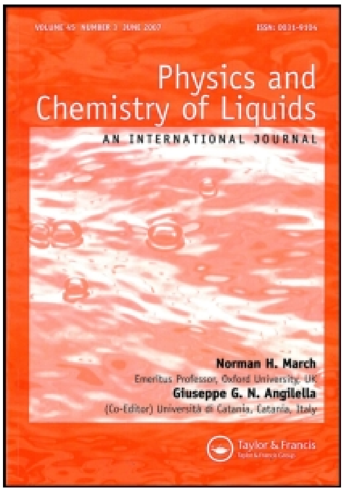

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On the Structure of Liquid Metals

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On the Structure of Liquid Metals

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The integral equation perturbation theory of Lado, Madden and Fitts(MF) was combined with the Optimized Cluster Theory (OCT) of Weeks-Chandler-Andersen in calculating the radial distribution functions for two oscillatory potentials suggested for liquid sodium and aluminium. These calculations properly take into account the softness of the repulsive part of these potentials. The results are compared with molecular dynamic simulations, the high temperature(HTA) and with Percus-Yevick and Mean spherical model results.

INTRODUCTION

Since to a good approximation liquid metals may be described by hard sphere forms, Ashcroft and Lekner[1] calculated the structure factors of liquid metals using the analytic solution of the Percus-Yevick[2] equation for hard spheres as obtained by Wertheim[3] and Thiele.[4] In these calculations the packing fraction (η) has been chosen as an adjustable parameter and good agreement was obtained for the major diffraction peak. Since then there was renewed interest in calculating the structure and thermodynamic properties of liquid metals.[5,6] The inter particle potential for liquid metals have long range oscillations and rather soft repulsive cores and it is the aim of the present study to obtain structural information for such potentials which treats properly the softness of the repulsive cores. Recent theoretical results[7,8] have shown that various parts of the interatomic potential have very different effects on the structure of a liquid. It was found that at high densities the repulsive part of the potential determines the structure factor for wave vectors larger than the location of the first maximum and it determines the location but not the height of the first maximum. The long range attractions affect the height but not the location and the behaviour of the structure factor for smaller values of the wave vector. Jones[19] has applied the variational theory of Mansoori and Canfield[10] to calculate the equation of state of liquid metals using hard sphere diameter as a variational parameter. Umar and Young[11] calculated the structure factors of liquid metals in the variational theory. Kumaravadivel and Evans[12] obtained the structure of liquid metals from Weeks–Chandler–Andersen (WCA) perturbation theory.[13] A method of obtaining the structure of liquid metals using Singwi–Tosi–Land–Sjolander (STLS) scheme[14] has been given by Ailawadi.[6] Recently, Rami Reddy *et al.*[15] presented the results for the radial distribution function for liquid metals using the Optimised cluster theory.[16] Various computer simulation studies such as the Monte-Carlo (MC) and Molecular dynamic (MD) methods were reported in the literature for liquid metals.[17,19] Blum and Narten[20] applied the Mean spherical model[21] and calculated the radial distribution function for liquid aluminium. Recently, Bratkovsky *et al.*[22] made a careful analysis of theory and the Hyper netted chain (HNC)[23] approximation. All the calculations carried out so far can be divided into three categories:

i) the computer simulation

ii) calculations based on the integral equations and

iii) those based on perturbation theory relative to some hard sphere system.

In the methods based on perturbation theory the structure of the reference part of the potential was calculated using zeroth order blip function theory.[24] Defining

$$y(r) = g(r)\exp[\beta u(r)] \tag{1}$$

where $g(r)$ is the radial distribution function, $u(r)$ is the interparticle potential and $\beta = 1/k_B T$ where k_B is the Boltzman constant and T is the temperature of the fluid. The zeroth order blip function expansion result in the expression

$$y(r) = y_d(r) \tag{2}$$

where $y_d(r)$ is the y-function for a fluid of hard spheres of diameter d. The density of the hard sphere fluid is equal to the density of the fluid being treated. The hard sphere diameter is chosen such that the following equation is satisfied:

$$\int d\mathbf{r}B(r) = 0 \tag{3}$$

The function $B(r)$ is defined by the relation

$$B(r) = y_d(r)\{\exp[-\beta u(r)] - \exp[-\beta u_d(r)]\} \tag{4}$$

where $u_d(r)$ is the hard sphere potential given by

$$\begin{aligned} u_d(r) &= \infty \qquad r < d \\ &= 0 \qquad r > d \end{aligned} \tag{5}$$

