IC/79/145
INTERNAL REPORT
(Limited distribution)

19306

International Atomic Energy Agency
and
United Nations Educational Scientific and Cultural Organization

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

STRUCTURE AND THERMODYNAMICS OF TWO-COMPONENT CLASSICAL PLASMAS IN THE MEAN SPHERICAL APPROXIMATION

G. Senatore, M. Rovere, M. Parrinello
Istituto di Fisica Teorica dell'Università e GNSM-CNR, Trieste, Italy,
and
M.P. Tosi
Istituto di Fisica Teorica dell'Università e GNSM-CNR, Trieste, Italy,
and
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

The analytic approximation applied by Gillan to a classical one-component plasma, in which short-range correlations are grafted onto a Debye-Hückel theory through a hard-sphere boundary condition on the pair correlation function, is examined in a two-component plasma over wide ranges of temperature, densities, and valences. The results for the thermodynamics and the structure of these systems are in good agreement with available Monte Carlo data and generally very close to those yielded by the hypernetted-chain approximation.

MIRAMARE - TRIESTE
October 1979

1. Introduction

Dense mixtures of fully or highly ionized light elements, such as H^{+} - He^{2+} mixture, have been the object of considerable attention in recent years. Of special interest are the thermodynamic properties of these systems and in particular the possibility that phase separation may occur in astrophysical conditions[1-3]. A relevant model is provided[4-6] by a two-component classical plasma of point charges on a uniform neutralizing background (TCP). Under appropriate conditions, perturbative techniques allow one to add onto this model the effects of screening by the electronic background and of departures from classical behaviour of the ions. The appearance of bound state for the electrons, however, may drastically alter[2,3] the thermodynamic behaviour.

The evaluation of static properties of the TCP has relied[4,5] on the numerical solution of the integral equations yielded by the hypernetted-chain approximation (HNC), which has been tested against Monte Carlo simulation results in a few cases. We examine in this paper how well the known static properties of the TCP are reproduced by the mean spherical approximation (MSA). In this scheme[7] the short range correlations between the charged particles are introduced onto a Debye-Hückel picture of long range correlations through a hard-sphere boundary condition on the pair correlation functions. The advantage of the MSA is that it leads to analytic expressions[8,9] for the thermodynamics and the structure of the charged fluid, whose full evaluation involves very little numerical work. This exactly soluble physical model has been shown[7] to produce results which are as good as those of the HNC in the case of the one-component classical plasma, and appears to be superior to other semi-analytic schemes[10]. As we shall see, the MSA and the HNC results are of closely comparable quality for the

TCP as well.

2. Structure of the TCP

We begin by recalling a few relevant results of the exact solution[9] of the MSA for a multi-component fluid of charged hard spheres with charges $Z_i e$, particle densities ρ_i, and diameters σ_i, embedded in a uniform background of density $\rho = \sum_i Z_i \rho_i$. These parameters, together with a temperature parameter $\Gamma = e^2/(a k_B T)$ with $a = \left(\frac{4\pi}{3}\sum_i \rho_i\right)^{-1/3}$, fully characterize the system. The solution of the MSA uses the factorization method of Baxter[11,12] to relate the matrix of direct correlation functions to a matrix of factor correlation functions $Q_{ij}(r)$, whose determination leads to a third-order polynomial,

$$Q_{ij}(r) = \tfrac{1}{3}\pi\rho a_j (r-\sigma_{ij})^3 + \tfrac{1}{2} Q''_{ij}(r-\sigma_{ij})^2 + Q'_{ij}(r-\sigma_{ij}) - Z_i a_j \qquad (r<\sigma_{ij}), \tag{2.1}$$

with $\sigma_{ij} = \frac{1}{2}(\sigma_i+\sigma_j)$. The coefficients of the polynomial are explicit functions of the parameters of the system and of a quantity γ (denoted by Γ in ref. 9) which is to be determined numerically from the parameters of the system by solving an algebraic equation. The equation for γ and the expressions for the coefficients a_i and Q'_{ij} are in fact formally identical to those found[12] in the solution of the MSA for the case $\rho = 0$, when the ionic valences are replaced by effective valences

$$Z_i^* = Z_i - \tfrac{1}{6}\pi\rho\sigma_i^3 . \tag{2.2}$$

These subtract from the bare valence the background charge enclosed in the ionic sphere.

