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► To cite this version:

Yaakov Rosenfeld. THE THEORY OF SIMPLE CLASSICAL FLUIDS : UNIVERSALITY IN THE SHORT RANGE STRUCTURE. Journal de Physique Colloques, 1980, 41 (C2), pp.C2-77-C2-81. 10.1051/jphyscol:1980212 . jpa-00219804

HAL Id: jpa-00219804

<https://hal.science/jpa-00219804>

Submitted on 4 Feb 2008

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THE THEORY OF SIMPLE CLASSICAL FLUIDS : UNIVERSALITY IN THE SHORT RANGE STRUCTURE

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Résumé.- Une théorie des fluides classiques simples est présentée dans laquelle à la fois la structure statique (au niveau des "paires"), et la thermodynamique de tous les systèmes pouvant être décrits par des potentiels de paires à symétrie sphérique peut être calculée par une approche unifiée. La théorie est fondée sur l'expansion diagrammatique de la fonction de distribution de paires conduisant à une équation intégrale HNC modifiée. Elle consiste en l'approximation que les "bridge functions" (c'est-à-dire la somme de tous les graphes élémentaires, annulés dans l'approximation HNC) constituent la même (universelle) famille de courbes, quel que soit le potentiel de paires adopté. En utilisant les simulations numériques paramétrisées du modèle des sphères dures comme donnée initiale dans l'équation intégrale il devient possible de reproduire un large éventail de données numériques calculées pour des potentiels d'interaction de particule à particule très différents (les plasmas à une et deux composantes en particulier). L'hypothèse d'universalité permet d'obtenir le potentiel de force moyenne à courte distance directement à partir de solutions de l'équation intégrale ; les facteurs d'améliorations des réactions nucléaires (dans le plasma dense) qui en remettent sont en bon accord avec les résultats récents de Jancovici (par une méthode indirecte) pour des charges identiques, et avec le modèle de la sphère ionique de Salpeter pour les mélanges.

Abstract.- A theory of simple classical fluids is presented in which both the static structure (on the "pair" level), and the thermodynamics, of all systems describable by spherically symmetric pair potentials, can be calculated by a unified approach. The theory is based on the diagrammatic expansion of the pair distribution function that leads to a modified hypernetted chain (HNC) integral equation. It consists of the approximation that the bridge functions (i.e. the sum of all elementary graphs, assumed zero in the HNC approximation) constitute the same (universal) family of curves, irrespective of the assumed pair potential. Using the parametrized computer simulation data for hard spheres as input in the integral equation, it was found possible to virtually duplicate a large body of computer simulation data compiled for a variety of quite disparate interparticle potentials (the one and two component plasma in particular). The statement of universality enables to obtain the potential of mean force at small separations directly from the solutions of the integral equation, and the resulting enhancement factors for nuclear reaction rates (in the dense plasma) are in excellent agreement with Jancovici's recent calculations (by an indirect method) for equal charges, and Salpeter's ion-sphere prediction for mixtures.

A theory for classical fluids is presented in which both the static structure (on the "pair" level), and the thermodynamics, of all system describable by spherically symmetric pair potentials, can be calculated by a unified approach. The theory is based on the diagrammatic expansion of the pair distribution functions that leads to modified hypernetted-chain (HNC) integral equations. It consists of the approximation that the bridge functions (i.e. the sum of all elementary graphs, assumed zero in the HNC approximation) constitute the same (universal) family of curves, irrespective of the assumed pair potentials. Using the parametrized computer simulation data for hard spheres as input in the integral equations, it was found possible to virtually duplicate a large body of

computer simulation data, compiled for a variety of quite disparate interparticle potentials (the one and two-component plasma in particular). The statement of universality enables to obtain the potential of mean force, at small separations, directly from the solutions of the integral equations. The resulting enhancement factors for nuclear reaction rates (in the dense plasma) are in excellent agreement with Jancovici's recent calculations (by an indirect method) for equal charges, and Salpeter's ion-sphere predictions for mixtures. Consider a mixture containing N_α particles of type α , interacting via the potentials $U_{\alpha\beta}(v)$. Let $N = \sum_\alpha N_\alpha$, V = total volume, $\psi = \frac{N}{V}$, $\psi_\alpha = \frac{N_\alpha}{V}$, $X_\alpha = \frac{N_\alpha}{N}$.