The zeroth order blip function theory works well for potentials whose repulsive cores approximate a hard sphere potential. But for potentials whose repulsive cores are softer than the Lennard Jones r^{-12} core the blip function expansion has to be taken to higher order. To carry out the perturbation to higher order terms one encounters higher order correlation functions, information about which is too meagre. Various prescriptions were made in the literature.[7,25] To overcome this difficulty Lado[26] and Madden and Fitts[27] (MF) have formulated perturbation theories in which the integral equation approximations were used to obtain the perturbation corrections. In this paper we have used the MF integral equation perturbation theory approach supplemented with the Percus-Yevick and HNC approximations for calculating the structure of the reference part of the potential. To calculate the structure of the fluid interacting with the potential $u(r)$ we used the Optimised cluster theory. Calculations were performed for the following potentials:

i) a potential suggested by Schiff[17] for liquid sodium and is given by

$$V_1(r) = \frac{\cos(2k_f r)}{r^3}\left(A + \frac{B}{r^2} + \frac{C}{r^4}\right) + \frac{\sin(2k_f r)}{r^4}\left(E + \frac{F}{r^2}\right) \tag{6}$$

The repulsive core of this potential is intermediate between the Born-Mayer soft core and the Lennard Jones r^{-12} core. The potential parameters were taken from Schiff.

ii) a potential also suggested by Schiff which has an inverse twelfth power repulsive core and is given by

$$V_5(r) = \frac{\cos(2k_f r)}{r^3}\left(A + \frac{B}{r^2} + \frac{C}{r^4}\right) + \frac{\sin(2k_f r)}{r^4}\left(E + \frac{F}{r^2}\right) + \frac{G}{r^{12}} \tag{7}$$

INTEGRAL EQUATION PERTURBATION THEORY

It is well known that in a dense fluid the repulsive forces dominate the structure and the effect of the attractive forces is to provide a uniform background of the mean field type. In the perturbation theory one divides the potential $u(r)$ into

$$u(r) = u_0(r) + \lambda u_1(r) \tag{8}$$

where $u_0(r)$ is the reference part of the potential and $u_1(r)$ is the attractive perturbation. An important aspect of the perturbation theory is that a judicious choice has to be made in the separation of $u(r)$ into $u_0(r)$ and $u_1(r)$. Following WCA we take the division such that

$$\begin{aligned} u_0(r) &= u(r) - u(R_m) \qquad && r < R_m \\ &= 0 && r > R_m \end{aligned} \tag{9}$$

$$\begin{aligned} u_1(r) &= u(R_m) \qquad && r < R_m \\ &= u(r) && r > R_m \end{aligned} \tag{10}$$

Here R_m is the position of the minimum in the potential. Verlet and Weis[28] have shown by numerical experiments that WCA separation leads to a converging perturbation series for the Helmholtz free energy. A perturbation series for $g(r)$ may be obtained by expanding $g(r)$ in a power series in λ about the reference system

$$\begin{aligned} g(r) &= g_0(r) + \sum_n \left(\frac{\partial^n g}{\partial \lambda^n}\right)_{\lambda=0} \frac{\lambda^n}{n!} \\ &= g_0(r) + \sum_n \lambda^n \Delta^n g(r) \end{aligned} \tag{11}$$

where $g_0(r)$ is the RDF of the reference system and $\Delta^n g(r)$ is the nth order perturbation correction. Approximating the perturbation corrections through integral equations Eq. (11) becomes

$$g(r) = g_0(r) + \sum_n \lambda^n \Delta^n g^{\mathrm{IE}}(r) \tag{12}$$

A similar expansion of $y_0(r)$ around that of the hard spheres and approximating the perturbation corrections through integral equation yields

$$y_0(r) = y_{\mathrm{HS}}(r; d) + \sum_n \alpha^n \Delta^n y^{\mathrm{IE}}(r) \tag{13}$$

Madden and Fitts approximated Eq. (13) by writing

$$y_0(r) = y_{\mathrm{HS}}(r; d) + y_0^{\mathrm{IE}}(r) - y_{\mathrm{HS}}^{\mathrm{IE}}(r; d) \tag{14}$$

In the zeroth order blip function theory one retains only the first term on the right hand side of Eq. (14).