Of particular relevance for the application of the MSA to the description of the TCP are the coefficients Q'_{ij}, since they give the values of the pair correlation functions $g_{ij}(r)$ at contact, i.e. for $r = \sigma_{ij}^+$. These functions must vanish continuously at short distances in the plasma, and we thus have a triplet of conditions,

$$Q'_{ij} = 0 , \tag{2.3}$$

for the determination of the two diameters σ_1 and σ_2 in terms of the other system parameters. It turns out that for limited values of the charge ratio $(Z_2/Z_1 = 2)$ and comparable concentrations of the two components $(\rho_2/\rho_1 \simeq 1)$ these conditions can all be satisfied with an accuracy of $\pm$ 0.02 on the values of $g_{ij}(\sigma_{ij}^+)$, except at small values of Γ $(\Gamma \leq 1)$. The accuracy progressively worsens as one moves away from the situation indicated above ; namely, non-additive diameters are needed to describe the correlation holes when the valences and/or the concentrations of the two components are vastly different. We have tried to minimize this source of error by adopting a least-squares procedure in the evaluation of additive diameters from the conditions(2.3). In the calculations reported below, which include values of Z_2/Z_1 as large as 8 and cover wide ranges of concentration and temperature, the deviations of $|g_{ij}(\sigma_{ij}^+)|$ from zero never exceed 0.4. We shall comment later on the ensuing inaccuracy in the calculation of the thermodynamic properties of the plasma.

A general qualitative feature of the results is that the correlation holes tend to shrink upon increasing the concentration of the component of higher valence, at given temperature and total particle density. The dependence on temperature and density is qualitatively as expected, namely the diameters increase with the plasma parameter Γ. A precise comparison of the calculated structure of the TCP with Monte Carlo simulation data and HNC results[4] is possible for the case $Z_2 = 2Z_1$, $\rho_2 = \rho_1$ and $\Gamma = 40$, and is reported in fig. 1. The MSA pair correlation functions were evaluated directly from the $Q_{ij}(r)$'s by an extension of the technique proposed by Perram[13]. The quality of the results is very much similar to those reported by Gillan[7] for the one-component plasma: the pair correlation functions yielded by the MSA are very close to those of the HNC, and both fail to give a close account of the Monte Carlo data in the region of the main peak.

A clearer visualization of the structure of the TCP is afforded by the pair functions which express the correlations between charge density fluctuation and concentration fluctuation variables. These are defined[14], respectively, by

$$q(\underline{r}) = Z_1\rho_1(\underline{r}) + Z_2\rho_2(\underline{r}) \tag{2.4}$$

and

$$c(\underline{r}) = (1-c)\,\rho_1(\underline{r}) - c\,\rho_2(\underline{r}) \tag{2.5}$$

where $c = \rho_1/(\rho_1+\rho_2)$ and $\rho_i(\underline{r})$ are the density fluctuation variables for the individual components of the plasma. The corresponding correlation functions can be written as

$$g_{qq}(r) = \bar{Z}^{-2}\left[c^2Z_1^2 g_{11}(r) + (1-c)^2 Z_2^2 g_{22}(r) + 2c(1-c)Z_1Z_2 g_{12}(r)\right], \tag{2.6}$$

$$g_{cc}(r) = c^2(1-c)^2\left[g_{11}(r) + g_{22}(r) - 2g_{12}(r)\right], \tag{2.7}$$

and

$$g_{cq}(r) = c(1-c)\bar{Z}^{-1}\left\{cZ_1\left[g_{11}(r) - g_{12}(r)\right] - (1-c)Z_2\left[g_{22}(r) - g_{12}(r)\right]\right\}, \tag{2.8}$$

where $\bar{Z} = cZ_1 + (1-c)Z_2$. The charge-charge correlation function (2.6) is obviously quite similar to that of the one-component plasma, which shows at these values of Γ a strong correlation hole followed by a sizable pile-up of charge. Subtler structural effects in the TCP are revealed by the other functions, which are reported in fig. 2. The definition (2.5) implies that a concentration fluctuation at the origin corresponds to a local excess of ions with lower valence and thus to a local excess of the negative background charge. It is then apparent from the form of $g_{cq}(r)$ that this is screened by a local pile-up of charge, and from the form of $g_{cc}(r)$ that the pile-up has an internal structure in which there is an excess of the lower-valence ions in an inner shell. The figure also serves to stress that the MSA involves discontinuities in the derivatives of the $g_{ij}(r)$'s at contact.