Consider a specific q component case with a given set X_1, X_2, \dots, X_q . The graphical analysis of the pair distribution functions $1/g_{\alpha\beta}(v)$ yields the following exact equations for the total correlation functions, $h_{\alpha\beta}(v) = g_{\alpha\beta}(v) - 1$, and the direct correlation functions $C_{\alpha\beta}(v)$:

$$h_{\alpha\beta}(v) + 1 = \exp \left[-U_{\alpha\beta}^{\text{eff}}(v)/k_B T + h_{\alpha\beta}(v) - C_{\alpha\beta}(v) \right], \quad (1)$$

$$\tilde{h}_{\alpha\beta}(k) - \tilde{C}_{\alpha\beta}(k) = \sum_{\gamma} \tilde{h}_{\alpha\gamma}(k), \quad \tilde{C}_{\alpha\beta}(k) \quad (2)$$

where

$$U_{\alpha\beta}^{\text{eff}}(v)/k_B T = U_{\alpha\beta}(v)/k_B T + B_{\alpha\beta}(v) \quad (3)$$

Eq. (2) is the Ornstein-Zernike relation for mixtures, written in terms of Fourier transforms. $B_{\alpha\beta}(v)$ denotes the functions represented by minus the sum of all elementary graphs with Mayer f -bonds, which have a particle of type α and a particle of type β as root points, while field points can belong to particles of any type. Note that $B_{\alpha\beta}(v)$ can be also represented by a subset of the elementary graphs, the "basic" set (consisting of all elementary graphs with at least triply connected field points) possessing instead of $f_{\gamma\delta}$ bonds only $h_{\gamma\delta}$ bonds (1).

Given the potential $U_{\alpha\beta}^{\text{eff}}(v)$, eqs. (1) and (2) represent the hypernetted chain (HNC) equations for the unknowns $h_{\alpha\beta}(v)$, $C_{\alpha\beta}(v)$. With the assumption $U_{\alpha\beta}^{\text{eff}}(v) = U_{\alpha\beta}(v)$ i.e. $B_{\alpha\beta}(v) = 0$, these equations constitute the usual HNC approximation. With a given (not necessarily the exact) set of functions $B_{\alpha\beta}(v)$, we refer to eqs. (1)-(3) as the modified HNC scheme (MHNC). Various integral equations that result from widely used approximations in the theory of liquids, can be cast in the MHNC form (2). In particular, the Percus-Yevick (PY) equations are obtained with

$$B_{\alpha\beta}^{\text{PY}}(v) = Y_{\alpha\beta}^{\text{PY}}(v) - 1 - \ln Y_{\alpha\beta}^{\text{PY}}(v), \quad (4)$$

where

$$Y_{\alpha\beta}(v) = g_{\alpha\beta}(v) \exp \left[\bar{U}_{\alpha\beta}(v)/k_B T \right] \equiv \exp \left[\bar{H}_{\alpha\beta}(v) \right]. \quad (5)$$

Eq. (5) defines the potentials of mean force, $H_{\alpha\beta}(v)$. From the way the MHNC equations have been written, the exact "bridge functions", $B_{\alpha\beta}(v)$, actually play the role of perturbing potentials in the usual HNC scheme, poten-

