Physics of isodesmic chemical equilibria in solution

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Exactly solvable one-dimensional lattice-gas model mixtures are used to develop a physics of isodesmic chemical equilibria. Potential distribution theory is used to solve directly for the equation of state and to obtain the cluster statistics needed to discuss self-assembly. A mapping of three-dimensional amphiphilic discotic solutions onto one-dimensional models is proposed and is found to explain the remarkable nature of previous computer simulation data. Here, at fixed pressure, the low concentration regime involves an extreme concentration dependence to solute aggregation, associated with a maximum in the equilibrium constant. This behavior is a class of colloidal phenomena, driven by solvent-solvent attractive interactions. In addition, the exact physics of isodesmic chemical equilibria is used to investigate a variety of conceptual issues concerning the phenomenology of self-assembly. One finds that $\bar{\mu}_n = n\mu_A$ is an exact consequence of statistical mechanics and that it is even possible to give a precise meaning to the chemical potential of an aggregate, that, for example, defines what is meant physically by the identity $\bar{\mu}_1 = \mu_A$. The nonuniqueness of the choice of cluster definition is considered in the context of solvent-excluded clusters; an explicit example appropriate to amphiphilic systems. Finally, the mapping to three-dimensional discotic solutions is extended to inhomogeneous phenomena whereby the disks prefer to adsorb flat onto a surface. This mapping implies that the sticky solvent regime is associated with an overwhelming driving force for chains to attach by one end to a solutelike wall.
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I. INTRODUCTION

Complex fluids and, in particular, solutions containing amphiphiles, exhibit the phenomena of self-assembly, as defined by an equilibrated aggregate distribution resulting from the exchange of amphiphiles between an aggregate environment and being isolated within a solvent

$$[1]+[n-1] \rightleftharpoons [n], \tag{1}$$

where $[n]$ denotes the concentration of aggregates composed of precisely n amphiphiles. The phenomenology of chemical equilibria (see, for example, [1–3]), based on the law of mass action, generates a set of equilibrium constants,

$$K_n \equiv \frac{[n]}{[n-1][1]}, \tag{2}$$

which in turn define the configurational free energy change involved when an amphiphile joins an aggregate

$$-\ln K_n = \beta \bar{\mu}_n^0 - \beta \bar{\mu}_{n-1}^0 - \beta \bar{\mu}_1^0, \tag{3}$$

$$\beta \bar{\mu}_n = \beta \bar{\mu}_n^0 + \ln[n]. \tag{4}$$

Here, β denotes $1/k_B T$ (T is temperature and k_B Boltzmann's constant) and the notation $\bar{\mu}_n$ indicates the identification of a chemical potential for aggregates of size n. The above language hides a multitude of sins, including: (i) for a two-component system, fixing two thermodynamic fields such as T and p (pressure), still leaves one thermodynamic degree of freedom (i.e., when is the concentration dependence of an equilibrium "constant" significant?), (ii) the nonuniqueness of cluster definitions used to define an aggre-

gate (even liquid argon contains aggregates at any instant in time), (iii) the chemical meaning of an amphiphile (how wide can one vary intermolecular interactions and/or molecular geometry and still obtain specific aggregates), and (iv) what precise statistical mechanical meaning can be attached to $\bar{\mu}_n$ the so-called aggregate chemical potential [after all, the only true chemical potentials are those of the solute (μ_A) and solvent (μ_B) molecules, with $\bar{\mu}_n = n\mu_A$ since the chemical potential of a molecule cannot distinguish between a temporarily isolated or aggregated environment]? One aim of this paper is to tackle these and related issues exclusively within the context of statistical mechanics; in short, to develop a physics of self-assembly. In particular, I shall rely heavily on an exact representation of liquid state physics, known as potential distribution theory, whereby either in the canonical or grand canonical ensemble, the chemical potential of species A is given by the sum rule [4]

$$\rho_A(\mathbf{r}) e^{-\beta \mu_A + \beta v_A^{ext}(\mathbf{r})} = \langle e^{-\beta \psi_A(\mathbf{r})} \rangle \tag{5}$$

and, hereafter, densities (ρ) are made dimensionless by taking all lengths to be divided by a hard-core diameter (with de Broglie wavelengths set to unity). On the left side of Eq. (5) the quantity v^{ext} denotes any one-body or external field, while the right side is the average of a Boltzmann factor involving the energy of a test particle of species A placed at position $\mathbf{r}$, i.e., ψ is the hypothetical energy of interaction between the test particle and the system, with the latter not actually physically affected by the test (or ghost) particle.