OPTIMISED CLUSTER THEORY

The optimised cluster theory (OCT) has been well discussed in the literature and hence we confine ourselves to giving a brief outline of the theory. In OCT the Mayer cluster series for the Helmholtz free energy and the pair correlation functions are transformed using topological reduction to a compact form involving a renormalised potential. Defining

$$\phi(r) = -\beta u_1(r) \tag{15}$$

and its fourier transform by

$$\hat{\phi}(k) = \int \phi(r) \exp[i\mathbf{k} \cdot \mathbf{r}]\, d\mathbf{r} \tag{16}$$

the renormalised potential is given by

$$C_L(r) = \frac{1}{(2\pi)^3} \int d\mathbf{k} \exp[i\mathbf{k} \cdot \mathbf{r}] \frac{\hat{F}_0^2(k)\hat{\phi}(k)}{[1 - \hat{F}_0(k)\hat{\phi}(k)]} \tag{17}$$

In the above equation the hyper vertex $F_0(r_1, r_2)$ is defined by

$$F_0(r_1, r_2) = \rho\delta(r_1, r_2) + \rho^2 h_0(r_1, r_2) \tag{18}$$

where

$$h_0(r_1, r_2) = g_0(r_1, r_2) - 1 \tag{19}$$

and $\delta(r)$ is the Dirac delta function. The RDF in the OCT is given by

$$g(r) = \exp[-\beta\{u_0(r) + u(r)\}] y_d(r) \exp[C_L(r) - \phi(r)] \tag{20}$$

In the high temperature approximation (HTA) valid at high densities the RDF is approximated by

$$g^{\mathrm{HTA}}(r) = \exp[-\beta u_0(r)] y_{\mathrm{HS}}(r; d) \tag{21}$$

INTEGRAL EQUATIONS

We made use of the Percus–Yevick (PY) and the Hyper netted chain (HNC) equations in Eq. (14). In PY theory

$$c(r) = f(r)y(r) \tag{22}$$

and in the HNC theory

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r) \tag{23}$$

where $c(r)$ is the direct correlation function defined in terms of the pair correlation function $g(r)[h(r) + 1]$ by the Ornstein–Zernicke relation

$$h(r) = c(r) + \rho \int h(r')c(r - r')\, d\mathbf{r}' \tag{24}$$

where ρ is the number density and the Mayer function is given by

$$f(r) = \exp[-\beta u(r)] - 1 \tag{25}$$

The mean spherical approximation for molecules with impenetrable cores of diameter d is usually written

$$\begin{aligned} g(r) &= 0 \qquad & r < d \\ c(r) &= -\beta u(r), \qquad & r > d \end{aligned} \tag{26}$$

Eq. (26) was first derived by Lebowitz and Percus[21] as the limit for continuum fluids of the mean spherical model for lattice systems.

For $y_{\mathrm{HS}}^{\mathrm{PY}}(r; d)$ we used the analytic representation of the PY solution as given by Smith and Henderson[29] and for $y_{\mathrm{HS}}(r; d)$ we used the Verlet–Weis formulation. $y_{\mathrm{HS}}^{\mathrm{HNC}}(r; d)$ was obtained by solving the HNC equation for the hard sphere potential of diameter d.

CHOICE OF R

Two different methods were adopted in the choice of R_m. In the first place R_m was chosen at the minimum of the potential as proposed by WCA. In the second case R_m was chosen from the following prescription:

Defining the blip function expansion parameter ξ by

$$\xi = \int d\mathbf{r}\,|B(r)|/4\pi d^3 \tag{27}$$

For inverse power potentials it was found that the approximation given by eq(2) is accurate provided $\xi \simeq 0.14$. The second choice for R_m was chosen such that

$$\xi(R_m) = 0.14 \tag{28}$$

where $\xi(R_m)$ is given by Eq. (27) with

$$B(r) = y_d(r)\{\exp[-\beta u_R(r)] - \exp[-\beta u_d(r)]\} \tag{29}$$

with

$$\begin{aligned} u_R(r) &= u(r) - u(R_m) \qquad & r < R_m \\ &= 0 \qquad & r > R_m \end{aligned} \tag{30}$$

