HYPERSCALING THEORY OF CHARGED SYSTEMS

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April 26, 2010

1 Abstract

The Hyperscaling (HYPERSCA) is a new analytical and amazingly accurate closure of the Ornstein-Zernike[1] which derives from the Scaled Particle Theory (SPT) [2]. The theory yields the *full angular* correlation functions [3] from which the *proper* molecular site-site correlation functions are obtained [4, 5, 6]. This theory summarizes the results for charged systems of close to 40 years research collaboration with Joel Lebowitz. The HYPERSCA [7, 8] uses the ESBIMSA [9] which is derived from scaled particle theory, and the 'illegal marriage' [10] of the PY[11] and MSA [12, 13] approximations. The idea of this marriage originated in a discussion with Joel Lebowitz (see the footnote of Blum and Narten [14], which was first called the soft MSA). Joel made then the observation that that this is a new approximation, which prompted the joint research with Yaacov Rosenfeld [10, 15, 16]: The proper way to extend the hard-core SPT to charged systems is to convert the hard core cavity into a charged core cavity, and that is an obvious extension of the Fundamental Measure Theory [17] to include the electrostatic interactions. The technical details are discussed in earlier work [10, 21, 22]. The new theory uses the EXP closure [18] as applied to unrestricted mixtures [19]. We then show that the new scaling parameters are directly related to the contact pair correlation function. Which makes the theory consistent with the full association asymptotics. Then contact pair distribution function agrees with the careful simulations of Bresme et al. [24] *is the only theory that satisfies the infinite charge limit* [9, 23] and explains the amazing agreement of the simulations of Orkulas et al. [25] with our theoretical predictions [26].

References

[1] L. Blum and D. V. Perez Veloz, 2007, *Cond. Matter Physics* , **10** 381. (ArXiv cond-mat 0707-3136).

[2] H. Reiss, H.L. Frisch , J.L. Lebowitz, 1959,*J. Chem. Phys.*, **31** 369, **33** 1379.

[3] Blum, L. and Torruella, A.J., 1972, *J. Chem. Phys.***56** , 303,**57**, 1862,**58**, 3295.

[4] Dyer, K.M., Perkyns, J. S., Stell, G., Pettitt, B. M., 2008, *J. Chem. Phys.*, **129** 104512.

[5] Blum, L. and Narten, A.H., 1976, *Adv. Chem. Phys* .**34**, 203.

[6] Chandler, D. , Silbey, R., and Ladanyi. B , 1982, *Mol. Phys.***46** , 1335.

[7] Blum L. and Arias, M., 2006, *J. of Phys.: Cond. Matt.*, **18**, S2437, (ArXiv cond-mat 0602477).

[8] Blum L. and Arias, M., 2006, *Mol. Phys.*, **104**, 3801.

[9] Blum, L., and Bernard, O., 2004, *Proc. International School of Physics "Enrico Fermi", Course CLV,* Mallamace, F. and Stanley, H. E., Editors, IOS Press, Amsterdam, **155**, 335.

[10] Blum, L., and Rosenfeld, Y.,1991, *J. Stat. Phys.*, **63**, 1177.

[11] Percus J.K. and Yevick G., 1964, *Phys. Revs.* ,**1** B290.

[12] Lebowitz, J.L. and Percus, J.K., 1966 *Phys. Revs*, **144**, 251.

[13] Waisman, E. and Lebowitz, J.L., (1970) *J. Chem. Phys.*, **52** , 4307, ibid, **56** , 3086, 3092 (1972).

[14] Blum, L. and Narten, A.H., 1972, *J. Chem. Phys.***56** , 5197,**60** , 3378.

[15] Rosenfeld, Y. and Blum, L. 1986,*J. Chem. Phys.*, **85** 1556.

[16] Rosenfeld, Y. and Blum, L. 1985,*J. Phys. Chem.*, **89** 5149.

[17] Rosenfeld, Y.,(1997), *Phys. Revs. E*, **55**, R4873.

[18] Andersen, H.C. and Chandler, D., 1972, *J. Chem. Phys.*, **57** , 1918.

[19] Blum L., Perez-Veloz,D.V., and Arias, M., 2009, *AIP Conference Proceedings TAC-C2008*,**1102** 52.

[20] Blum, L. 1975, L. *Mol. Phys.* **30**, 1559.

[21] Blum, L. and Hoye, J.S.,*J. Phys. Chem.*, **81** 1311.

[22] Hiroike, K. 1977, *Mol. Phys.* **33**, 1195.

[23] Bernard, O. and Blum L.,(1996),*J. Chem. Phys.* , **112**, 7227.

[24] Bresme, F., Lomba, E., Weis, J.J., Abascal, J.L.F., 1995 *Phys. Rev.* E **51** 389.

[25] Orkulas, G., Kumar, P. and Panagiotopoulos, A.Z., 2003,*Phys. Revs. Letters*, **90**, 048303.

[26] Jiang J. W., Blum L., Bernard, O., Prausnitz, J. M., Sandler, S. I. 2002, *J. Chem. Phys.* **116**, 7977.

PACS: 61.20.Gy