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Thermodynamics of a Set of Closed Curved Surfaces and Noether's Theorem

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ABSTRACT

For a set of closed curved surfaces that resemble a Langmuir monolayer an energy is defined that depends only on the curvature of the surfaces interacting with the dimensions normal to the surfaces, that is, the thickness of these surfaces. The thickness, or depth, of the surfaces originates because of surface-particles with chains, that move freely on the inside of the surfaces at a certain depth. This is a purely geometrical description that does not depend on the introduction of ad hoc constants like the elastic constant. With a statistical mechanical model the equations of state are calculated for a gas of non-connected sphere-like surfaces in a volume. There are two states of which the lower temperature state is depending mostly on the interaction energy and surface properties, and the higher temperature state is depending mostly on sphere kinetic and volume properties. This results in aggregation of the sphere-like surfaces from many small ones to few large ones when lowering temperature and vice versa. The model allows for the calculation of the partition function and, when the emergence of the curvature - depth interaction is described as a phase-transformation, for the application of Noether's theorem. Because of these properties the model is interesting in its own right apart from being an addition to existing elastic descriptions of surfaces.

Keywords: thermodynamics; surfaces; curvature

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1. INTRODUCTION

Collections of random curved surfaces have applications in field theory [ref.1-3] and for biological membranes and micro-emulsions [ref.4-7]. Curved biological membranes are described with elastic curvature surface-energy. Changes of shape, thermal fluctuations, influence properties like the rigidity of membrane surfaces [ref.8]. The wavelength of the fluctuations relative to the characteristic sizes of the surface, that is the total size and the size of the component parts, is decisive for these systems. Spherical membranes, vesicles, can be regarded as an ideal gas with a fixed vesicle number. In this way one has described sets of spherical membrane surfaces, starting from elastic curvature, with as result size distributions [ref.6]. Another concept is higher-order, i.e. non-Hookean, bending elasticity.

In this article a set of spherical Langmuir monolayer surfaces is described starting from the size properties of a number of asymmetric surfactants on one side of the, closed, surfaces, without referring to *a priori* knowledge of curvature surface energies. This is a purely geometrical description that uses only physical measures of the sizes of the spheres and surfactants, in contrast to existing [ref.4-7] theories. The description includes a statistical mechanical model of a gas composed of a variable number of non-connected individually varying sphere-like surface parts of constant total surface area in a volume. Instead of superimposing elastic curvature for the surface parts now introduced are surfactants that are treated as a gas of surface particles, with chains that stick out on the inside of the spheres thus giving the surface thickness. The free area for the surfactants is taken to be lying in a plane at a certain constant depth (d) beneath the sphere surface and thus to be smaller than the sphere surface area itself, and dependent on individual curvature radius (R_i). From this dependence originates the interaction between curvature and depth. In fact the free area is proportional to $(1 - d/R_i)^2 \propto \exp(-2d/R_i)$ for d small compared to R_i. For the whole sphere-like surface part there are a number of ($\propto R_i^2$) surfactants on it, thus giving an interaction factor proportional to $\exp(-2dR_i)$.

Thus because of only entropy considerations the asymmetric surfactants cause an interaction energy for the curved surface parts that is different from usual elastic curvature. In fact the interaction energy turns out to be formally equivalent to the energy of spontaneous curvature, proportional locally to the curvature tensor instead of the square of the curvature tensor, but then without the main elastic curvature term along with it and without an ad hoc elastic curvature constant.

Another difference with existing descriptions is that the sphere-like surface parts are treated as a collective in a volume with a constant total surface area and a variable number of surface parts. The spheres themselves are treated as an excluded volume gas and this results in extra free energy factors. The volume in which the sphere surfaces are situated returns as a parameter in the equations for the partition function and the equations of state. Instead of the wavelengths of shape fluctuations now the variables are the variable sizes, radii (R_i), of the individual sphere-like surface parts, and the variable number of sphere-like surface parts (q).

Not included in the description are interface interactions, like for instance electrostatic interactions, that are, in most descriptions, used to explain the existence of interface layers. This model restricts itself to geometrical interactions in order to concentrate on their effect on aggregation of surface parts.

