A stable local density functional
approach to ion-ion correlations

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Abstract. – We propose a new approach for incorporating counterion correlations into Poisson-
Boltzmann like theories, which is based on a local density functional for the system of counte-
rions. Our derivation is inspired by the Debye-Hückel approach to the one-component plasma
(OCP). An artificial instability due to the OCP's homogeneous background charge – which is
absent in the original counterion system – is overcome by excluding the background from the
vicinity of a central ion. The resulting free energy density is convex and thus applicable within a
local density approximation. For the simple example of a strongly charged stiff rod surrounded
by its counterions we demonstrate that the Poisson-Boltzmann free energy functional augmented
by our new correction accounts for the correlations present in this system when compared to
molecular dynamics simulations.

A widespread starting point for the statistical description of ionic systems is the Poisson-
Boltzmann (PB) equation. Charge density and electrostatic potential are connected via
the Poisson equation and the assumption that the ion density is locally proportional to the
Boltzmann-factor. This mean-field approach is equivalent to a local density functional theory,
which expresses the free energy as a functional of the ionic density and takes into account only
electrostatic energy and entropy of this density field.

An important example is the screening of a highly charged macroion by oppositely charged
counterions [1]. One attempt to improve onto the PB density profiles [5, 6, 7, 8, 9, 10, 11] is to
locally approximate the correlation contribution beyond mean-field theory by the free energy
of a uniform counterion system with a homogeneous background charge, *i.e.*, a one-component-
plasma (OCP) [2, 3, 4]. There is, however, a fundamental problem: Already for moderately
high densities the free energy of a homogeneous OCP is a concave function of density [12], a
situation which favors the development of inhomogeneities. In the plain OCP this is opposed
by the homogeneous background charge. However, this mechanism does not exist when instead

dealing with individual macroions. The corresponding instability of the screening atmosphere collapsing onto the surface of the macroion has been termed "structuring catastrophe" in this context [9, 10].

An exact expression for the OCP free energy is not known. However, there exists e.g. an approximation on the level of Debye-Hückel (DH) theory [13], called Debye-Hückel plus hole (DHH) [14]. Although constructed as a low density approximation, it also displays the asymptotic concavity at high density and gives rise to the abovementioned instability.

At this point there are two alternative directions in which one could proceed: The first is to keep the OCP correction but employ *nonlocal* theories [5, 6, 10, 15], the second is to remain local but find a correlation functional which is *convex* in the density. In this paper we pursue the second way and derive a convex functional, based on a modification of the DHH theory. The basic idea will be *(i)* to exclude the homogeneous background from a region of radius a around the central particle during the Debye charging process and *(ii)* to use this fixed distance a as a lower bound for the artificial correlation hole of radius h introduced in the DHH theory (see below). The new theory, referred to as the Debye-Hückel-Hole-Cavity (DHHC) approach, remains simple and can be used within a local density approximation (LDA) to account for counterion correlations. This will be shown in an example at the end of the paper, where we compare its predictions to simulational results of a model system.

Since the necessary changes to DHH will turn out to be surprisingly small, it is worthwhile to briefly recall the way in which DHH theory arrives at a free energy for the OCP. For definiteness, we assume a system of N identical point-particles of valence v and (positive) unit charge q inside a volume V with a uniform neutralizing background of charge density vqn_{B} and dielectric constant ε. According to the Debye-Hückel approach, the potential ϕ created by a central ion (*i.e.*, fixed at the origin) and all its surrounding ions results from solving the spherically symmetric Poisson equation

$$\nabla^2\phi(r) = \phi''(r) + \frac{2}{r}\,\phi'(r) = -\frac{4\pi}{\varepsilon}\rho(r), \tag{1}$$

subject to the requirements that *(i)* the charge density is $qv\delta(\boldsymbol{r})$ at the central ion and *(ii)* the rest of the mobile ions rearrange in the uniform background in accordance with the Boltzmann distribution $\rho(r) = vqn_{\mathrm{B}}(\exp\{-\beta vq\phi(r)\} - 1)$. Combining this with eq. (1) yields the nonlinear PB equation. Linearization of the exponential function gives $\rho(r) = -\varepsilon\kappa^2\phi(r)/4\pi$ together with the famous Debye-Hückel solution for the potential, $\phi(r) \sim e^{-\kappa r}/r$, illustrating the rearrangement of the other ions around the central one in order to screen the Coulomb interaction. Here, $\kappa \equiv \sqrt{4\pi\ell n_{\mathrm{B}}}$ is the inverse screening length, $\ell = \ell_{\mathrm{B}}v^2$, with $\ell_{\mathrm{B}} = \beta q^2/\varepsilon$ being the Bjerrum length, and $\beta = 1/k_{\mathrm{B}}T$.

