Compressibilities in bilayers of charged particles

2006 J. Phys. A: Math. Gen. 39 4625

(http://iopscience.iop.org/0305-4470/39/17/S49)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **39** (2006) 4625–4629 doi:10.1088/0305-4470/39/17/S49

Compressibilities in bilayers of charged particles

Stamatios Kyrkos[1,2], **Gabor J Kalman**[2] **and Kenneth I Golden**[3]

[1] Department of Chemistry and Physics, Le Moyne College, 1419 Salt Springs Rd., Syracuse, NY 13214, USA
[2] Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
[3] Department of Mathematics and Statistics and Department of Physics, University of Vermont, Burlington, VT 05405, USA

E-mail: kyrkoss@lemoyne.edu

Received 20 September 2005, in final form 28 December 2005
Published 7 April 2006
Online at stacks.iop.org/JPhysA/39/4625

Abstract

The isothermal compressibility plays a central role in determining the characteristics of the static response in plasma systems. In a charged particle bilayer this role is assumed by L_{ij}, the matrix of inverse compressibilities. For weak coupling, the inverse compressibilities of a bilayer of charged particles can be calculated analytically in the Debye limit from the equation of state through the chemical potential. There are two different charging procedures to obtain the latter. We present the results of a rather lengthy analytical calculation, exploring both approaches. The limits of the validity of the Debye description are discussed, and we compare the weak coupling results with L_{ij} values inferred from $S(k\rightarrow 0)$ through the compressibility sum rule, where the structure function $S(k)$ is generated for strong coupling both through molecular dynamics simulations and by HNC calculations.

PACS numbers: 51.35.+a, 51.30.+i

1. Introduction

Charged particle bilayers are remarkable physical systems with interesting static and dynamic properties [1–6]. The intralayer and interlayer compressibilities play a key role in determining the character of the static response and the screening properties (antiscreening and overscreeening versus normal screening) of a bilayer system [7, 8]. While the compressibilities can be derived in principle from the equation of state, they can also be deduced from the small k behaviour of the static structure functions $S_{ij}(k)$. Whereas in an exact theory the two approaches should provide identical results, in an approximate description of the system this is not assured. In fact, consistency may be regarded as a useful check on the reliability of a particular approach. For strongly coupled classical bilayers, compressibilities have been

deduced from the static structure function $S(k)$, this latter having been generated by HNC calculations [9]. So far, however, no direct calculations from the equation of state have been available. Here we calculate the compressibilities from a weak coupling equation of state, established earlier in an exact Debye-like calculation [10]. We give a careful definition of the bilayer compressibilities in terms of the chemical potential μ, derive two different charging procedures that can be used for the calculation of μ, give a semi-analytic expression for the compressibilities as a function of the coupling strength Γ, connect the results with the strong coupling results and show the trend that is responsible for the anomalous screening properties.

2. Compressibility calculations

The bilayer that we examine consists of two 2D layers of densities n_1 and n_2, separated by a distance d. The partial density response functions are defined by

$$\delta n_i(\mathbf{k},\omega) = \chi_{ij}(\mathbf{k},\omega)\Phi_j(\mathbf{k},\omega), \tag{1}$$

where $\chi_{ij}(\mathbf{k},\omega)$ satisfies the compressibility sum rule

$$\chi_{ij}(\mathbf{k}=0,\omega=0) \equiv \chi_{ij} = \chi_0 L_{ij}^{-1} \tag{2}$$

and $\Phi_i(\mathbf{k},\omega)$ is the perturbing potential for layer i. Partial pressures do not constitute a useful concept in layered systems. For the compressibility, one has to revert to the definition in terms of the chemical potential. Then, the inverse compressibilities are

$$L_{ij} = \chi_0 \frac{\partial \mu_i}{\partial n_j} \tag{3}$$

where μ_i is the chemical potential for layer i, and $\chi_0 = -\beta n$, for a classical system. The chemical potential is derived from the free energy F:

$$\begin{aligned} \mu_i &= \frac{1}{V}\frac{\partial}{\partial n_i}\left\{\sum_m F_m^0 + \sum_{m,n} F_{mn}\right\} \\ F_m^0 &= -V n_m T \log\left(\zeta \frac{T^{3/2}}{n}\right), \qquad F_{mn} = \int_0^1 \mathrm{d}\lambda \frac{E_{mn}(\lambda e^2)}{\lambda}. \end{aligned} \tag{4}$$

Charging parameter λ is associated with charge e^2 and ζ is the chemical constant. Since the correlation energy E_{mn} is expressible in terms of the correlation functions $h_{mn}(r)$,

$$E_{mn} = \frac{1}{2} V n_m n_n \int \phi_{mn}(r) h_{mn}(r)\, \mathrm{d}^3 r, \tag{5}$$

μ is expressible in terms of the integrals

$$K_{mn} = \int_0^1 \mathrm{d}\lambda \int \phi_{mn}(r) h_{mn}(r;\lambda e^2)\, \mathrm{d}^3 r. \tag{6}$$