3. Thermodynamics of the TCP

The MSA yields the following expression[9] for the potential energy u per particle of the TCP,

$$u(\Gamma', c) = \frac{e^2}{\rho_1+\rho_2}\left(-\gamma\sum_i \frac{\rho_i Z_i^{*2}}{1+\gamma\sigma_i} - \frac{\pi}{2\Delta}\Omega P_n^2 - \frac{1}{2}\pi\rho\varphi_2 + \frac{\pi^2}{3a}\rho^2\zeta_5\right). \tag{3.1}$$

Here, $\Gamma' = \Gamma\left[\rho/(\rho_1+\rho_2)\right]^{1/3}$ and

$$P_n = \frac{1}{\Omega}\sum_i \frac{\rho_i Z_i^* \sigma_i}{1+\gamma\sigma_i}, \tag{3.2}$$

$$\Omega = 1 + \frac{\pi}{2\Delta}\sum_i \frac{\rho_i\sigma_i^3}{1+\gamma\sigma_i}, \tag{3.3}$$

$$\varphi_n = \sum_i \rho_i Z_i \sigma_i^n, \tag{3.4}$$

$$\zeta_n = \sum_i \rho_i \sigma_i^n, \tag{3.5}$$

and $\Delta = 1-\frac{1}{6}\pi\zeta_3$. The comparison of the results for $Z_2 = 2Z_1$ with the available Monte Carlo and HNC results[4] is reported in table 1. The table reports also the excess energy of mixing Δu, defined as the difference between u and the potential energy u_0 of the independent components at the same background density ρ,

$$u_0(\Gamma', c) = c\, u(\Gamma', c=1) + (1-c)\, u(\Gamma', c=0) . \qquad (3.6)$$

It is apparent that the MSA results are in closer agreement with the Monte Carlo data at all values of Γ except the lowest ones ($\Gamma \lesssim 1$) , and that the simple superposition (3.6) of the one-component energies is a very accurate approximation to u_{MSA}. The uncertainties in the MSA results arising from the determination of the correlation diameters, as we discussed in the preceding section, are of the order of one unit in the significant figure for Δu .

Further examination of the poor performance of the MSA at low values of Γ shows that its results are rapidly approaching those of the linear Debye-Hückel theory for $\Gamma \simeq 0.1$. This defect is probably due to the fact that the sizes of the correlation holes are shrinking to zero without allowing for a smooth vanishing of the pair correlation functions at short distances.

A comparison between the MSA values of the internal energy and HNC results[5] for larger values of the valence ratio Z_2/Z_1 is reported in table 2. The MSA values are somewhat more negative, as was the case for the systems illustrated in table 1. The uncertainties in u arising from the determination of the correlation diameters are now comparable in magnitude to Δu , so that the MSA results are still represented, within their reliability, by the simple interpolation formula (3.6).

The MSA expression for the equation of state of the plasma given in ref. 9 cannot be applied to the TCP, since the correlation

diameters are now functions of temperature and densities. The expression for the pressure in the TCP can, however, be derived through the use of the virial theorem,

$$P = (\rho_1+\rho_2)\, k_B T \left(1+\tfrac{1}{3}u\right), \qquad (3.7)$$

at least for those cases in which the residual values of the pair correlation functions at contact are very small. The isothermal compressibility χ obtained by differentiating this expression with respect to volume is reported in fig. 3 as a function of Γ. The MSA and HNC results are indistinguishable and in excellent agreement with the Monte Carlo data[4].

The alternative route to the evaluation of χ is through thermodynamic fluctuation theory, which relates χ to the long-wavelength limit of the partial structure factors of the TCP. This relation reads[4]

$$\chi_0/\chi = 1 - \lim_{k\to 0} \sum_{ij} \frac{(\rho_i\rho_j)^{1/2}}{\rho_1+\rho_2}\left[c_{ij}(k) + \frac{4\pi e^2}{k_B T k^2}(\rho_i\rho_j)^{1/2} Z_i Z_j\right] \qquad (3.8)$$

where the $c_{ij}(k)$'s are the Fourier transforms of the direct correlation functions. A lengthy but straightforward calculation for the MSA yields

$$\chi_0/\chi = \frac{1}{\Delta^2} + \frac{1}{(\rho_1+\rho_2)\Delta^4}\left[\tfrac{1}{4}\pi^2\zeta_2^3 + \pi\Delta\zeta_1\zeta_2 - \pi\Gamma a P_n^2 \Delta^2\right] \qquad (3.9)$$
$$+ \frac{4\pi\rho\Gamma a}{\rho_1+\rho_2}\left[\frac{P_n}{2\Delta\gamma} - \frac{P_n}{3\gamma} + \frac{\pi}{180}\rho\zeta_5 - \frac{1}{12}\varphi_2 + \frac{\varphi_1}{6\gamma} + \frac{\pi\rho\zeta_4}{36\gamma}\right],$$

and the results are also reported in fig. 3. Clearly the MSA is, as the HNC, affected by "thermodynamic inconsistency", namely the equation-of-state and the fluctuation-theory values for the compressibility differ appreciably from each other.