The problem with Debye-Hückel theory is that the condition for linearization is obviously not satisfied for small r, where the potential is large [16] Indeed, the particle density becomes negative and finally diverges at the origin. A solution of this defect was suggested in the DHH theory [14], which artificially postulates a correlation hole of radius h around the central ion where no other ions are allowed. In this case the charge density is given by

$$\rho(r) \;=\; \begin{cases} vq\left(\delta(\boldsymbol{r}) - n_{\mathrm{B}}\right) & : \quad r \le h \\ -\varepsilon\kappa^2\phi(r)/4\pi & : \quad r > h \end{cases}. \tag{2}$$

The solution of the linearized PB equation with the appropriate boundary conditions (continuity of electric field and potential) yields the potential for both regions. The free parameter h has to be fixed on physical grounds: At low temperatures the electrostatic repulsion dominates and the minimum ion separation essentially becomes the mean separation, so $h = (4\pi n_{\mathrm{B}}/3)^{-1/3}$. At high temperatures, the hole size can be estimated by balancing Coulombic and thermal energy,
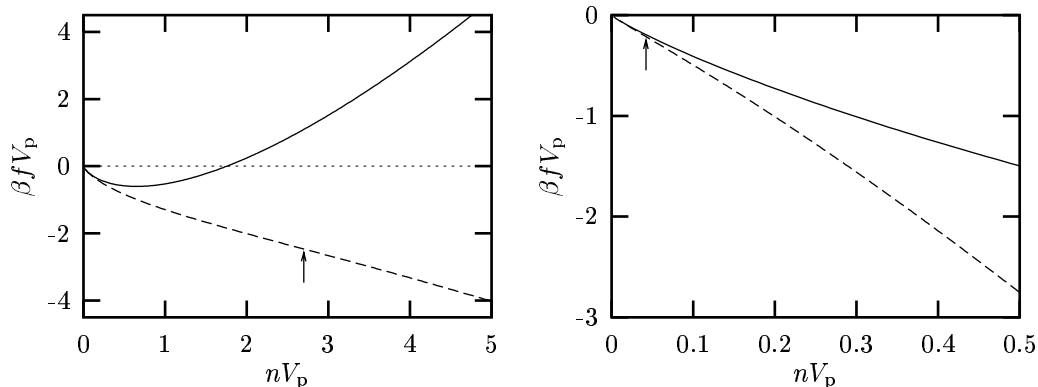
Fig. 1. – Free energy density f of the homogeneous OCP within DHH approximation (dashed, eq. (4) plus entropy) as a function of density for Bjerrum length $\ell_B = 7.14\,\text{Å}$ and monovalent/divalent ions (left/right). The arrows mark the points at which f changes from convex to concave. The solid line results from using the DHHC expression (12). A particle volume of $V_p = (5\text{Å})^3$ was assumed.

which gives $h = \ell$. A systematic way to interpolate between these two limits results from excluding particles from a region where their potential energy is larger than some threshold. A natural choice is the thermal energy k_BT, which leads to

$$\kappa h = \omega - 1 \qquad \text{with} \qquad \omega = (1 + 3\ell\kappa)^{1/3}. \tag{3}$$

Incidentally, this assumption also gives a continuous charge density across the hole boundary.