NUMERICAL CALCULATIONS

The PY and HNC equations were solved in the r-space by transforming the integral in Eq. (24) to bipolar coordinates. A step size of 0.05σ was used in the numerical integrations of these equations. Convergence was enhanced by using Broyle's mixing technique. The iterations were truncated when

$$|y^{n}_{\text{in}}(r) - y^{n+1}_{\text{out}}(r)| \leq 0.001 \tag{31}$$

These results were used in calculating $y_0(r)$ from Eq. (14). In the OCT the contributions of the ring diagrams to the free energy is given by

$$a_{\text{ring}} = \frac{-1}{2(2\pi)^3} \int d\mathbf{k}\{\hat{F}_0(k)\hat{\phi}(k) + \ln[1 - \hat{F}_0(k)\hat{\phi}(k)]\} \tag{32}$$

It is obvious that the properties of the fluid of particles interacting through the potential $u = u_0 + u_1$ must be independent of the value of the perturbation u_1 for the physically impossible interparticle separations $r < d$. This unphysical behaviour was eliminated by choosing u_1 in such a way that

$$C_L(r) = 0, \qquad r < d \tag{33}$$

This implies that

$$\frac{\delta V a_{\text{ring}}}{\delta \phi} = \tfrac{1}{2}\rho^2 C_L(r) = 0, \qquad r < d \tag{34}$$

The solution u_1 to the above equation was found in the following manner. For $r < d$, $u_0(r)$ was expanded as

$$u_0(r) = \sum_{m=1}^{n} a_m (r - d)^{m-1} \tag{35}$$

where n is a positive integer. The vector $(a_0, a_1, \ldots, a_n)$ which is the solution of the set of equations which follows was found:

$$\frac{\partial V a_{\text{ring}}}{\partial a_m} = 0 \tag{36}$$

The set of equations were solved by using Newton–Raphson method. All the integrals were evaluated using Simpson's rule and the fourier transforms were evaluated using Filon's method. The function $y_{\text{HS}}(r; d)$ inside the core was obtained from the equation

$$\ln y_{\text{HS}}(r; d) = A + B\left(\frac{r}{d}\right) + C\left(\frac{r}{d}\right)^2 + D\left(\frac{r}{d}\right)^3 \tag{37}$$

Equation (37) is an interpolation formula. The coefficients A, B, C and D were determined as suggested by Grundke and Henderson[30].

RESULTS

The results of the calculations based on the present method for the RDF for liquid sodium and aluminium for the potentials $V_1(r)$ and $V_5(r)$ are presented in Figures 1–8. The molecular dynamic calculations for $V_1(r)$ at $T^* = 0.97$ and $\rho = 0.83$ were reported by Paskin and Rahman[32] and for aluminium MD calculations were performed by Schiff at $T^* = 0.78$ and $\rho = 0.89$. In Figures

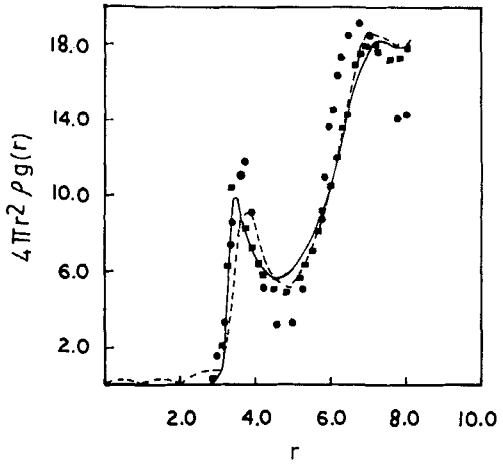

FIGURE 1 $4\pi r^2 \rho g(r)$ for liquid sodium for $V_1(r)$ at $T^* = 0.97$, $\rho = 0.83$. ——— Present theory using PY-IEPT with R_m chosen such that $\xi = 0.14$. ● ● ● MD, ■ ■ ■ HTA, – – – – Neutron diffraction experiments.