tials that are to be determined self consistently via the functions $h_{\alpha\beta}(v)$, by an iterative procedure. Let the symbol $\{ \}$ denote the set of all $\alpha\beta$ pairs. Let us denote the solution of eqs. (1)-(3) with a given set $\{B_{\alpha\beta}(v)\}$ by $\{h_{\alpha\beta}(v); \{B_{\alpha\beta}(v)\}\}$, and let $\{\sum_{\beta} h_{\alpha\beta}^{(i)}\}$ represent the bridge functions, $\{B_{\alpha\beta}^{(i)}(v)\}$, obtained by the summation of the infinite set of basic diagrams with the $h_{\gamma\delta}(v)$ bonds chosen from a given set $\{h_{\alpha\beta}^{(i)}(v)\}$. The iterative self consistency scheme may take the following form :

$$\{h_{\alpha\beta}^{\text{HNC}}(v); \{B_{\alpha\beta}(v) = 0\}\}, \{h_{\alpha\beta}^{(1)}(v); \{\sum_{\beta} h_{\alpha\beta}^{\text{HNC}}\}\}, \{h_{\alpha\beta}^{(2)}(v); \{\sum_{\beta} h_{\alpha\beta}^{(1)}\}\}, \dots \quad (6)$$

The overall quantitative similarity between the HNC and "exact" computer simulation results for the structure, together with the highly connected nature of the "basic" diagrams, suggests that the series (6) is fastly convergent. We make the following proposition /2,3/ :

$$\left| h_{\alpha\beta}^{(1)}(v) - h_{\alpha\beta}^{\text{exact}}(v) \right| < < 1 \quad (7)$$

As it stands, this proposition is of no practical significance since even one iteration requires to sum an infinite number of diagrams. A way out is suggested as follows : A well founded notion, on which the physical understanding of simple classical fluids is based, is manifested pictorially in the possibility to scale both $g(v)$ and $S(k)$ (the structure factor), for quite disparate systems (potentials varying between, say v^{-1} , and $v^{-\infty}$) so that they are nearly congruent (4). In other words, there exists a "first order" universality of structure

$$\{h_{\alpha\beta}(v); \psi, T\} \approx \text{independent of} \{U_{\alpha\beta}(v)\}, \quad (8)$$

provided we consider the whole set as function of density and temperature. This first order universality provides the basis for the successful application of the variational method with one universal reference system (e.g. the hard-sphere system), for

a variety of potentials including the coulomb plasma, with good results for the thermodynamics /5/. The deviations from (8) are, however, the main object of interest in the theory of classical fluids. These deviations are relatively small, of the same order of magnitude as the derivations $h_{\alpha\beta}^{\text{HNC}}(v) - h_{\alpha\beta}^{\text{exact}}(v)$. Thus if we maintain proposition (7). i.e. the "one iteration" assumption, we expect that the accuracy of $\{h_{\alpha\beta}^{(1)}(v)\}$ can be achieved also if we choose the bridge functions from a universal set appropriate to one (any one) particular choice of the potentials $\{U_{\alpha\beta}(v)\}$:

$$\{B_{\alpha\beta}(v) ; \psi, T\} \approx \text{independent of } \{U_{\alpha\beta}(v)\}. \quad (9)$$

The approximation of universality as embodied in (8) provides, in the context of the variational scheme, reasonably accurate results for the thermodynamics. We iterate this notion of universality, and expect that (9) in the context of the MHNC scheme will give the corresponding first order corrections to the statement (8). It turns out, however, that these "corrected" results are nearly indistinguishable from the best computer simulation data presently available, for all physical systems considered.

How the bridge functions look like? In the absence (indeed the nonfeasibility) of any diagram summation that will be meaningful for a dense fluid, we focus attention on the computer simulation data for, $g_{\alpha\beta}^{\text{exact}}(v)$, and the thermodynamics. These "exact" results suffer from two (among others) intrinsic limitations: (i) $g_{\alpha\beta}(v)$ is given only in the range $0 < v < L^{-1/3}$ (where L^3 is the volume of the basic simulation cube) that usually covers only the first few peaks. This prohibits the unambiguous determination of $S(k)$ or $C(v)$. This problem is treated more or less satisfactorily by joining the tails of $\{g_{\alpha\beta}^{\text{exact}}\}$ to the solution of some approximate integral equation (PY, HNC, etc)/6/. (ii) In the region of very strong repulsion where (say) $g(v) \lesssim 10^{-3}$ it is numerically impossible to calculate $H(v)$ directly from the data via $h g(v)$. The importance of this quantity stems from the fact that $\exp |H_{\alpha\beta}(0)|$ is the first order approximation for the enhancement factors for nuclear reactions rates in dense ionized matter