Once the potential at the position of the central ion is known, the electrostatic contribution to the Helmholtz free energy density can be obtained by the Debye charging process [13], as was done previously by Penfold *et al.* [9]:

$$\frac{\beta f_{\text{DHH}}}{n_B} = \frac{1}{4}\left[1 - \omega^2 + \frac{2\pi}{3\sqrt{3}} + \ln\left(\frac{\omega^2 + \omega + 1}{3}\right) - \frac{2}{\sqrt{3}}\arctan\left(\frac{2\omega + 1}{\sqrt{3}}\right)\right]. \tag{4}$$

Within a local density approximation the total free energy is thus approximated by

$$F[n(\boldsymbol{r})] \simeq \int \mathrm{d}^3r\left\{k_BT\,n(\boldsymbol{r})\ln(n(\boldsymbol{r})V_p) + f_{\text{el}}[n(\boldsymbol{r})] + f_{\text{DHH}}[n(\boldsymbol{r})]\right\}. \tag{5}$$

The first term accounts for the entropy (V_p is the particle volume). The second term describes the mean-field electrostatic energy generated by a charge density $vq(n(\boldsymbol{r}) - n_B)$. This part vanishes for a homogeneous system. The third term finally accounts in a local fashion for the free energy difference between the charged and a corresponding neutral system having the same density. The equilibrium density profile is obtained by functional minimization of F under the constraint of global charge neutrality.

For the *homogeneous* case the free energy is plotted in Fig. 1. It is concave beyond the density $n^\star \approx 7.8618/\ell^3$ and asymptotically behaves like $-n^{4/3}$. The development of inhomogeneities this would cause is balanced by the global electrostatic energy, which acts against a charge separation. This prevents the system from collapsing, but requires a description going beyond the homogeneous situation. An extension of DHH theory towards slowly varying nonuniform densities and a comparison with Monte-Carlo simulations can be found in ref. [17].

As discussed in the introduction, an attempt to improve PB theory is to extend its density functional to include a correlation term. The free energy for a macroion surrounded by its counterions is thus partitioned into two terms:

$$F[n(\boldsymbol{r})] = F_{\mathrm{PB}}[n(\boldsymbol{r})] + \int \mathrm{d}^3 r \; f_{\mathrm{corr}}[n(\boldsymbol{r})]. \tag{6}$$

The first part

$$F_{\mathrm{PB}}[n(\boldsymbol{r})] = \int \mathrm{d}^3 r \left\{ k_{\mathrm{B}} T \, n(\boldsymbol{r}) \ln \left(n(\boldsymbol{r}) V_{\mathrm{p}} \right) + \frac{1}{2} \, qv \, n(\boldsymbol{r}) \phi[n(\boldsymbol{r})] \right\} \tag{7}$$

contains the entropy of the small ions and the global electrostatics, *i.e.*, the interaction of the small ions with the macroion potential and the mean-field interaction between the counterions. Minimization of eq. (7) under the constraint of global charge neutrality gives – together with the Poisson equation – the PB equation. The interparticle correlations are taken into account by applying a similar variational approach to eq. (6).

Unfortunately, it is impossible to use the term f_{DHH} from eq. (4) as a correlation correction f_{corr} in eq. (6). The reason is that, contrary to the case of a plain OCP, the global electrostatic energy does not act against the development of inhomogeneities. Rather, it favors a distribution in which all ions sit on the surface of the macroion. Since beyond $n^\star$ the entropy plus DHH contribution is concave and favors phase separation, this gives rise to the "structuring catastrophe" mentioned in the introduction. We point out that it is the *interplay* between the LDA and the asymptotically concave DHH correction which is responsible for this phenomenon. Note also that in situations, for which the density $n^\star$ is nowhere exceeded, the theory does not necessarily "realize" its asymptotic instability and gives a finite (yet, meta-stable) answer. It has in fact been applied to account for correlations in cases of systems with low ionic strength [5, 6, 9]. For instance, in aqueous solutions ($T = 300\,\mathrm{K}$, $\varepsilon_{\mathrm{r}} = 78.5$, giving $\ell_{\mathrm{B}} \approx 7.1\,\text{Å}$) $n^\star \approx 36\,\mathrm{mol/l}$ for monovalent ions, while it is $0.56\,\mathrm{mol/l}$ and $0.049\,\mathrm{mol/l}$ for di- and trivalent ions, respectively.

To circumvent the instabilities, a number of *nonlocal* free energies have been proposed [5, 6, 10, 15]. In these *weighted density approximations* (WDA) the local density is replaced by a spatially averaged quantity. The main problem with these methods is that the choice of the weighting function is somewhat arbitrary. In most cases it is obtained by relating the second variation of the free energy with the direct correlation function. At this point the WDA requires prior information about this function, which is not yet available and thus has to be calculated using different approaches (like, *e.g.*, integral equation theories). Whatever choice one takes, it is still *(i)* quite arbitrary and *(ii)* leads to a series of approximations which *(iii)* instead of clarifying the physics tend to obscure it.