This model, with a geometrical surface energy, allows for the calculation of the partition function and, as a main result, the equations of state for a set of sphere-like surface parts for a low and a high temperature state. There are found to be two asymptotic states relative to a critical temperature (paragraph 3.1). In state I, for high temperature, there are many small spheres and thus the surface is relatively curved and in state II, for low temperature, there are relatively few large spheres and the surface is more flat. The limit totally flat is not reached because even for low numbers the spheres remain closed. In state I the emphasis is on the gas of spheres in the volume with individual radii and in state II on the surface with the surfactants. Only in state II the effect of the depth of the surface is noticeable in the equation of state and in the average energy per sphere, with the interaction energy as described above (paragraph 3.2). Also derived is an approximation for the size distributions of the radii for the individual spheres in both states (paragraph 3.3).

As a final result a description of the emergence of the interaction of surface depth with curvature in terms of a phase-transformation is given, and Noether's theorem is applied to discuss time-

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dependence (paragraph 4). In this case, quantisation seems justified, because the surfactants are not further specified and the sphere-surfaces are treated as a collective.

The discussion section (paragraph 5) contains the following subjects. Firstly the description is generalised to other dimensions than two surface dimensions. It is shown how this model can be a useful intermediary between higher dimensional spaces of different dimension. Besides this the derived size-distributions are compared with the ones found in [ref.6] where elastic curvature is used. Also packing considerations and a critical parameter are discussed.

2. DEFINITIONS

2. 1. SURFACE PROPERTIES AND THE PARTITION FUNCTION

The surface is a simple form of a Langmuir monolayer [ref.9] of constant total area. Surfactants move freely on a surface part, a sphere, with chains that stick out on the inside of the surface at a certain depth d. Inside and outside the sphere-like parts there is a gas with a density that is constant everywhere. The mass and surface density, and thus the total number, of the surfactants remains constant.

Curvature influences the free area of the surfactants, measured at the depth d away from the sphere surface, and causes a curvature originating free energy. Chosen is for chains that stick out on the inside to achieve a balance between interaction- and kinetic- depending entropy for the spheres. As a result the free area is smaller by a factor $(1 - d/R_i)^2 \sim \exp(-2d/R_i)$, where R_i is the variable individual sphere radius. This factor, for all surfactants on all spheres, is included in the configuration integral.

For each sphere-like surface part the interaction energy can be predicted to be proportional to $d\,R_i/a$, with (a) the average surface area per surfactant, by multiplying the factor $-2d/R_i$ by the number of surfactants on the sphere R_i^2/a. One notices that this interaction factor is large for large sphere-like surfaces and small for small sphere-like surfaces. This will also be derived directly from the partition function, later in the text, in paragraph 3.2 in equations (5, 6).

The partition function for the system is calculated with the spheres treated as an excluded volume gas for the collective movement of their surfactants, and the surfactants as free particles on a sphere as described above. The in-between gas can permeate through the surface and does not add anything new to the results and is left out in the following. To keep the total surface area constant it is necessary that the total number of spheres and the average (not the individual) sphere-surface radius depend on each other.

The spheres are perfectly round. It is possible to describe shape fluctuations, deviations from this perfect form, with spherical harmonics. These cause an extra energy, that however totally depends on the number of degrees of freedom for the deviations that is supposed to be equal to the total number of surfactants which remains constant.

Applied is the thermodynamical limit where the system and in proportion with it the volume and the total number of surfactants, and in this way the total surface area, are being greatly enlarged.

To derive the partition function first the configuration integral Q, that contains all integration with constant q, the number of sphere-like surface parts, is calculated. Then all the factors depending on q that are not included yet in Q are added to give the partition function Z(q) for constant number of spheres. Finally there follows summation over q ranging from 1 to N, N the total number of surfactants, to derive the partition function Z from Z(q). From the definitions of the model it follows that there is:

1 $$Q = 1/2\pi \int d\gamma \int \prod_i d\check{R}_i \exp(\, i\gamma(\check{R}_i^2 - 1)\,)\ (\, \check{R}_i^3\,)\ \exp(\, - 8a^3/w \sum \check{R}_i^3 - 8\pi\, ad\, /a\ \sum \check{R}_i\,)$$

Here used are the abbreviations average radius a with $a^2 = 1/q \sum_i R_i^2$ with R_i the individual sphere radius for sphere i with i = 1 … q, q the number of spheres, $R_i = a\, \check{R}_i$ and the average volume per sphere $w = 3V/4\pi q$ with V the overall volume. The upper limit of the second integral depends on the volume V and does not return in the final result. The abbreviations are introduced to facilitate notation when actually calculating Q.