/7/. A general scheme to extract the bridge functions from the simulation data may consist of: (i) assuming a form for $\{B_{\alpha\beta}(v)\}$ with some free parameters, (ii) solving the MHNC equations (1)-(3) to find the corresponding $\{g_{\alpha\beta}(v)\}$, (iii) altering the free parameters until best fit for the computer data is achieved. In particular, thermodynamic consistency between the compressibility equation of state via $\{C_{\alpha\beta}(v)\}$ and the energy equation of state via $\{g_{\alpha\beta}(v)\}$ should be imposed. Even without reference to bridge functions as a key quantity, this scheme provides a numerically sound procedure for obtaining $\{S_{\alpha\beta}(k)\}$ from $\{g_{\alpha\beta}^{\text{exact}}(v)\}$, better in fact than all previous methods used. A particular such fit will reproduce $\{g_{\alpha\beta}^{\text{exact}}\}$ and yield also $\{C_{\alpha\beta}(v)\}$, but in view of the relation $h_{\alpha\beta}(v) = C_{\alpha\beta}(v) + H_{\alpha\beta}(v) + B_{\alpha\beta}(v)$, only the sum $H_{\alpha\beta}(v) + B_{\alpha\beta}(v)$ can be determined for small v , and not each function separately. This fitting scheme is not sensitive at all to the values of the fitting functions $\{B_{\alpha\beta}(v)\}$ at small v , since a finite perturbation on an effectively infinite (since $g(v) \ll 1$) potential has no effect on the structure. For values of v beyond the first peak of $g_{\alpha\beta}(v)$, $B_{\alpha\beta}(v)$ is of order $\frac{1}{2} h_{\alpha\beta}^2(v)$. In the context of the MHNC scheme this corresponds to a weak and long range perturbing potential, whose effect on $g_{\alpha\beta}(v)$ is very small, within the noise of present day simulations (about ± 0.01 , i.e. 1%). We thus arrive at the conclusion that from the standpoint of its structural consequences, the important region for which $B_{\alpha\beta}(v)$ is to be specified, in any theory, is the region of the first peak. Moreover, in that narrow region, $B_{\alpha\beta}(v)$ has the universal property of being effectively a repulsive potential. This last result is obtained by comparing published HNC and "exact" results for a large variety of systems. At this point universality (9) seems very plausible and even a family of straight lines should do a fine job of fitting the simulation data /8/. The statement of universality (9) allows the determination of $H(v)$ at small v provided we know the exact bridge functions for at least one system. There is only one fluid system for which one can rigorously obtain the values of

$H_{\alpha\beta}(v)$ at small v in terms of computationally feasible thermodynamic quantities, and that is the system composed of hard spheres with diameters $\sigma_1, \sigma_2, \dots, \sigma_q$. In particular /9/, $H_{\alpha\beta}(0) = \frac{\mu_{\alpha\beta}^E}{k_B T}$ where $\mu_{\alpha\beta}^E$ denotes the excess chemical potential for type α particles and $\sigma_{\alpha} \leq \sigma_{\beta}$. The computer simulation data for hard spheres have been parametrized /9/ as corrected versions of the analytic solution of the PY equations, with an accuracy that enables to infer the corresponding bridge functions $\{B_{\alpha\beta}^{HS}(v; \sigma_1, \dots, \sigma_q) ; \psi\}$. For a q -component system these represent a q -parameter family of curves. For the sake of comparison we also construct the corresponding bridge function family from the analytic PY results via eq.(4). A most interesting observation is the fact that except for a relabelling of the parameters σ_{α} , the two families $B_{\alpha\beta}^{HS, \text{exact}}$ and $B_{\alpha\beta}^{HS, PY}$ are nearly identical /2/. In other words, a set $(\sigma_1, \dots, \sigma_q)$ in one family corresponds, with a high accuracy to some set $(\sigma'_1, \dots, \sigma'_q)$ in the other. That means that incorporating the PY bridge functions in the MHNC scheme, we can duplicate the computer simulation data for hard sphere mixtures, for the pair structure and thermodynamics, including a direct determination of $H_{\alpha\beta}(0)$. According to the conjecture of universality, we should use in such a scheme (for any potentials) the exact hard sphere bridge functions. Our latest observation implies that the MHNC calculations can be performed with the analytic input from PY, thus making the whole procedure free from any "noisy" input.