4. Concluding remarks

The main conclusions that can be drawn from the foregoing detailed comparisons can be summarized as follows:

i) the MSA for the TCP fares as least as well as the HNC whenever a comparison with Monte Carlo data is possible, except for very low values of the plasma parameter Γ ($\Gamma \lesssim 1$) where the MSA approaches too rapidly the limiting law of linear Debye-Hückel theory;

ii) the MSA values for the internal energy are in close agreement with the HNC over a sizable range of values for the valence ratio Z_2/Z_1;

iii) the excess energy of mixing at fixed background density is usually smaller in the MSA than in the HNC, and lies within the uncertainty of the determination of the correlation diameters at large values of Z_2/Z_1.

If these conclusions are combined with the detailed analysis of the phase separation problem given by Hansen et al[4,5], it appears that the MSA and the HNC will lead to similar results for the phase diagrams, at least for moderate values of Z_2/Z_1. Point iii) above will imply a sizable uncertainty in the estimation of the critical temperature.

Acknowledgments. Two of us (G.S. and M.R.) wish to acknowledge the holding of fellowships by the Scuola Normale Superiore di Pisa and by the CISRIF of Trieste, respectively.

References

1. D.J. Stevenson, Phys. Rev. B12, 3999 (1975).
2. E.L. Pollock and B.J. Alder, Phys. Rev. A15, 1263 (1977).
3. E.L. Pollock and B.J. Alder, Nature 275, 41 (1978).
4. J.P. Hansen and P. Vieillefosse, Phys. Rev. Letters 37, 391 (1976); J.P. Hansen, G.M. Torrie and P. Vieillefosse, Phys. Rev. A16, 2153 (1977).
5. B. Brami, J.P. Hansen and F. Joly, Physica 95A, 505 (1979).
6. H.E. De Witt, in "Strongly Coupled Plasmas" (edited by G. Kalman; Plenum Press, New York 1978), p. 81; J.P. Hansen, ibidem p. 117.
7. M.J. Gillan, J. Phys. C7, L1 (1974).
8. R.G. Palmer and J.D. Weeks, J. Chem. Phys. 58, 4171 (1973).
9. M. Parrinello and M.P. Tosi, Chem. Phys. Letters 64, 579 (1979).
10. M. Baus and J.P. Hansen, J. Phys. C12, L55 (1979).
11. R.J. Baxter, J. Chem. Phys. 52, 4559 (1970).
12. L. Blum, Molec. Phys. 30, 1529 (1975); L. Blum and J.S. Høje, J. Phys. Chem. 81, 1311 (1977).
13. J.W. Perram, Molec. Phys. 30, 1505 (1975).
14. A.B. Bhatia and D.E. Thornton, Phys. Rev. B2, 3004 (1970).

Table 1. Excess internal energy u and excess energy of mixing Δu for ionic mixtures with $Z_1 = 1$ and $Z_2 = 2$ (in units of $k_B T$).

		MSA		MC[4]		HNC[4]	
Γ	κ	$-u$	Δu	$-u$	Δu	$-u$	Δu
40	1	34.125	0	34.232	0	34.000	0
40	0.75	57.541	0.004	-	-	-	-
40	0.5	83.240	0.006	83.643	-0.024	83.161	0.004
40	0.25	110.90	0.004	-	-	-	-
40	0	140.28	0	-	-	-	-
20	0.5	41.035	0.004	41.191	0.006	40.919	0.004
10	0.75	13.793	0.002	13.777	-0.002	13.670	0.003
10	0.5	20.101	0.003	20.134	-0.010	19.975	0.005
10	0.25	26.898	0.002	26.964	-0.001	26.771	0.004
5	0.5	9.7552	0.003	9.715	0.000	9.638	0.004
1	0.5	1.7045	0.002	1.645	0.008	1.639	0.005

Table 2. Excess internal energy u and excess energy of mixing Δu for ionic mixtures with $Z_1 = 1$ (in units of $k_B T$).