The integral representation of the deltafunction $\delta\, (\sum_i \check{R}_i^2 - q)$ is included for constant total surface area. The factor $\prod_i \check{R}_i^3$ is included in Q for the momentum integral for each sphere. A factor a^{3q} among other terms will be included later in Z(q). The excluded volume interaction between the spheres in the volume V contains a factor $8 = 2^3$ because the radii R_i of the spheres are doubled to $2R_i$ to approximate exclusion at the rim between two average spheres. The factor for the change of free surface area $-2\, d\, /R_i$ for one surfactant because of curvature, as it was indicated above, is included in the exponent at the end, now for all the ($\propto R_i^2/a$) surfactants together on one sphere (the surfactant density $\propto 1/a$ where (a) is the average area for each surfactant on the surface) [note1]. All these factors are purely geometrical in origin following the specifics of the model.

2. 2. CALCULATION OF THE PARTITION FUNCTION AND THE ORIGIN OF THE TWO STATES

To derive the partition function first the configuration integral Q is calculated. This, in a natural way, leads to the definition of the two states the system can be in.

First one rewrites Q in the form $Q = 1/2\pi \int d\gamma\, (\, \int dR \exp(\, i\gamma\, R^2 + F(R)\,)\ )^q$ leaving out the accent on R. There is $F(R) = 3\log R - 8a^3/w\, R^3 - 8\pi\, ad\, /a\ R$ summarising all factors dependent of R. F(R) can be approximated with $F(R) = F(R_0) - g(R - R_0)^2$. This leads to a third order equation for R_0 because of $\partial_R F(R) = 0$ for the maximum of the integrand at $R = R_0$. The second order derivative of F(R) at R_0 is negative and equal to $-2g$. The third order equation is $R_0^3 + \pi\, wd\, /3aa^2\ R_0 - w\, /8a^3 = 0$.

When calculating Q one uses the solutions R_0 of this equation for which one has to approximate a term $(1+q_c/q)^{1/2}$. The system is defined to be in state I for lowest order in q_c/q and in state II for lowest order in q/q_c where there is $q_c \equiv 3\, V\, d^3 / a^3$, the transition number. This is the origin of the two states I and II. The term q_c/q is the result of balancing the two factors in F(R) for the interaction entropy effect and for the momentum of the spheres. When the chains of the surfactants are taken to stick out on the outside instead of on the inside of the sphere surfaces, this leads to a positive sign for the change of the free surface area factor in both equation (1) and F(R). This situation is discussed in [note2].

The further calculation of Q is as follows. By applying a contour transformation for the integral over R in Q one achieves:

$Q = 1/2\pi \exp\, (q\, F(R_0)) \int d\gamma \exp(\, -iq\, \gamma\,)\, X^q$

where there is now $X = 1/gR_0 \exp(-gR_0^2) \times \exp(x^2)\,(1/2\pi^{1/2} + \int dt \exp(-t^2))$ with $x = g R_0 /(g - i\gamma)^{1/2}$ and the integral over t in X is from zero to x. Then one writes $\exp(-iq\,\gamma)$ and $x^q \exp(qx^2)$ in Q both as power series in $(g - i\gamma)$ while the integral over t is approximated with its lowest term. Due to the residue theorem, the integral in Q, when taken over $(g - i\gamma)$ instead of γ and reduced to a closed one, equals zero for all powers in $(g - i\gamma)$ except one. Thus the two power series combine with the integral in Q to one power series that is recognised as a Bessel function expansion. The result is

$Q = (\pi/4)^{q/2} \exp(q\,(F(R_0) - g - g R_0^2))\,(g R_0)^{1-q/2}\, I_{q/2-1}(2qg R_0)$

with $I_{q/2-1}$ a Bessel function, for even number q and a similar expression for odd number q, taking only factors of order (e^q) since q, the number of spheres, is expected to be large.