An alternative way to avoid the instability in the local density approach is the use of a *convex* correlation correction instead of the asymptotically concave f_{DHH}. We now demonstrate how such a term can be derived on physical grounds. Starting with the DHH approximation of the OCP, we demand the following two additional requirements:

1. There exists a spherical region of radius a around the central ion which is free of background charge.

2. The size h of the artificial correlation hole is bounded below by a.

The parameter a acts similarly to the excluded region in the original Debye-Hückel theory [13] and we will therefore interpret it as an ion diameter. The charge density, which for the usual

DHH theory is given by eq. (2), has now three regions:

$$\rho(r) = \begin{cases} vq\delta(\boldsymbol{r}) & : \quad r < a \\ -qvn_{\mathrm{B}} & : \quad a \leq r \leq h \\ -\varepsilon\kappa^2\phi(r)/4\pi & : \quad r > h. \end{cases} \tag{8}$$

The solution of the linearized PB equation with appropriate boundary conditions yields

$$\psi(r) = \frac{ve_0}{4\pi\varepsilon r} \times \begin{cases} 1 - \dfrac{r}{2\ell}\left[(\kappa h)^2 - (\kappa a)^2\right] - \kappa r C_h & : \quad 0 \leq r < a \\ 1 - \dfrac{r}{2\ell}\left[(\kappa h)^2 - (\kappa r)^2\right] - \dfrac{1}{3\ell\kappa}\left[(\kappa r)^3 - (\kappa a)^3\right] - \kappa r C_h & : \quad a \leq r < h \\ C_h\,\mathrm{e}^{-\kappa(r-h)} & : \quad h \leq r < \infty, \end{cases} \tag{9}$$

with the abbreviation

$$C_h = \frac{1}{1+\kappa h}\left(1 - \frac{(\kappa h)^3 - (\kappa a)^3}{3\ell\kappa}\right). \tag{10}$$

In order to obtain the old theory in the limit $a \to 0$, we choose the hole size h to yield the same screening (*i.e.*, the same amount of charge within h) as the DHH theory. This results in

$$\kappa h = \left[(\omega - 1)^3 + (\kappa a)^3\right]^{1/3}. \tag{11}$$

This expression has four important physical limits: zero/infinite temperature and low/high density. At low temperature the exclusion hole has maximum size and behaves as $h = (3/4\pi n_{\mathrm{B}} + a^3)^{1/3}$. As the temperature is increased, the hole size shrinks, but contrary to DHH theory it does not vanish and $h \to a$ as $T \to \infty$. At small densities, entropic effects compete with the Coulombic repulsion and $h = \ell + a$; for high densities, the exclusion hole decreases but is again limited below and $h \to a$. Using this prescription for h, the Helmholtz free energy can be obtained by Debye-charging the system:

$$\frac{\beta f_{\mathrm{DHHC}}}{n_{\mathrm{B}}} = \frac{(\kappa a)^2}{4} - \int_1^\omega \mathrm{d}\bar\omega\left\{\frac{\bar\omega^2}{2(\bar\omega^3 - 1)}\Omega(\bar\omega)^{2/3} + \frac{\bar\omega^3}{(1 + \Omega(\bar\omega)^{1/3})(\bar\omega^2 + \bar\omega + 1)}\right\} \tag{12}$$

with the abbreviation

$$\Omega(\bar\omega) = (\bar\omega - 1)^3 + \frac{(\kappa a)^3}{3\ell\kappa}(\bar\omega^3 - 1) \tag{13}$$

and where ω is the same as in eq. (3). The integral can be solved numerically for given values of ℓ_{B}, v and a. Since f_{DHHC} is a convex function of density (see also fig. 1), it can be used within local density approximation as the correlation correction f_{corr} to the PB free energy functional from eq. (6). A low density expansion of the DHHC and the DHH functional coincides with an exact expansion of the hard core OCP [18] up to order $\rho^{3/2}$. The next term of order ρ^2 differs, since *e.g.* the second virial coefficient of hard spheres is not fully accounted for in the DHHC approach. If one wishes, this effect can easily be included along the lines of ref. [19]. The markedly different high density asymptotic of the DHHC correction compared to the DHH theory might seem worrying at first sight. One should, however, keep in mind that a Debye-Hückel approach always provides a low density theory, whose high density limit is not reliable. All we need is that the asymptotics should not cause the LDA to fail.

