j)}{1+\lambda_1\lambda_j f(1j)}\frac{\rho(1,2,\cdots,n,j;\boldsymbol{\lambda})}{\rho(1,2,\cdots,n;\boldsymbol{\lambda})}d\mathbf{r}_j$$
$$-\frac{1}{N(N-1)}\sum_{j=2}^{N}\int_V \frac{\lambda_j f(1j)}{1+\lambda_1\lambda_j f(1j)}\rho(1,j;\boldsymbol{\lambda})d\mathbf{r}_1 d\mathbf{r}_j. \quad (4)$$

Here $\rho(1,2,\cdots,n,j;\boldsymbol{\lambda})$ is the distribution function of $n+1$ particles, $1, 2, \cdots, n$, and j. We now subtract from Eq. (4) the corresponding equation for $\rho(1, 2, \cdots, n-1;\boldsymbol{\lambda})$, introduce the dimensionless distribution functions $g(1,2,\cdots,n;\boldsymbol{\lambda})=\rho(1,2,\cdots,n;\boldsymbol{\lambda})/\rho^n$ (with $\rho=N/V$), and neglect terms of $O(1/N)$, thus obtaining an integral equation for distribution functions

$$\frac{\partial}{\partial\lambda_1}\ln g(1,2,\cdots,n;\boldsymbol{\lambda})=\frac{\partial}{\partial\lambda_1}\ln g(1, 2, \cdots, n-1, \boldsymbol{\lambda})+\frac{\lambda_n f(1n)}{1+\lambda_1\lambda_n f(1n)}$$
$$+\frac{1}{V}\sum_{j=n+1}^{N}\int_V \frac{\lambda_j f(1j)}{1+\lambda_1\lambda_j f(1j)}\left[\frac{g(1,2,\cdots,n,j;\boldsymbol{\lambda})}{g(1,2,\cdots,n;\boldsymbol{\lambda})}-\frac{g(1, 2, \cdots, n-1, j;\boldsymbol{\lambda})}{g(1, 2, \cdots, n-1;\boldsymbol{\lambda})}\right]d\mathbf{r}_j \quad .(5)$$

The treatment is similar to that of Kirkwood,[1] except that the term $f(ij)/[1+f(ij)]$ appears everywhere instead of $U(\mathbf{r}_{ij})$. As usual in this type of problem, Eq. (5) is not closed because it involves functions of order $n+1$ in addition to those of order n. However, it can be solved exactly through a given order in the coupling parameters. We expand $g(1,2,\cdots,n;\boldsymbol{\lambda})$ and $g(1, 2, \cdots, n-1;\boldsymbol{\lambda})$ in λ_1, and remember that when $\lambda_1=0$ we have $g(1,2,\cdots,n;\boldsymbol{\lambda})=g(2,\cdots,n;\boldsymbol{\lambda}^1)$, with $\boldsymbol{\lambda}^1=\lambda_2, \cdots, \lambda_N$. Thus we write

$$g(1,2,\cdots,n;\boldsymbol{\lambda})=g(2,\cdots,n;\boldsymbol{\lambda}^1) \times\left[1+\sum_{\mu\geq 1}\frac{\lambda_1{}^\mu}{\mu!}g_\mu(1,2,\cdots,n)\right]. \quad (6)$$

The functions $g(1,2,\cdots,n,j;\boldsymbol{\lambda})$ and $g(1,2,\cdots,n-1,j;\boldsymbol{\lambda})$ are similarly expanded in λ_j. By retaining terms of appropriate orders in λ_1 and λ_j we can, in principle, solve Eq. (5) to a desired order in the coupling parameters. The fact that $g(1,\cdots,n;\boldsymbol{\lambda})$ can be expanded in λ_1 is not immediately apparent since the functions $f(ij)/[1+\lambda_i\lambda_j f(ij)]$ in Eq. (5) cannot be expanded in λ_i for small r_{ij} when $f(ij)=-1$. We note, however, that the left side of Eq. (5) involves $\ln g(1,\cdots,n;\boldsymbol{\lambda})$, not $g(1,\cdots,n;\boldsymbol{\lambda})$ itself. When the equation is transformed into one for $g(1,\cdots,n;\boldsymbol{\lambda})$ it is seen that each term $f(ij)/[1+\lambda_i\lambda_j f(ij)]$ is multiplied by the distribution function involving the corresponding particles. Each such function contains the factor $1+\lambda_i\lambda_j f(ij)$ which cancels out the corresponding singular denominator. Furthermore, we should remember that we are expanding the distribution function, not the kernel; the existence and convergence of such an expansion is proven in subsequent paragraphs.