The Bessel function can be approximated for large q as

$I_{q/2-1}(2qg R_0) = I_{q/2-1}((q/2-1)\,2gR_0/(1/2-1/q)) = (2gR_0/(1/2-1/q))^{q/2-1} \exp((q/2-1)(z - \log(1+z)))$

with $z = (1+ (4g R_0)^2)^{1/2}$.

These approximations result in the following expressions for $Q_{I/II}$ in the two states I and II:

$Q_I = (\pi e/2)^{q/2} \exp(q\,(F(R_0) - g - gR_0^2))$

$Q_{II} = (\pi)^{q/2} \exp(q\,(F(R_0) - g - gR_0^2 + 2gR_0))$.

where there is used that $z \approx 1$ for state I and $z - \log(1+z) \approx z \approx 4g R_0$ for state II.

The final derivation of $Q_{I/II}$ is done by insertion of $F(R_0)$, g and R_0 and then the calculation of the partition functions $Z_{I/II}(q)$ and $Z_{I/II} = \sum_q Z_{I/II}(q)$ is straightforward. In paragraph 3.1 the equations of state (equations 3, 4) are given as the main result of this paper. Below are given the expressions for Z_I and Z_{II} where the $c_{I/II}$ are unspecified dimensionless constants that re-occur in equation (4) and $K = (MkT/h^2)^{3/2}$ with M the mass of the surfactants, T the temperature, k is the constant of Boltzmann and h the constant of Planck [note3]:

2 $\quad Z_I = \exp(2c_I\,(V^2 K / a^{3/2})^{1/2})$

$\quad Z_{II} = \exp(c_{II} V a^{3/2} K / d^3 + 4\pi d^2 N / a + (16\pi c_{II} V N a^{1/2} K / d)^{1/2})$

3. RESULTS

3. 1. THE EQUATIONS OF STATE

The average number of spheres $< q >$ and pressure P are calculated for the states I and II using $< q > = (1 / Z) \sum_q q\, Z(q)$ and $P = kT\, \partial_V \ln Z$. This gives as result the equations of state:

3 $\quad P_I V = 2\, kT < q_I >$

$\quad P_{II} V = kT\,(< q_{II} > + q_0)$

4 $\quad < q_I > = c_I\, V K^{1/2} / a^{3/4}$

$\quad < q_{II} > = c_{II}\, V K a^{3/2} / d^3$

$q_0 = (4\pi N d^2 / a < q_{II} >)^{1/2}$, c_I and c_{II} are the numerical constants and $K = (MkT/h^2)^{3/2}$ as above.

Equations (3) and (4) can be discussed in the following way.

The transition number $q_c = 3\,V\,d^3 / a^3$ corresponds with a temperature T_c such that for $T > T_c$ the system is in state I and for $T < T_c$ in state II. T_c is defined by $< q_I (T_c) > = q_c = < q_{II} (T_c) >$.
For q near q_c the approximations for Z and thus for equations (3) en (4) are not very precise. Using anyhow $< q (T_c) > \cong q_c$ it then follows that $kT_c = \text{constant}\ d^4 h^2 / Ma^3$. It is clear from equation (4) that not simply the limit $d \to 0$ can be taken, and this agrees with the condition for which state II exists, that is $q < q_c \propto d^3$. From equation (3) and (4) it follows that at every temperature T there is an average surfactant surface area $a = a_c$, that marks the transition from state I to state II such that $T_c(a_c) = T$, for which the volume pressure for the spheres has a maximum.
At first instance the interaction dependent part q_0, caused by the depth of the surface, is expected to occur for both states and for state I (small spheres) even more than for state II (large spheres). However, for state I , $q > q_c$ and the average radius $< R_I^2 > = Na/< q_I >$ corresponding to q is relatively small so the number of surfactants per sphere is low and $q_0 = < R_I^2 >^{1/2} d / a << 1$ and this agrees with equation (3) [note4] where q_0 does not appear for state I.
Equation (3) suggests that the number of degrees of freedom for state I and II differ by a factor two. Indeed state I has three directions of movement for each sphere in the volume plus one for the sphere radius, while state II has only two directions of movement, for the surfactants on the sphere surface. Further in state II it is as if there is an extra number of spheres, q_0. However, notice that $q_0 (T_c) = (4/3\pi\ Na^2 / V\,d)^{1/2} << 1$ at the transition from II to I so there is no discontinuity from state II to state I because of q_0.
Both $< q_I >$ and $< q_{II} >$ are $\propto V$ and thus, when the volume V is made larger, the number of spheres becomes larger too and the average radius of the spheres decreases. This is not at all a trivial result since the number of surfactants N and the total surface area are kept constant and one would expect that with an increase of V the gas of spheres just would become more dilute while keeping the average sphere radius constant. Instead of this now together with a constant surface density for the surfactants there is also maintained a constant volume density for the spheres.

