APPROXIMATION METHODS IN CLASSICAL STATISTICAL MECHANICS

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Numerical experiments on the thermodynamic parameters and pair distribution function of a classical fluid in thermal equilibrium, as well as x-ray diffraction analysis, have produced rather reliable information[1] with which a number of theoretical approximations may be compared. Such comparisons have recently been carried out[2] with the aid of large computing machines, and the results over a considerable range of intensive variables have strongly favored the Percus and Yevick[3] (P.Y.) equation for the pair distribution function as opposed to the Bogoliubov, Born, Green, Kirkwood, and Yvon[4] (B.B.G.K.Y.) and hypernetted chain[5] equations. This has occasioned some surprise, since the former appears to require a sequence of linked but ill-defined approximations, while the latter involve single well-defined mathematical truncations. It is the object of this Letter to validate on firm physical grounds the numerical results obtained and to point out directions in which further progress may confidently be expected.

The qualitative basis of our argument is not novel. It resides in the representation of multiparticle coordinate distribution functions n_s as ordinary (one-) particle densities $n(y)$ under the imposition of suitable external potentials. Specifically, it is readily shown that in a grand canonical ensemble,

$$n_s(y,x_1\cdots x_{s-1})/n_{s-1}(x_1\cdots x_{s-1})=n(y\,|\,U),\quad (1)$$

where

$$U(x)=V(x,x_1)+\cdots+V(x,x_{s-1});$$

here $V(x,y)$ is the interparticle potential and the additional external potential U has been set off by a vertical bar. One must now carry out the process of "turning on" the external potential, and we will accomplish this by a functional Taylor series expansion about the value $U(x)=0$. The burden of the physics is to choose the dependent variable or function to be observed [it need not be $n(y)$] and the independent variable or function to be varied [it need not be $U(x)$] such that the expansion converges very rapidly. An optimal choice depends both upon the system being considered and upon the parameter range of interest.

Changing the external potential has an effect upon the distributions which is easily deduced by comparing the iterative definition of the Ursell distribution functions ($\beta=1/kT$):

$$\mathfrak{F}_{s+1}(y,x_1\cdots x_s)=e^{-\beta U(x_1)}\cdots e^{-\beta U(x_s)}\times\delta^s n(y\,|\,U)/\delta e^{-\beta U(x_1)}\cdots\delta e^{-\beta U(x_s)},\quad (2)$$

with the explicit $\mathfrak{F}_2(x_1,x_2)=n_2(x_1,x_2)-n(x_1)n(x_2)$, etc. Equally important is the effect of varying the one-body density. On the basis of (2), it suffices to compute $\delta U(y)/\delta n(x)$. One finds

$$-\delta n(x)/\delta\beta U(y)=n_2(x,y)-n(x)n(y)+n(x)\delta(x-y),\quad (3a)$$

$$-\delta\beta U(y)/\delta n(x)=\delta(x-y)/n(x)-c(x,y),\quad (3b)$$

where $c(x,y)$, the direct correlation function, may be regarded as defined by the pair (3).

Now consider $n(y\,|\,U)e^{\beta U(y)}$ as a functional of $n(y\,|\,U)$, as U is changed from 0 to its final value. The relation is strictly linear outside the range of the potential U, and in addition, $ne^{\beta U}$ continues its boundary value and slope (i.e., that of n itself) for some distance inside the range. Hence a Taylor series expansion,

$$n(y\,|\,U)e^{\beta U(y)}=n(y)+\int[n(z\,|\,U)-n(z)]\delta n(y\,|\,U)e^{\beta U(y)}/\delta n(z\,|\,U)\big|_{U=0}dz+\cdots,\quad (4)$$

truncated at first order as indicated, is particularly appropriate for a hard core at moderate pressure, where $ne^{\beta U}$ proceeds approximately linearly to the origin. Taking $U(y)=V(y,x)$ as in (1), Eq. (4) works out to

$$n_2(x,y)[e^{\beta V(x,y)}-1]=-n(x)n(y)c(x,y),\quad (5)$$

precisely the P.Y. equation.[3] Selecting U as an s-point potential with $s>1$ recovers the "superposition" hypothesis consistent with (5). Further terms in the Taylor series are very easily accommodated.

Expansions similar to (4) may be written down and similarly truncated at first order. Unless chosen with care, however, the dependent and independent functions will not bear a fixed linear relation over a substantially complete region of space as the external potential is turned on. For example, if one expands $\ln[ne^{\beta U}]$ in terms of n, large density fluctuations outside the range of U will not be well represented. Indeed, this particular choice gives rise to

$$\beta V(x,y)+\ln[n_2(x,y)/n(x)n(y)]+1-n_2(x,y)/n(x)n(y) = -c(x,y), \qquad (6)$$

which is the hypernetted chain approximation.[5] On the other hand, the same development applied to the relation between $n\nabla\beta U$ and $\ln[ne^{\beta U}]$ yields the B.B.G.K.Y. equation[4] in the form

$$\nabla_x \ln[n_2(x,y)e^{\beta V(x,y)}/n(x)]$$
$$+[\nabla_x \ln n(y)]\ln[n_2(x,y)e^{\beta V(x,y)}/n(x)]$$
$$+\int[n_2(x,z)/n(x)]\nabla_x\beta V(x,z)[n_2(y,z)/n(y)n(z)-1]dz=0. \qquad (7)$$

While $n\nabla\beta U$ does vanish outside the range of force, the required linear relation within simply does not obtain; the precise effect is not easy to assess.

The superiority of the P.Y. equation for short-range forces and moderate densities is no longer obvious in other domains, with characterizations as diverse as: long-range forces, phase transitions, quantum fluids, etc. A detailed elaboration of the present viewpoint for the more general situation is now being prepared for publication.

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IS THE PHOTON AN ELEMENTARY PARTICLE?*

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The idea that all strongly interacting particles are nonelementary in the technical sense of not being associated with quantized wave fields is a very attractive one. The possibility of associating such particles with trajectories of so-called Regge poles of the S matrix regarded as an analytic function of a complex angular momentum has been widely discussed.[1-4] Unfortunately, it has not yet been possible to establish theoretically any of the "desired" properties of Regge trajectories in a relativistic theory.

It has been conjectured by Chew and Frautschi[2] that all of strong interaction physics (including predictions of particle masses, baryon conservation, strangeness, isotopic spin, etc.) will "flow" from the principles of maximal analyticity of the S matrix, unitarity, and the concept of maximum strength of interactions compatible with unitarity. An attempt to axiomatize an S-matrix theory which makes no reference to fields has been made by Stapp.[5] From the standpoint of theoretical physics, the flow has thus far been more of a trickle than a deluge. Whether or not we know, yet, the proper basis for the Regge pole hypothesis, the concept seems to be a very useful one for high-energy physics phenomenology[6] and the question of "elementarity" can be tested experimentally.[4]

It is somewhat disturbing that any theory founded on such general principles as unitarity and analyticity should single out only strong interactions. The outstanding omission from the scene is the photon. Interestingly enough, this is the only object for which the field concept seems to have a very firm foundation in the theory of measurement. We would like to argue that since photons interact with all charged particles (including the