As an example, we apply the correlation correction f_{DHHC} to the theoretical description of screening of a charged rod, which is a simple model of biologically relevant stiff polyelectrolytes like DNA, actin filaments or microtubules. Much of the thermodynamic behavior of these
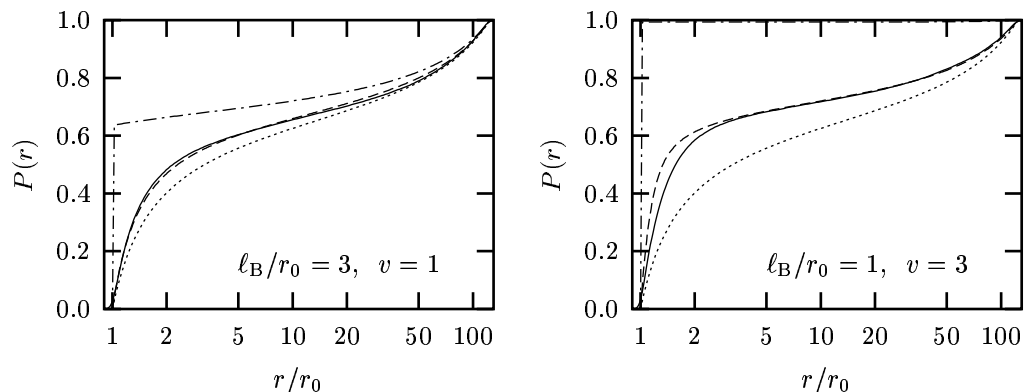
Fig. 2. – Counterion distribution function $P(r)$ from eq. (14) for two cylindrical cell models with $R/a = 123.8$, $\lambda = 0.959\,q/a$ and the values for Bjerrum length and valence as indicated in the plots. The solid line is the result of an MD simulation [21] while the dotted line is the prediction from PB theory. The increased counterion condensation visible in the simulation is accurately captured by the extended PB theory (dashed line) using the DHHC correction from eq. (12). An approach using the DHH correction from eq (4) (dash-dotted line) evidently fails to correctly describe the ion distribution.

molecules is determined by the distribution of the counterions around the polyion. As a model system we take a rod of diameter a and line charge density $\lambda = 0.959\,q/a$ embedded in a cell of outer radius $R = 123.8\,a$. The counterions also have a diameter a, giving them a distance of closest approach to the rod of a. Complementary values $\ell_{\mathrm{B}}/a = 3$, $v = 1$ and $\ell_{\mathrm{B}}/a = 1$, $v = 3$ have been investigated, which on the plain PB level give the same charge distribution and, in particular, a fraction of (Manning-)condensed counterions of roughly 65% [20, 21]. This system is thus strongly charged and one expects ionic correlations to become relevant. Indeed, a comparison between the distributions obtained by simulation [21] and the ones from PB theory shows that the mean-field approach fails in the limit of high ionic strength. In reality the ions do not just interact with the average electrostatic field but if an ion is present in a position r, it tends to push away other ions from that point. This effect becomes important at high densities, low temperatures and for multivalent ions.

In the following we will be interested in the fraction of ions within a distance r from the rod axis

$$P(r) = \frac{1}{\lambda} \int_a^r \mathrm{d}\bar{r}\; 2\pi\bar{r}\, vq\, n(\bar{r}). \tag{14}$$

Figure 2 shows the PB prediction for this observable, the results from a computer simulation [21] of the same system and the prediction of the f_{DHHC}-corrected free energy functional from eq. (6). The radius of the cavity excluding the background charge has been identified with the distance of closest approach between two ions. The equilibrium ion distribution minimizing such a functional is most easily found using a Monte-Carlo solver [22].