$\phi_{11}(r) = \phi_{22}(r) = \frac{e^2}{r}$ and $\phi_{12}(r) = e^2(r^2+d^2)^{-\frac{1}{2}}$. The elements of the L-matrix now become

$$L_{ij} = \delta_{ij} + \beta n \left\{ K_{ij} + n(K_{11,j} + K_{12,j}) + \frac{n^2}{2}(K_{11,ij} + 2K_{12,ij} + K_{22,ij}) \right\} \tag{7}$$

where $K_{11,i} \equiv \frac{\partial}{\partial n_i} K_{11}$, $K_{11,ij} \equiv \frac{\partial^2}{\partial n_i \partial n_j} K_{11}$ etc.

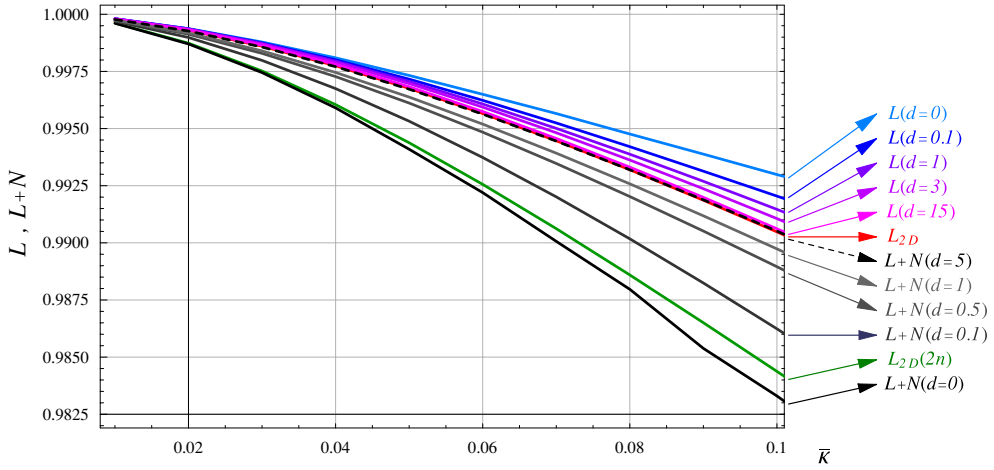

Figure 1. L and $L+N$ ($L_{11} \equiv L, L_{12} \equiv N$) as a function of $\bar{\kappa}$ in the Debye approximation, showing the $d \to 0$ and $d \to \infty$ limits.

Since the second-order derivatives are not convenient to work with numerically, an alternative expression in terms of first derivatives has also been obtained:

$$\begin{aligned} \mu_i &= \mu_i^0 + T \log n_i + \sum n_m G_{mi} \\ G_{mn} &= \int_0^1 \mathrm{d}\xi \int \phi_{mn}(r) h_{mn}(r; \xi q_n)\, \mathrm{d}^3 r. \end{aligned} \tag{8}$$

Here the charging parameter ξ [11] is associated with charge of species i, rather than with the overall e^2. The elements of the L-matrix now become

$$L_{ij} = \delta_{ij} + \beta n \left(G_{ij} + \sum n G_{mi,j} \right). \tag{9}$$

The equivalent of the Debye theory for a bilayer provides the Fourier transform of the pair correlation functions [10]:

$$h_{11}(\mathbf{k}) = h_{22}(\mathbf{k}) = \frac{\kappa^2 \,\mathrm{e}^{-2kd} - \kappa(k+\kappa)}{(k+\kappa)^2 - \kappa^2 \,\mathrm{e}^{-2kd}}, \qquad h_{12}(\mathbf{k}) = \frac{-k\kappa \,\mathrm{e}^{-kd}}{(k+\kappa)^2 - \kappa^2 \,\mathrm{e}^{-2kd}}. \tag{10}$$

$\Gamma = \beta e^2/a$ and $\kappa = 2\pi n \beta e^2$ are the coupling parameter and Debye wavelength respectively; a is the lattice constant, so that $\bar{\kappa} \equiv \kappa a = 2\Gamma$. Using these functions, μ can be calculated via (7) and (9). In the first case, the $\int \mathrm{d}\lambda$ integrations can be performed explicitly in k-space:

$$\begin{aligned} K_{mn} &= \int_0^1 \mathrm{d}\lambda \int \phi_{mn}(r) h_{mn}(r; \lambda e^2)\, \mathrm{d}\mathbf{r} = \frac{1}{4\pi^2} \int_0^1 \mathrm{d}\lambda \int \phi_{mn}(k) h_{mn}(k; \lambda e^2)\, \mathrm{d}\mathbf{k} \\ &= \int_0^\infty f_{mn}(k, \kappa)\, \mathrm{d}k; \end{aligned} \tag{11}$$

but the f_{mn} functions are the furthest one can go analytically. Further calculations, such as the 1st and 2nd derivatives $K_{11,i}$, $K_{11,ij}$ etc, can only be done numerically. One proceeds similarly