3. 2. THE CURVATURE - DEPTH INTERACTION ENERGY

The average energy for an average sphere is calculated with $U / < q > = (1/< q >)\, T^2\, \partial_T\, k \ln Z$.

5
$$U_I / < q_I > = 3/2\, kT\, (1 + < N_I >)$$
$$U_{II} / < q_{II} > = 3/2\, kT\, (1 + < N_{II} > + q_0)$$

$q_0 = (4\pi < N_{II} > d^2 / a)^{1/2} = 4\pi < R_{II}^2 >^{1/2} d / a$ with $< R_{II}^2 >^{1/2}$ the radius of a sphere with $< N_{II} >$ surfactants, and $< N_{I/II} > = N / < q_{I/II} >$.
Equation (5) is interpreted for the factor 3/2kT times 1 because of the movement of the centre of a sphere and a factor $kT< N_{I/II} >$ because of the movement of the surfactants on a sphere surface. For shape fluctuations, when the surface can change locally along the normal, the number of degrees of freedom is N_i for a sphere i, with the corresponding average extra energy $1/2kT< N_{I/II} >$ also as expected present in (5). The $3/2kTq_0$ part is the average interaction energy due to the depth d and the curvature of the surface. Just like before, with the equations of state, by considering that for state I

there is $q > q_c$ and $q_0 = < R_I^2 >^{1/2} d / a << 1$, one notices that there is no discontinuity from state II to state I caused by q_0.

Generalising from equation (5) for state II and using the expression for q_0 above, defined now in equation (6):

6 $\alpha(R_i) = 6\pi\, kT\, R_i\, d / a$

is $\alpha(R_i)$ as an approximation for the individual interaction energy for a sphere i with radius R_i where i = 1,…, $< q_{I/II} >$. There is assumed $< R_i > = < R_i^2 >^{1/2}$ together with $< \alpha(R_i) > = 3/2kTq_0$, so the average individual interaction energy is the same as the average interaction energy.

3. 3. DISTRIBUTION OF SPHERE RADII

For both states I en II, $e_i = 3/2\ kT\ (\ 1\ +\ N_i\ ) + \alpha_{I/II}$ with $\alpha_I = 0$ and $\alpha_{II} = \alpha(N_i)$ is an approximation for the total energy for a sphere i with a number N_i of surfactants or radius R_i where i = 1,…, $< q_{I/II} >$. Assuming Bose statistics, that is the number of spheres with the same number of surfactants N_i is not limited, then it follows that the distribution is

$P(N_i) = (1/ < q_{I/II} >)\ 1/ (\exp\ (e_i - \mu)/kT\ - 1)$ so that for the corresponding radius R_i with

$P(R_i) \propto P(N_i)dN_i/dR_i$ there is:

7 $P(R_i) \propto\ (R_i /a) \exp -6\pi/a\ (\ R_i^2 - R_{min}^2\ )$

$P'(R_i) \propto\ \exp -(\ R_i /< R_{I/II}^2 >^{1/2} - 3/4\ )^2$

A chemical potential μ is added that is defined with the restriction $\sum_i P\,(N_i) = 1$ where there is summed over $N_i = N_{min} \ldots N$. The dependence of $P(R_i)$ on T is completely included in R_{min}, corresponding to N_{min}, that may be estimated with an assumption like $R_{min} = < R_{I/II}^2 >^{1/2}$ /constant. Always few large spheres with $R \geq < R_{I/II}^2 >^{1/2}$ are accompanied by many small spheres with $R \sim R_{min}$. The alternative $P'(R_i)$ is the Gauss distribution that follows from the assumptions of [note5] for the variance of R. For this alternative distribution, in state I for small spheres the deviation is much smaller than in state II for large spheres.