			MSA		HNC[5]	
Z_2	Γ	κ	$-u$	Δu	$-u$	Δu
3	1	0.75	1.9393	0.004	1.8741	0.011
3	10	0.25	57.905	0.006	57.804	0.005
3	10	0.5	39.201	0.009	39.090	0.010
3	10	0.75	22.409	0.007	22.289	0.012
8	1.6758	0.9	6.7599	0.003	6.6683	0.028
8	4	0.9	16.654	0.008	16.546	0.027
8	4	0.95	9.3751	-0.004	9.2649	0.016
8	10	0.95	24.144	0.000	24.019	0.021

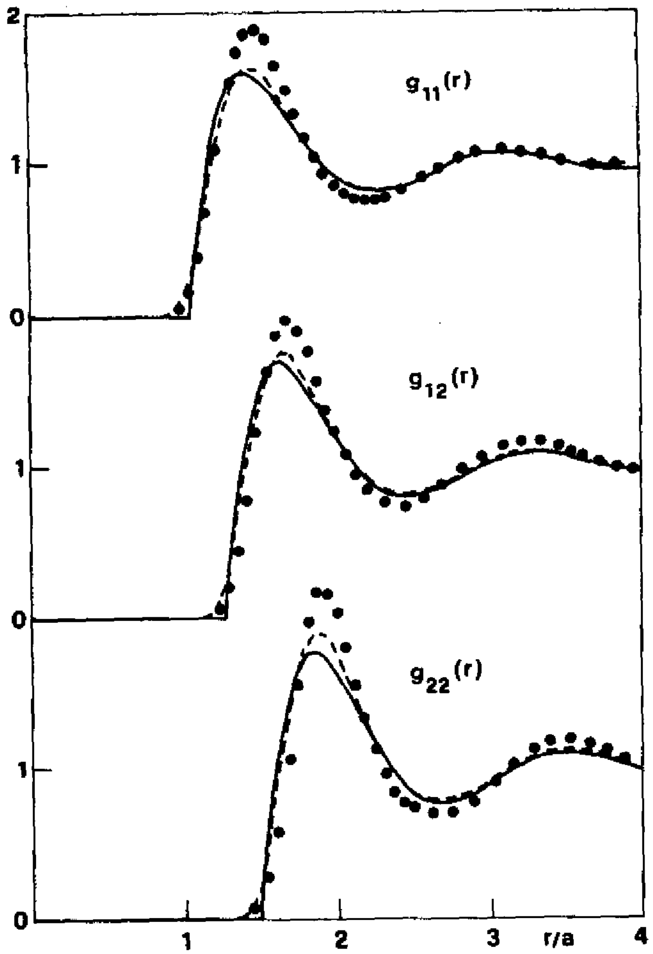

Fig. 1. Pair correlation functions in an ionic mixture with $Z_1=1$, $Z_2=2$, $\Gamma=40$ and $\rho_2=\rho_1$. Full curves: MSA results; broken curves: HNC results[4]; dots: Monte Carlo results[4].