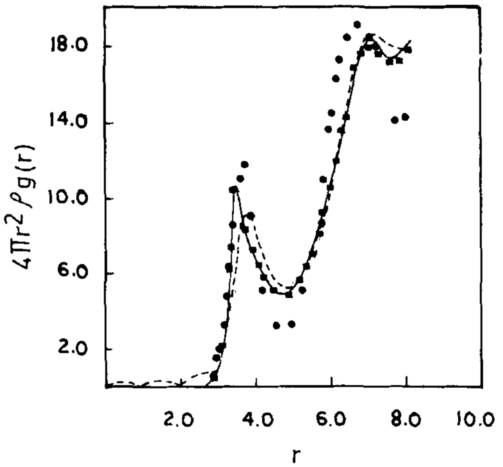

FIGURE 2 Same as Figure 1 but using HNC-IEPT.

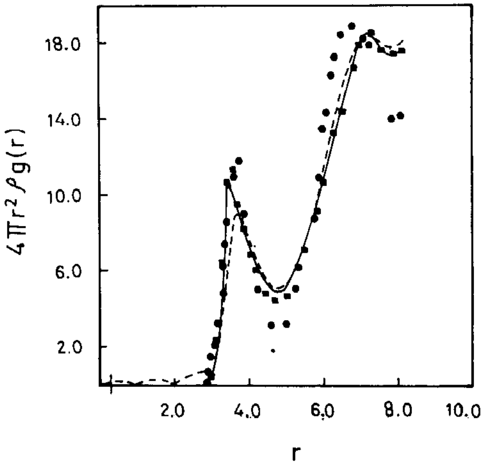

FIGURE 3 Same as Figure 2 but R_m was chosen using WCA criterion.

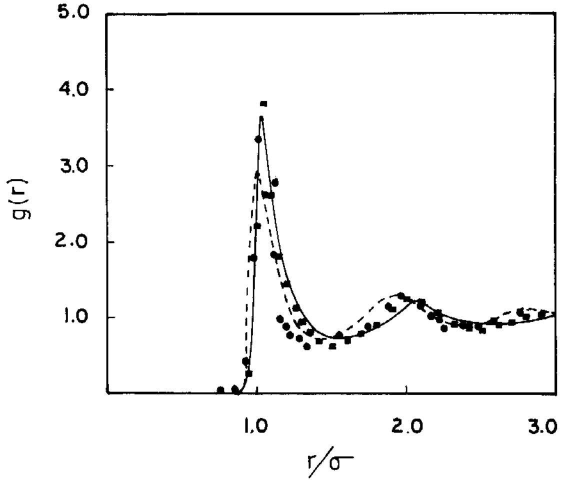

FIGURE 4 RDF for liquid aluminium for $V_5(r)$ at $T^* = 0.78$, $\rho = 0.89$. ——— Present theory using PY-IEPT with R_m chosen such that $\xi = 0.14$. For other symbols see Figure 1.

1 and 2 the RDF for $V_1(r)$ calculated from the present theory with PY and HNC integral equation perturbation theory with R_m chosen from Eq. (28) was compared with the MD calculations, the high temperature approximation and with diffraction experiments. In Figure 3 the HNC IEPT results when R_m is chosen from the WCA criterion was compared with other results. In Figures 4–6 similar comparison was made for the RDF of liquid aluminium. In Figures 7 and 8 RDF of liquid sodium and aluminium obtained from the

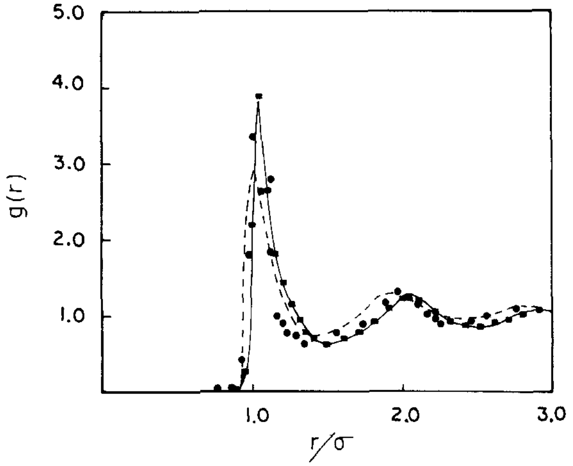

FIGURE 5 Same as Figure 4 but for HNC-IEPT.