We performed the MHNC calculations for a large variety of potentials. The following single component systems we considered /2/ : hard spheres, Lennard-Jones, inverse fifth power (v^{-5}) potential applicable to the helium ground state problem, Coulomb (i.e. the classical one component plasma), Yukawa, charged hard spheres, and an oscillatory potential proposed for liquid metals. The calculations for binary mixtures include /10/ : hard-spheres, Lennard-Jones, Coulomb (the two component plasma). For each system considered at a given temperature and density, a single bridge function, from the PY hard sphere set, could be found, such that a thermodynamically consistent solution of the

MHNC equations reproduces both the structure and the equation of state as obtained by computer simulations to within their noise. This solution also provides a prediction for $H_{\alpha\beta}(0)$, in fact the only direct prediction for this quantity available at present.

Unlike the hard spheres, the possibility of obtaining $H_{\alpha\beta}(0)$ for a dense plasma (positive ions immersed in a compensating uniform charge background) relies on specific physical considerations. For the

$$\frac{U_{\alpha\beta}(v)}{k_B T} = \frac{Z_{\alpha} Z_{\beta} e^2}{k_B T v} \equiv Z_{\alpha} Z_{\beta} \frac{\Gamma}{(v/a)}$$

(where $a = (3/4\pi\eta)^{1/3}$), the dominant strong coupling ($\Gamma \gg 1$) contribution to the excess free energy is expected to have the following form :

$$\frac{F^{\text{ex}}}{N k_B T} (x_1, \dots, x_q) = -E_{\mu} \langle Z \rangle^{1/3} \langle Z^{5/3} \rangle \Gamma \quad (10)$$

where,

$$\langle Z^S \rangle = \sum_{\alpha} x_{\alpha} Z_{\alpha}^S$$

and the "Madelung" constant is well approximated by the ion-sphere model /11/, $E_{\mu}^{\text{IS}} = 9/10$. A rigorous consequence of (10) is

$$H_{\alpha\beta}(0) = E_{\mu} \langle Z \rangle^{1/3} \Gamma \cdot \left[(Z_{\alpha} Z_{\beta})^{5/3} - Z_{\alpha}^{5/3} - Z_{\beta}^{5/3} \right] \quad (11)$$

Jancovici /7/ made use of Monte Carlo data /12/ to improve Salpeter's ion-sphere prediction for the case of the one-component plasma. For $\Gamma \gg 1$ both results are very close and agree very well with our direct predictions /2/ using the MHNC scheme with PY bridge functions. Our direct predictions for a binary mixture /10/ with $Z_1 Z_2 = 2$ agree well with (11). These results provide a severe test for both the accuracy of the theory and its diagrammatic interpretation.

In view of the statement of universality and its apparent confirmation by computer simulations, the formulation of a procedure for an a priori calculation of both the structure (including the otherwise inaccessible $H(v \ll 1)$) and the thermodynamics of any physically conceivable pair potentials $U_{\alpha\beta}(v)$, can be carried out in many ways. For one component systems,

for which the hard sphere bridge functions constitute a one parameter family of curves, this is easily achieved by imposing thermodynamic consistency in order to obtain the appropriate value of this parameter as function of density and temperature. An essentially similar procedure can be used for mixtures but it involves more technical details.

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