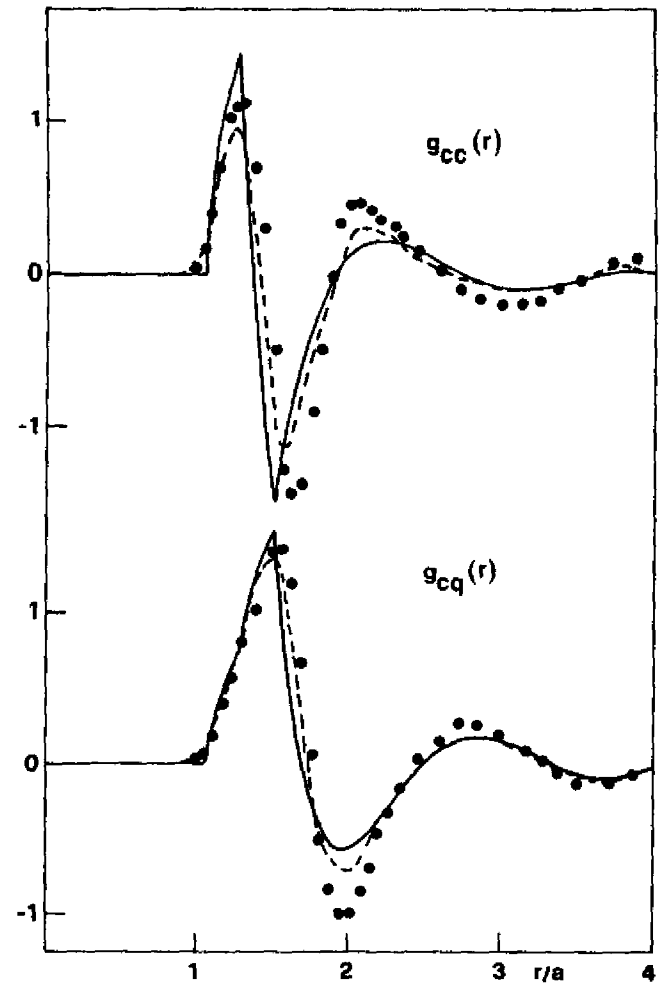

Fig. 2. The concentration-charge correlation function $g_{cq}(r)$ (bottom, in units of $c(1-c)/\bar{Z}$)and the concentration-concentration correlation function $g_{cc}(r)$ (top, in units of $c^2(1-c)^2$) for the TCP illustrated in fig. 1. The meaning of the curves is as in fig. 1.

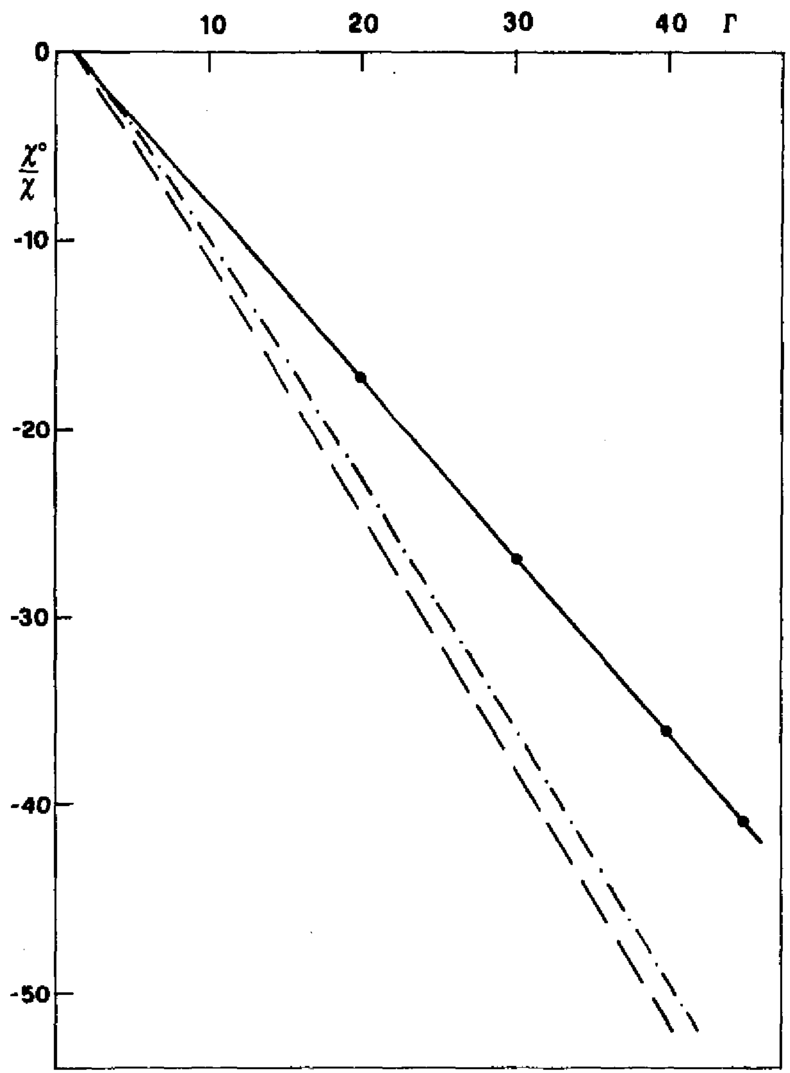

Fig. 3. The ratio $\chi_\circ/\chi$ between the ideal-gas compressibility $\chi_\circ$ and the compressibility χ of an ionic mixture with $Z_2 = 2$, $Z_1 = 1$ and $c = 1/2$, plotted against Γ. The full line gives both the MSA and the HNC results obtained through the virial theorem, and the dots are Monte Carlo data[4]. The other curves report the values of $\chi_\circ/\chi$ obtained by fluctuation theory; dashed curve, HNC results[4]; dash-dot curve, MSA results.