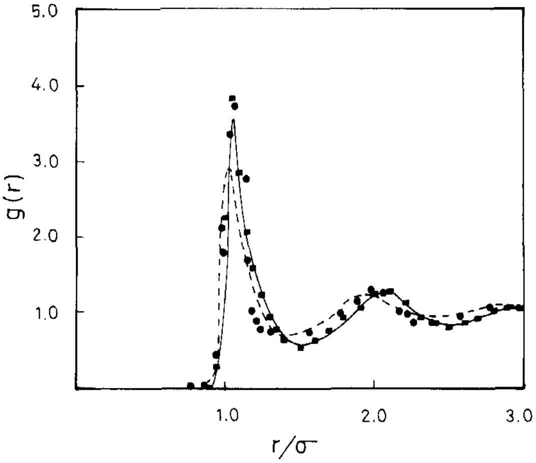

FIGURE 6 Same as Figure 5 but for R_m chosen using WCA criterion.

PY and HNC integral equations were compared with the simulation results. These comparisons clearly indicate that when the structure of the reference part of the potential was well represented (beyond the zeroth order blip function theory) then OCT provides a good representation of the structure of liquid metals.

A comparison of Figures 1 and 2 and Figures 4 and 5 shows that for soft core fluids the HNC approximation is superior than the PY approximation. Further, provided the structure of the soft core fluid is represented properly the two different choices of R_m give quantitatively the same result.

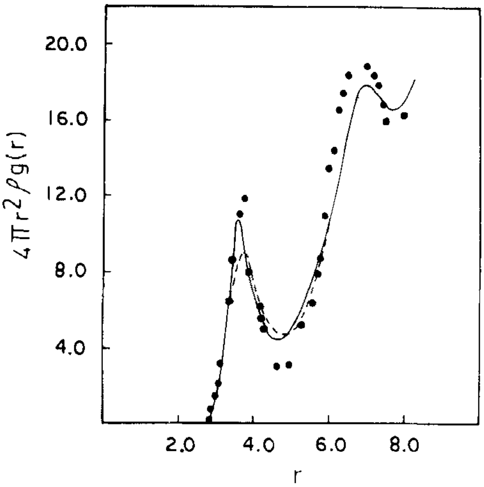

FIGURE 7 $4\pi r^2 \rho g(r)$ for liquid sodium for $V_1(r)$ at $T^* = 0.97$, $\rho = 0.83$. ——— PY, - - - - MSM, ● ● ● MD.

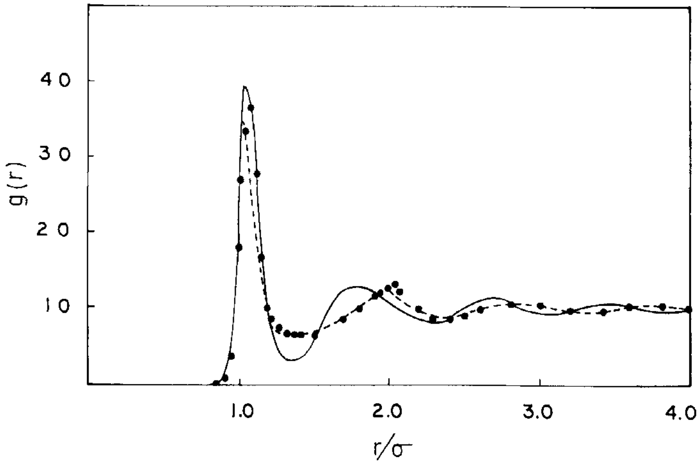

FIGURE 8 RDF for liquid aluminium for $V_5(r)$ at $T^* = 0.78$, $\rho = 0.89$. See Figure 7 for symbols.

CONCLUSIONS

We presented a method for calculating the reference part of the potential for liquid metals based on the integral equation perturbation theory supplemented with the PY and HNC approximations which takes in a rough way the higher contributions in the blip function expansion. These calculations provide an accurate representation for the reference part of the potential for liquid metals. Further it was shown that when the reference part of the potential was well represented then OCT will provide a good representation of the structure of the liquid metal. A similar conclusion was made for other liquid metals by Swamy and Reddy.[31]

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