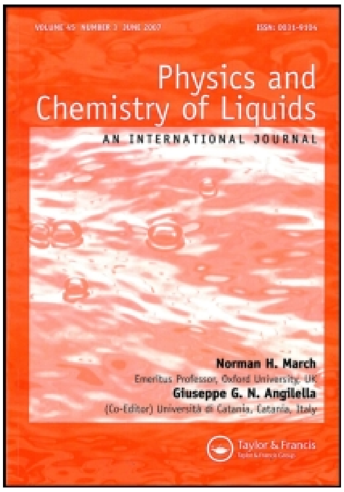

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Liquid Structural Theories Related via a Force Correlation Function

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Liquid Structural Theories Related via a Force Correlation Function

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Four approximate theories of dense liquid structure are cast into directly comparable form using a force correlation function. Numerical comparisons via computer simulation data are proposed as a result.

1 INTRODUCTION

Dense liquids continue to present problems for analytical theories of structure. A number of such theories are by now available, but it seems unlikely that any one of these will be adequate to span a physical regime of force laws going from a liquid like argon near its triple point, characterized by a hard core plus a short-range attractive tail, through to relatively soft cores and long-range interactions appropriate for simple liquid metals such as rubidium.

The present work has been motivated by the desire to understand the relation between the study of de Angelis and March[1] and that of Liboff.[2] Whereas Ref. 1 was directed towards the so-called "inverse problem" in which one attempts to extract a pair potential $\phi(r)$ from a measured structure factor $S(k)$, Liboff's work had the more customary aim of calculating the pair correlation function $g(r)$ from a given pair potential.

2 RELATION BETWEEN LIQUID STRUCTURE THEORIES

The equation proposed by de Angelis and March[1] has the form

$$\frac{\phi(r) - U(r)}{k_B T} = \frac{1}{8\pi^3 \rho} \int [S(k) - 1]^2 \exp(i\mathbf{k} \cdot \mathbf{r})\, d\mathbf{k} \tag{1}$$

where the potential of mean force $U(r)$ is defined in terms of $g(r)$ in a classical liquid by the Boltzmann form

$$g(r) = \exp(-U(r)/k_B T). \tag{2}$$

Evidently, Eq. (1) yields a solution, albeit very approximate, to the "inverse problem" referred to above.

We turn next to Liboff's structural theory.[2] Following the notation used by the writer in relating Liboff's equation to vacancy properties in a hot close-packed crystal near its melting point,[3] this equation takes the form, with the total correlation function $h(r) = g(r) - 1$ introduced,

$$\frac{\partial h}{\partial r} + \frac{1}{k_B T}\frac{\partial \phi}{\partial r} g + \frac{\rho}{k_B T}\frac{\partial F(r)}{\partial r} = 0 \tag{3}$$

where $F(r)$ is defined by

$$F(r) = \int d\mathbf{r}' \phi(\mathbf{r} + \mathbf{r}') g(\mathbf{r}') \tag{4}$$

Equation (3) can be integrated to yield[3]

$$h(r) + \frac{\rho F(r)}{k_B T} = E(r) \tag{5}$$

where the function $E(r)$ enters the Born–Green structural theory and is defined by

$$E(r) = \frac{1}{k_B T}\int_r^\infty g(r)\phi'(r)\, dr \tag{6}$$

$-\phi'$ denoting the pair force.

Because of the function $E(r)$ common to the Liboff and the Born–Green theories, we combine them through the Born–Green equation[4]:

$$\frac{U(r) - \phi(r)}{k_B T} = -\rho \int h(\mathbf{r} - \mathbf{r}') h(\mathbf{r}')\, d\mathbf{r}' - \frac{\rho^2}{k_B T}\int F(\mathbf{r} - \mathbf{r}') h(\mathbf{r}')\, d\mathbf{r}'. \tag{7}$$

Since $S(k) - 1$ is, essentially, the Fourier transform of the total correlation function $h(r)$, the use of the convolution property of Fourier transforms shows that the neglect of the second term on the right-hand-side of Eq. (7) leads back to Eq. (1).

3 FORCE CORRELATION FUNCTION AND STRUCTURAL THEORIES

One can pose the approximate Eqs (1) or (7) somewhat more generally in terms of a force correlation function G, through[4]

$$\frac{U(r)-\phi(r)}{k_B T} = -\rho \int G(\mathbf{r}-\mathbf{r}')h(\mathbf{r}')\,d\mathbf{r}'. \tag{8}$$

Plainly, from Eq. (7) we can write then

$$G(r) \doteqdot h(r) + \frac{\rho F(r)}{k_B T}. \tag{9}$$

As we summarize in the Table, in the original Born-Green theory $G(r)$ becomes $E(r)$, while to recover Eq. (1) of de Angelis and March, G is replaced by h.

TABLE

Structural theories related by $G(r)$ in Eq. (8)

Theory	Liboff + Born-Green	Hypernetted chain	Born-Green	de Angelis and March
Form for $G(r)$	$h(r) + \frac{\rho}{k_B T} F(r)$	$c(r)$	$E(r)$	$h(r)$

4 DISCUSSION AND SUMMARY

It has been shown in this paper that four liquid structure theories can be linked through a force correlation function $G(r)$ defined by Eq. (8). In Born-Green theory, G is replaced by $E(r)$ defined in Eq. (6) etc., as in the Table.

Liboff's equation does not fall naturally into this framework, but it has been shown, by combining this with the Born-Green approximation, that Eq. (9) represents a possible alternative approximation to the force correlation function G.

Presumably, computer simulation data, say for argon or krypton on the one hand, and a liquid metal like Rb on the other, could be used to extract $\tilde{G}(k)$ from Eq. (8), though it has not been proved to date that such a procedure would lead to a singularity-free Fourier transform $\tilde{G}(k)$.

While $E(r)$ and $c(r)$ both tend to $-\phi(r)/k_BT$ for sufficiently large r, for thermodynamic states far from the critical point, it is not clear what their relation is at small r. Further numerical studies, via the common ground of the force correlation function $G(r)$, seem therefore called for, using computer simulation data for $g(r)$ and $\phi(r)$.

References

1. U. de Angelis and N. H. March, *Phys. Letts.*, **56A**, 287 (1976).
2. R. L. Liboff, *Phys. Rev.*, **A31**, 1883 (1986).
3. N. H. March, *Phys. Chem. Liquids*, 1986 (in press).
4. See, for instance, N. H. March, *Liquid Metals* (Pergamon, Oxford), 1968.