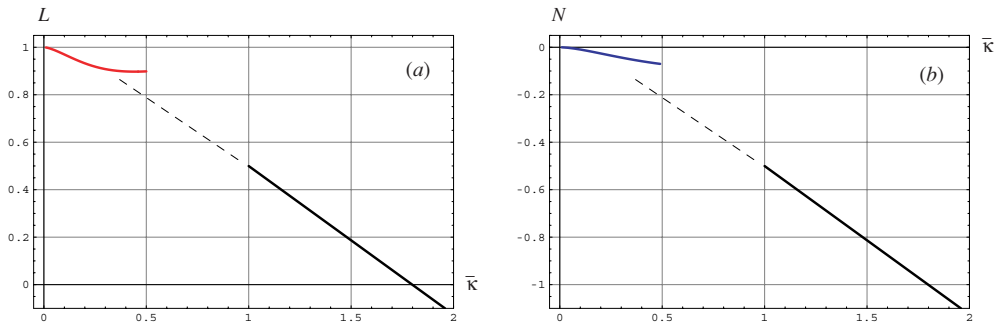

Figure 2. (*a*) $L_{11} \equiv L$ as a function of $\bar{\kappa}$ in the Debye approximation. (*b*) $L_{12} \equiv N$ as a function of $\bar{\kappa}$ in the Debye approximation. The solid straight lines indicate the HNC results.

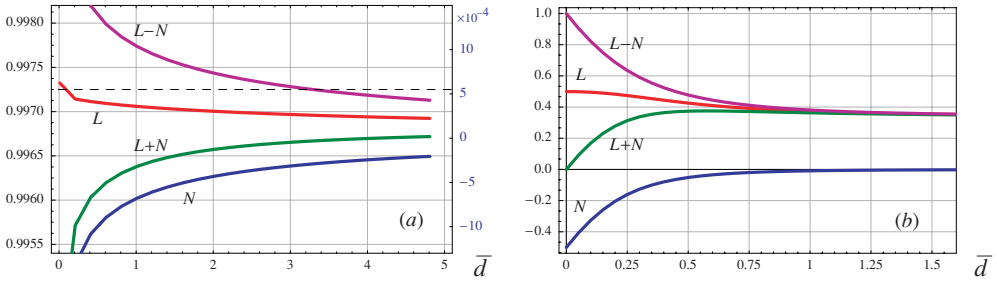

Figure 3. (*a*) L, N, $L+N$, $L-N$ as a function of $\bar{d}$ in the Debye approximation, for $\bar{\kappa} = 0.05$. The right axis label applies to N. (*b*) L, N, $L+N$, $L-N$ as a function of $\bar{d}$ in the HNC approximation, for $\Gamma = 1$.

with the functions G_{mn}. Figure 1 displays the calculated inverse compressibilities for weak coupling. At the $d \to 0$ and $d \to \infty$ limits they display the expected behaviour, i.e.,

$$L + N \xrightarrow{d\to 0} L_{2D}(2n), \qquad L \xrightarrow{d\to\infty} L_{2D}(n), \quad N \xrightarrow{d\to\infty} 0. \tag{12}$$

The results appear reliable for values of $\kappa \approx 0.1$ or less (figure 2), where the behaviour of L_{11} and L_{12} as a function of d mirrors the strong coupling behaviour derived from the HNC approximation (figure 3).

Acknowledgments

This work has been partially supported by the National Science Foundation under grants no PHY-0206695, PHY-0514619, PHY-0206554 and PHY-0514618.

References

[1] Goldoni G and Peeters F M 1996 *Phys. Rev.* B **53** 4591
[2] Kalman G J, Valtchinov V and Golden K I 1999 *Phys. Rev. Lett.* **82** 3124
[3] Kalman G J and Donko Z 2001 *Phys. Rev.* E **63** 061504
[4] Donko Z, Kalman G J, Hartmann P, Golden K I and Kutasi K 2003 *Phys. Rev. Lett.* **90** 226804
[5] Schweigert I V, Schweigert V A and Peeters F M 1999 *Phys. Rev.* B **60** 014665

[6] Schweigert I V, Schweigert V A and Peeters F M 1999 *Phys. Rev. Lett.* **82** 005293
[7] Valtchinov V, Kalman G J and Blagoev K B 1997 *Phys. Rev.* E **56** 4351
[8] Kyrkos S and Kalman G J 2003 *J. Phys. A: Math. Gen.* **36** 6235
[9] Kalman G J, Donko Z, Golden K I and McMullan G 2001 *Condensed Matter Theories* **16** 51
[10] Golden K I, Kalman G J and Kyrkos S 2002 *Phys. Rev.* E **66** 031107
[11] Hill T L 1960 *An Introduction to Statistical Thermodynamics* (Reading, MA: Addison-Wesley)