The specific purpose of this work is to address the physics involved in modeling linear self-assembly by chain-forming discotic amphiphiles. One class of experimental system that has received much attention consists of solutions of disk-

shaped triphenylene based molecules dissolved in water. In particular, an NMR technique has been developed to measure the aggregation distribution [5] and simulation modeling undertaken [6]. The physics of these systems was first tackled by carrying out an extensive series of computer simulations of a generic simplified model of discotic solutions, both to confirm the presence of lyotropic nematic and columnar liquid crystal states at high concentration and, relevant to this paper, to measure the cluster statistics of isotropic solutions [7]. To simulate a cluster distribution requires that one achieve equilibrium of the set of chemical equilibria defined in Eq. (1), for all physically significant values of n. Clearly, the model needs to be highly simplified to achieve this goal, but this should not effect the underlying physics driving linear self-assembly. Note also, that the aggregate ends each consist of a single discotic molecule, so one does not anticipate the presence of a critical micelle concentration and Eq. (2) reduces to isodesmic chemical equilibria (after desmo, meaning bond)

$$K_n = K; \quad n = 2,3,\ldots. \tag{6}$$

In pure systems, the density dependence of an equilibrium constant can only arise from cluster-cluster interactions, which usually lead to a shift in K towards larger clusters. Thus, it was natural for the authors of Ref. [7] to anticipate that K would become independent of concentration at low concentration, where it would presumably be a minimum. However, the simulation study found precisely the opposite physics. Attard [8] was the first to suggest that a strong concentration dependence in the dilute limit of linear self-assembly could be understood by analogy with colloidal systems at fixed pressure (cf. clay swelling). Attard used an effective medium approximation to one-dimensional models to discuss, amongst a variety of issues, why at fixed pressure the isodesmic equilibrium constant should be at least a local maximum at zero concentration. The use of exactly solvable one-dimensional models to elucidate the physics of linear aggregation was pioneered for single component systems by Mitchell, Barnes, and Ninham [9]. In Secs. II and III below, I shall extend this approach to encompass a general two-component lattice-gas mixture [10]. Of course, such models can always be solved exactly, for example by transfer matrix methods [11], but for present purposes I shall develop a direct route to the equation of state and cluster statistics, using the absolute minimum of mathematical formalism. This, in turn, will enable me to extract a significant amount of exact physics, directly relevant to the physical chemistry of linear self-assembly in solution (Secs. IV–VIII). In particular, Sec. IV proposes a mapping of three-dimensional systems onto one-dimensional models, which is capable of a semiquantitative explanation of the simulation data of Ref. [7]. This success appears to be due to the fact that in a three-dimensional solution, a linear aggregate is sheathed by solvent and thus in the absence of aggregate-aggregate interactions is indeed a quasi one-dimensional object. When a chain is broken, solvent interposes between two solute disks, in a manner directly analogous to inserting a disk of solvent. For this mapping to hold, I require solute-solute, solvent-solvent, and solute-solvent interactions consistent with the exclusion of solvent molecules between aggregated solute in one direction alone (along the chain but not between chains). This, then, will be our working definition of a discotic amphiphile in the physical world.

II. TWO COMPONENT LATTICE-GAS EQUATION OF STATE

Consider a two-component lattice-gas (LG) mixture, with attractive well depths and their associated Boltzmann factors denoted

$$\epsilon_A \equiv \epsilon_{AA}; \quad \epsilon_B \equiv \epsilon_{BB}; \quad \epsilon_C \equiv \epsilon_{AB}; \tag{7}$$

$$1 + a_A \equiv e^{\beta \epsilon_A}; \quad 1 + a_B \equiv e^{\beta \epsilon_B}; \quad 1 + a_C \equiv e^{\beta \epsilon_C}. \tag{8}$$