It can be seen that the simulated distribution functions lie above the PB prediction, indicating an increased condensation. Moreover, this effect is more pronounced for the trivalent system. In both cases the increase is reproduced by the f_{DHHC}-corrected functional from eq. (6). While in the case $\ell_{\mathrm{B}}/a = 3$, $v = 1$ the theoretical prediction practically overlaps the simulation, it somewhat overestimates correlations in the complementary case $\ell_{\mathrm{B}}/a = 1$, $v = 3$. Still, the general fact that deviations from PB theory are stronger for the multivalent system

is accurately accounted for. For comparison, fig. 2 also shows the ion distributions which would have been predicted by using the DHH correction instead. The strong deviation from the correct result is evident. Particularly for the trivalent case the collapse of the screening atmosphere onto the macroion can clearly be seen.

In conclusion, we have argued that within a local density approximation the asymptotically concave OCP correlation correction fails due to the absence of a stabilizing homogeneous background. As an alternative to nonlocal weighted density theories we suggested a different solution to this instability problem by using a correlation correction which is convex in density. Starting from the DHH treatment of the OCP we derived such a term by incorporating a background-free region around the central ion which also acts as a lower bound to the artificial correlation hole. The local density functional theory derived from this assumption is able to correctly account for the correlations between small ions in the presence of a strongly charged macroion. This was demonstrated for the case of a stiff rodlike polyelectrolyte by comparing the integrated charge density to simulation results.

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REFERENCES

[1] GOUY G. L., *J. Phys.*, **9** (1910) 457. CHAPMAN D. L., *Phil. Mag.*, **25** (1913) 475. FUOSS R. M., KATCHALSKY A., and LIFSON S., *Proc. Natl. Acad. Sci. USA*, **37** (1951) 579. LE BRET M. and ZIMM B. H., *Biopolymers*, **23** (1984) 287.
[2] SALPETER E. E., *Ann. Phys.*, **5** (1958) 183
[3] ABE R., *Prog. Theory Phys.*, **22** (1959) 213
[4] BAUS M. and HANSEN J.-P., *Phys. Rep.*, **59** (1980) 1
[5] STEVENS M. J. and ROBBINS M. O., *Europhys. Lett.*, **12** (1990) 81.
[6] DIEHL A., BARBOSA M. C., TAMASHIRO M. N. and LEVIN Y., *Physica A*, **274** (1999) 433.
[7] ALEXANDER S., CHAIKIN P. M., GRANT P., MORALES G. J., PINCUS P. and HONE D., *J. Chem. Phys.*, **80** (1984) 5776.
[8] KREMER K., ROBBINS M. O. and GREST G. S., *Phys. Rev. Lett.*, **57** (1986) 2694.
[9] PENFOLD R., NORDHOLM S., JÖNSSON B. and WOODWARD C. E., *J. Chem. Phys.*, **92** (1990) 1915.
[10] GROOT R., *J. Chem. Phys.*, **95** (1990) 9191.
[11] LEVIN Y., BARBOSA M. C. and TAMASHIRO M. N., *Europhys. Lett.*, **41** (1998) 123; TAMASHIRO M. N., LEVIN Y. and BARBOSA M. C., *Physica A*, **258** (1998) 341.
[12] LIEB E. H. and NARNHOFER H., *J. Stat. Phys.*, **12** (1975) 291. Erratum: *J. Stat. Phys.*, **14** (1976) 465.
[13] DEBYE P. and HÜCKEL E., *Phys. Z.*, **24** 185; 305; McQUARRIE D. A., *Statistical Mechanics*, Harper-Collins, New York, 1976, chapter 15.
[14] NORDHOLM S., *Chem. Phys. Lett.*, **105** (1984) 302.
[15] PATRA C. N. and YETHIRAJ A., *J. Phys. Chem.*, **103** (1999) 6080.
[16] VIEILLEFOSSE P., *J. de Physique*, **42** (1981) 723.
[17] TAMASHIRO M. N., LEVIN Y. and BARBOSA M. C., *Physica A*, **268** (1999) 24.
[18] NETZ R. R. and ORLAND H., cond-mat/9902220.
[19] BORUKHOV I., ANDELMAN D. and ORLAND H., *Phys. Rev. Lett.*, **79** (1997) 435. LUE L., ZOELLER N. and BLANKSCHTEIN D., *Langmuir*, **15** (1999) 3726.
[20] MANNING G. S., *J. Chem. Phys.*, **51** (1969) 924; 934; 3249.
[21] DESERNO M., HOLM C. and MAY S., *Macromolecules*, **33** (2000) 199.
[22] DESERNO M., *Physica A*, **279** (2000) 405.