Solution through $O(\lambda_1)$ is obtained immediately on setting $\lambda_1=0$ in Eq. (5), and retaining only terms of order λ_j in $g(1,2,\cdots,n,j;\boldsymbol{\lambda})$ and $g(1, 2, \cdots, n-1, j;\boldsymbol{\lambda})$. Setting all $\lambda_j=\lambda$ for simplicity, and taking the limit $N,\ V\rightarrow\infty$, we obtain

$$g_1(1,2,\cdots,n)=g_1(1,2,\cdots,n-1)+\lambda_n f(1n)$$
$$+\lambda^2\rho\int f(1j)[g_1(2,\cdots,n,j)-g_1(2,\cdots,n-1,j)]d\mathbf{r}_j \tag{7}$$

which is exactly solved by superposition

$$g_1(1,2,\cdots,m)=\sum_{j=2}^{m} g_1(li),$$
$$g_1(2,\cdots,m,j)=\sum_{i=2}^{m} g_1(ji). \tag{8}$$

The coefficient $g_1(12)$ is given by Eq. (7) with $n=2$, and the pair distribution function by

$$g'(12)=g(2)[1+\lambda_1 g_1(12)].$$

This expression is exact through first order in λ_1 and λ_2, and through *second* order in $\lambda_j=\lambda$, the coupling parameters of the remaining particles of the system.[7] For crystals, we thus have two coupled equations, Eq. (5) for $g(2)$ and Eq. (7) for $g_1(12)$. For fluids we have $g(i)=1$, and $g_1(i)=0$. The pair distribution function is then given by the single equation

$$g_1(\mathbf{R})=\lambda_2 f(\mathbf{R})+\lambda^2\rho\int f(\mathbf{r})g_1(\mathbf{R}-\mathbf{r})d\mathbf{r} \tag{9}$$

which is analogous to the linearized Kirkwood,[1] approximation—with the important difference that the kernel $f(\mathbf{r})$ is finite at all values of $|\mathbf{r}|$ and yields convergent solutions for realistic pair potentials with a repulsive core.

The solution of Eq. (9) is

$$g_1(\mathbf{k})=\frac{f(\mathbf{k})}{1-\rho f(\mathbf{k})} \tag{10}$$

where $f(\mathbf{k})$ and $g_1(\mathbf{k})$ are the Fourier transforms of $f(\mathbf{r})$ and $g_1(\mathbf{r})$, respectively, and we set $\lambda_2=\lambda=1$. Solution of Eq. (5) through nth order in λ_1, in general, involves $n+1$ coupled equations (n for fluids). In this connection we note that the linear Eq. (10) is equivalent to a Montroll-Mayer[4] summation over f-bond chains connecting particles 1 and 2, including, however, the *direct* f bond $f(\mathbf{r}_{12})$. Neither the chain summation nor its generalization by nodal expansions,[5] have a recognizable parameter, in contrast with the present procedure. Furthermore, since we do *not* use a virial expansion, or results should apply to condensed phases as well.

We now outline the proof that $g(1,2,\cdots,n;\lambda_1)$ is the ratio of finite polynomials in λ_1, when all the remaining coupling parameters are set equal to unity (as is actually done in practical applications). First we note that

$$\frac{Z(\lambda_1)}{Z(\lambda_1=0)}=\frac{\rho}{z_1}. \tag{11}$$

Here $z_1=z(\lambda_1)$ is the activity of particle 1. From Eq. (2) we have, in the limit N, $V\rightarrow\infty$,

$$\frac{\rho}{z_1}=\xi(\lambda_1)=1+\sum_{\mu\geq 1}\frac{\lambda_1{}^{\mu}\rho^{\mu}}{\mu!}\int g(2,3,\cdots,\mu+1)\prod_{i=2}^{\mu+1} f(1i)d\mathbf{r}^{\mu}. \tag{12}$$