4. PHASE-TRANSFORMATION AND NOETHER'S THEOREM

When quantising in a naïve way, the de Broglie wavelengths for the individual sphere i and the surface particles on it and their momenta hk_i and hk can be introduced, while the individual mass $M_i = N_i M$, and thus also the related surface radius R_i and number N_i of surfactants, of the sphere is the quantity to be determined. It follows that for the sphere i there is the equation $d\omega_i/dk_i = hk_i/M_i$, with

$M_i = h^2k_i^2 / kT$, and this, for three directions together, gives for the energy the result

$h\omega_i = 3/2kT\ (1+ \ln N_i/< N_i >) \approx 3/2\ kT\ N_i/< N_i >$.

For each of the N_i surfactants on sphere i one has $dv/dk = hk/M$, and this gives, for the two directions along the sphere surface and one direction perpendicular to it, for the N_i surfactants together

$3N_i h\nu = 3/2\ kT N_i$. Assumed now is, in agreement with paragraph 3.2, an extra interaction surface energy $A = 3/2\ kT N_i\, d / R_i$. This energy is equal to $A = (\pi\ d^2 / a)^{1/2} h^2\, \mathbf{k}\mathbf{k}_i / M$ where now $\mathbf{k}_i$ and $\mathbf{k}$ are isotropic 3-dim. vectors. In this way A can be included in the total energy
$h\omega_i = 3/2\ kT (N_i/< N_i > + N_i) + A = (1/B)\, h^2\, \mathbf{k}_i^2 / 2M + A$ for sphere i like a vector potential (with
$B = < N_i >/ 1+< N_i >$):

$$8 \qquad h\omega_i = (1/B) (h\, \mathbf{k}_i + B (\pi\, d^2 / a)^{1/2} h\, \mathbf{k})^2 / 2M - B (\pi\, d^2 / a)\, h^2\, \mathbf{k}^2 / 2M$$

The result of introducing the interaction of the depth with the curvature of the surface can thus be described with a phase-transformation for the wave-function of the sphere.
With proper boundary conditions, conservation of the energy when applying the phase-transformation in state I where the interaction energy is negligible, means according to Noethers theorem that the Noether charge ($\propto < 1/R_i > = < \mathrm{Tr}\ h >$ = average curvature) is a constant in time. The Noether charge is derived by assuming that the Lagrangian depends on the first derivatives of the phase-transformation only and that the Noether current is linear in k_i only.
In state II the total energy $h\omega_i$ does depend on d and the interaction energy significantly, and the Noether charge can change in time. In this way the time dependence makes it possible to differentiate between state I and II. Equation (8) can be assumed to be a good approximation for both asymptotic states I and II, since the interaction energy in state II decreases when approaching state I. When one considers equation (8) to be describing the real physical situation in both states (and that the interaction energy in state I is only relatively small compared to state II) the time-dependence of the Noether charge in state I is expected to be only small relative to the time dependence in state II rather than it being strictly conserved.

5. DISCUSSION

It follows from the equations of state that both states I and II (equations 3, 4) have the property that the volume density of the spheres is independent of the volume itself. In fact the number of spheres q is proportional to the overall volume V when expanding according to the equations of state, in both states.
Thus the equations of state are partly equivalent to a new constraint for the surface, that is: the volume density for the sphere-like surface parts the total surface is composed of, in the overall volume, is constant whereas the number of sphere-like surface parts is not.
On the other hand the constraints for the total surface itself as a two-dimensional space for the surfactants can be summarised as: the surface density 1/a of the surfactants and the total number N of surfactants are both constant. Surprisingly, when the overall volume V changes while respecting these two surface constraints, according to the equations of state the total number of spheres changes accordingly and the volume density of the spheres remains constant.
This suggests the definition of a continuation of constraints when transferring two-dimensional surface properties to three-dimensional volume properties: The constraint for density is maintained while the constraint for number is not. For a surface with thickness and depth, continuation of constraints is the link towards a description with volume-like properties i.e. spheres in a volume. It is conjectured that

continuation of constraints can be generalised towards the transition between any kind of lower to higher dimensional spaces, when the lower dimensional space has some ‘depth’ property normal to it relating it to the higher dimensional space. It is characterised by the maintenance of density constraints while number constraints are lost.

For the thermodynamical limit (TL) there is the requirement that parts of the system that are apart far enough have no interaction [ref.10]. Here the range of the interaction is equal to the radius of the sphere surface (for an excluded volume system there is only interaction when spheres touch each other). From equation (4) it is noticed that the average area for a sphere is $Na / < q > \propto N/V$ and this is a constant in the TL. But this means that consequently for this kind of system the mentioned requirement is always fulfilled. This is due to the existence of q_c and the possibility of defining for this system a continuation of constraints as an alternative for the equations of state.

The results concerning size distributions, depending only on surface depth and density of the surfactants on the sphere-like surface parts, could be qualitatively descriptive for closed membranes. Helfrich [ref.6] describes distributions depending on elastic curvature and he expects combinations of few large spherical surfaces with many small ones, as is expected in this paper as well. However, his distributions, apart from having a different origin (elastic curvature instead of depth-curvature interaction), are also different because Helfrich’s description does not allow for the emergence of two states I and II. The emergence of the two states I and II with a critical temperature T_c and transition number q_c as described in paragraph 3.1 is one main result of this paper.

Because the surfactants are treated as a gas and the spheres as a collective, the model deviates from the usual packing considerations as they are described in [ref.11]. The average surface area per surfactant is larger than it usually is. The usual packing parameter is proportional to $v_0 / a\, d_c$ where v_0 is the surfactant chain volume and d_c the maximal chain length. Instead now the critical parameter is $<q_{I/II}>/ q_c$ where $q_c = 3 V d^3 / a^3$ is the transition number. Notice that $<q_{I/II}>$ is proportional to V, equation (4), as well as q_c so $<q_{I/II}>/ q_c$ is independent of V. The critical parameter depends mainly on the depth d relative to a, and on temperature. It is typical for this geometrical model that the temperature enters the critical parameter. In the usual packing parameter, v_0 depends on the effective chain length (chain deformation) and surface curvature. Small spherical surfaces have high curvature and the packing parameter will be low whereas larger surfaces have a relatively high packing parameter until the critical value 1/3 is reached when spherical surfaces change to another shape (cylindrical surfaces). For the critical parameter described in this article the situation is different. Sphere-surfaces with a depth d large relative to a, will have a relatively high q_c and thus will be mainly in state II where the emphasis is on surface properties like the interaction energy. This corresponds to a state with mainly large spheres until by decreasing depth d or increasing temperature, $<q_{II}>/ q_c$ approaches the value = 1 and state I is reached. Note however that when crossing the transition value = 1 the shape of the surfaces remains spherical, it is the equation of state that changes.
Starting from state II and lowering surface pressure in such a way that a and <q> both increase following equation (4), one approaches state I but never reaches it since in state I, <q> again

decreases with increasing a. A change of surface pressure never can lead to a change of state (from I to II or vice versa) whereas a change of volume pressure can lead to such a change, volume pressure being always proportional to <q>, in both states. This kind of pressure behaviour, when studying aggregates of surfaces with surfactants that behave like a gas, is predicted by this theory.

NOTES

[1] Because of the curvature of the sphere surface, for a sphere with radius R, the free area for the surfactants changes with a factor $(1-d/R)^2 \sim (1-2d/R) \sim \exp(-2d/R)$. This applies for all $4\pi R^2/a$ particles on the sphere so eventually a factor $\exp(-8\pi R\, d/a)$ in Q results. Generally for just one irregularly shaped sphere with surface area $4\pi R^2$ in the same way a free energy factor $\exp(-d/a \int (g)^{1/2} \,\mathrm{Tr}\, h)$ results, with g the metric and Tr h the trace of the curvature tensor (indices left out). The expression in the exponent is, now without a factor kT, known as a symmetry breaking term for elastic curvature. One higher order in d/R gives for a surface the Euler constant that depends on its topological shape.