For $\lambda_1=1$, Eq. (12) is just the first equation of the Kirkwood-Salsburg hierarchy.[3,8] For repulsive core systems $\xi(\lambda_1)$ contains a small number m of terms[3] because the integrals vanish for $\mu\geq m$ since $f(1i)=0$ for large $|r_{1i}|$ while $g(2,3,\cdots,\mu+1)$ vanishes for small separations. *Thus the thermodynamics function $\xi(\lambda_1)$ is a low order polynomial in λ_1* (e.g., for hard spheres $m=12$). This fact may be important for phase transitions where limiting processes and convergence problems are troublesome. From Eq. (3) we similarly obtain

$$g(1,2,\cdots,n;\lambda_1)=\frac{S(\lambda_1)}{\xi(\lambda_1)}\prod_{j=2}^{n}[1+\lambda_1 f(1j)], \tag{13}$$

$$S(\lambda_1)=g(2,3,\cdots,n)$$
$$+\sum\frac{\lambda_1{}^{\mu}\rho^{\mu}}{\mu!}\int g(2,3,\cdots,n+\mu)\prod_{i=n+1}^{n+\mu} f(1i)d\mathbf{r}^{\mu}. \tag{14}$$

For $\lambda_1=1$ this is the general Kirkwood-Salsburg equation. The series $S(\lambda_1)$ is a mth order polynomial just like the $\xi(\lambda_1)$ series, which proves our statement. Equation (13) also provides an explicit expansion parameter for the Kirkwood-Salsburg hierarchy, and, in conjunction with Eq. (6), yields many useful relations for solving Eq. (5). The most attractive feature, however, is the assurance of obtaining finite polynomial solutions, at least by machine computations.

From the above discussion we see clearly the advantages of exponential coupling as compared with the usual potential coupling. The individual terms of the expansion Eq. (6) are all finite even for strongly singular (e.g., hard sphere) potentials, where the Kirkwood coupling parameter expansion is not valid. The

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[7] This is entirely analogous to the rigorous derivation of the Debye screening potential for Coulombic systems [J. G. Kirkwood and J. C. Poirier, J. Phys. Chem. **58**, 591 (1954)]. For such systems our Eq. (9) yields the Debye potential when the f bonds are linearized. This also follows from the fact that for the linearized f bonds our coupling parameter becomes identical with that of Kirkwood.

[8] See also J. E. Mayer, J. Chem. Phys. **15**, 187 (1947); L. Sarolea and J. E. Mayer, Phys. Rev. **101**, 1627 (1956).

integral equation for $g(1,\cdots,n)$ Eq. (5) is likewise considerably better behaved than the Kirkwood or Born-Green ones because the kernel goes rapidly to zero as $|\mathbf{r}_{1j}|\rightarrow\infty$. In fact, the actual region of integration is small, and cell-theory type approximations may thus be useful in the solution of this equation. This fact is not surprising when we note that Eq. (5) is entirely equivalent to the Kirkwood-Salzburg hierarchy.[3]

It should be noted that, even though the distribution functions are given by the ratio of two practically finite polynomials Eq. (13), the expansion of $g(1,\cdots,n)$ in λ_1 is an infinite series because the ratio $S(\lambda_1)/\xi(\lambda_1)$ itself is such a series. It is possible to define "activity distribution functions" which can be expanded directly in practically finite polynomials in the new coupling parameters. Many other manipulations with exponential coupling parameters are possible. Thus, for example, the coupling can be employed in such a manner as to ensure that $g(12)\rightarrow 0$ as $r_{12}\rightarrow 0$ to any order in λ_1. The present approximation does not fulfill this condition: the distribution function remains in general finite and nonzero as interparticle separation goes to zero. Of course, such a behavior is still better than that obtained from linearized potential coupling (e.g., the Debye approximation), when the distribution function becomes infinite at zero separation. A detailed analysis of these new approximations will be published separately,[9] including calculations for hard sphere fluids. A modified form of the coupling has been applied to fused salts.[10] Among further possible applications we should like to mention ion pairing in semiconductors, equation of state of the classical electron gas, theory of electrolytes, and problems of phase transitions. For this last application, the assured convergence of exponential coupling expansions may prove particularly useful since limiting processes and interchanges of limits prove troublesome in the critical region. However, the question of the physical meaning of exponential coupling is as yet unanswered, and is at present under investigation.

Finally, we should like to note the possibility of applying the exponential coupling procedure to quantum-mechanical systems, e.g., by coupling the reaction matrix or the Yang-Lee "activity bond."[11]

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[9] E. Meeron (to be published).

[10] J. L. Katz and E. Meeron (to be published).

[11] C. N. Yang and T. D. Lee, Phys. Rev. **113**, 1165 (1959).