The elastic curvature energy is proportional to $(\mathrm{Tr}\, h)^2$ and generalisation to other dimensions than 1 or 2 is solved by arguing that $(\mathrm{Tr}\, h)^2 = (\nabla^2 X^2)^2$ (X surface-co-ordinate). For the curvature energy proportional to $(\mathrm{Tr}\, h = n \cdot \nabla^2 X^2)$ generalised from the above factor this is not possible and the normal vector n to the surface has to be derived using in d dimensions d linear equations and normalisation.

[2] When the chains stick out on the outside of the sphere surfaces the factor $a/d_a R$ is positive in equation (1) and F(R). Then the term q_c/q still occurs with the same q_c as before. State I and II are defined in the same way and for state I the calculation remains the same. However for state II with $q_c/q > 1$ the solution of the third order equation has to be derived now balancing the interaction entropy factor and the excluded volume factor. This leads to a slightly different partition function, equation (2), and different average number of spheres $< q_{II} >$, equation (4), for state II.

[3] A typical summation is $Z_I = \sum_q Z_I(q)$. The derivation of Z_I shows the origin of the factor 2 in equation (2) for the partition function for state I that re-occurs in equation (3) for the equation of state in state I. $Z_I(q)$ can be written as $Z_I(q) = q^{-2q} \exp(q\, \varepsilon_I)$ with ε_I = constant + $\ln(V^2/a^{3/2} K)$.

One has $Z_I = \sum_q q^{-2q} \exp(q\, \varepsilon_I) = \pi^{1/2} \sum_q 1/q!\, \exp(q(\varepsilon_I - 2)) / \Gamma(q+1/2)$. Now by considering that the value of q, the number of spheres, for which $Z_I(q)$ is maximal is very large in state I but not as large as the total number of surfactants N, it follows that the summation $\sum_q$ can approximately be taken from zero to ∞ instead of from q_c to N. With help of the expansion definition of the Bessel function $I_{-1/2}(z) = \sum_q 1/q!\, (z/2)^{2q-1/2} / \Gamma(q+1/2)$ one derives that $Z_I = \pi^{1/2} \exp(1/4(\varepsilon_I - 2))\, I_{-1/2}(2\exp(1/2(\varepsilon_I - 2)))$. One now assumes that $\exp(\varepsilon_I)$ is large because it contains the volume V and the gas of spheres is taken to be dilute. Inserted is the approximation for the Bessel function for large values $I_{-1/2}(z) \approx (2\pi z)^{-1/2} \exp(z)$ and the final result is $Z_I = 1/2 \exp(2\exp(1/2(\varepsilon_I - 2)))$. One notices the factor 2 before the second exponent due to the expansion definition of the Bessel function. In the case of Z_{II} the intermediate step using the Bessel function does not occur and a similar factor is absent.

[4] $<R_q^2>^{1/2} d/a$ can be estimated considering that $q_c / q < 1$ for state I and $<R_q^2>^{3/2} q << V$ and $1/q << 1$. It then follows from $q_c = 3 V d^3 / a^3$ that $<R_q^2>^{1/2} d/a << 1$ for this state. The assumption $<R_q^2>^{3/2} q << V$ only means that the volume density of the spheres is very low, a requirement for treating the spheres as an excluded volume system when calculating the partition function.

[5] For the definition of α it is assumed that $< R >^2 = < R^2 >$. However, generally $< R >^2 = < R^2 > - < \Delta R >^2$, ($< \Delta R >^2$ variance of R). When equating the average interaction energy $\alpha = 6\pi kT < R^2 >^{1/2} d/a$ to the average free energy for one sphere and letting it resemble the factor in the exponent $8\pi kT < R > d/a$ in [note1] it follows that $< \Delta R >^2 = 1/2 < R^2 >$. This value for the variance of R is used to derive the alternative distribution for R. This is only likely to be an acceptable approximation for low temperature, thus only for state II, but nevertheless assumed to be true for both states.

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