The particular example considered in Ref. [10] is the special case $a_A = a_B \equiv a$ and $a_C = -1$, i.e., when the unlike interaction is purely repulsive and of range twice that of the solute-solute (AA) and solvent-solvent (BB) repulsion. For a standard LG mixture, all repulsive interactions act over a single lattice spacing (which hereafter is our unit of length) and then each a_i appearing in Eq. (8) is non-negative. In one dimension an exact solution of the general model can essentially be written down by inspection of the potential distribution theorem. To grasp how this arises, first note that the right side of Eq. (5) splits into two factors

$$P_c(\mathbf{r}) \langle e^{-\beta \psi_A(\mathbf{r})} \rangle_c, \tag{9}$$

where the first factor is the probability of inserting the hard core of a particle of type A into the fluid at position $\mathbf{r}$ and the Boltzmann factor average is now to be carried out in the presence of a hard core fixed at $\mathbf{r}$; hence, the subscript c, which for one-dimensional systems I shall write as w (for wall). Evaluating each of these factors separately, we have

$$P_c(\mathbf{r}) = 1 - \rho, \tag{10}$$

$$\langle e^{-\beta \psi_A(\mathbf{r})} \rangle_c = [1 + a_A x_w \rho_w + a_C (1 - x_w) \rho_w]^2, \tag{11}$$

where the squared form of the right side of Eq. (11) has arisen because the presence of a hard wall (i.e., a fixed cavity) splits a one-dimensional system into two independent ensembles (provided attractive interactions do not reach across the wall). Here, the total density of solute and solvent in the square adjacent to a hard wall is denoted ρ_w, with x_w and $1 - x_w$ the associated mole fractions of solute and solvent, respectively. The left side of the potential distribution theorem (5) is, in similar notation,

$$x \rho e^{-\beta \mu_A}. \tag{12}$$

To evaluate the wall quantities and, hence, solve the model exactly, all one needs to do is apply the potential distribution theorem once more, this time evaluating the chemical potential in a square adjacent to a hard wall (obviously it is the same chemical potential, since switching from an infinite to a semi-infinite system does not alter the chemical potentials)

$$x_w \rho_w e^{-\beta \mu_A} = (1 - \rho_w)[1 + a_A x_w \rho_w + a_C (1 - x_w) \rho_w]. \tag{13}$$

Note that this time there is no squared factor, since interactions do not reach across the boundary wall. Dividing Eq. (13) by the first result, Eqs. (12), (10), and (11), eliminates μ_A to give

$$x_w \rho_w (1-\rho)[1 + a_A x_w \rho_w + a_C (1-x_w) \rho_w] = x\rho(1-\rho_w).$$
(14)

Of course, the same analysis applies to measuring the solvent chemical potential; this just leads to Eq. (14), but with a_A replaced with a_B, and x and x_w replaced by $1-x$ and $1-x_w$, respectively. Adding this latter result to Eq. (14), eliminates x to give the key identity

$$\rho_w(1-\rho)\{1 + [a_A x_w^2 + a_B(1-x_w)^2 + 2a_C x_w(1-x_w)]\rho_w\}$$
$$= \rho(1-\rho_w).$$
(15)

At this point, we have achieved an efficient solution for the equation of state in either of the standard phase spaces (T,ρ,x) or (T,μ_B,x). For example, choosing T sets the values of a_A, a_B, and a_C, so that for a specified ρ one has $\rho_w(x_w)$ from Eq. (15), which when substituted into Eq. (14) gives $x(x_w)$ and hence, from say Eq. (13), $\mu_A(T,\rho,x)$ as desired. Clearly, all values of x are obtained by varying x_w between 0 and 1. At a set value of the solvent chemical potential, one can use the solvent analog of Eq. (13) to obtain $\rho_w(x_w)$ and then substitute into Eq. (15) to get $\rho(x_w)$ and thus $x(x_w)$ from Eq. (14). In both the above cases, one is only required to solve a quadratic, which in fact always possess a single physical root ($0 < \{\rho,\rho_w\} < 1$). This uniqueness of the solution space guarantees the complete absence of phase transitions, as one expects for all short-ranged one-dimensional models, no matter how amphiphilic. By far the simplest phase space to work in, however, is (T,p,x) as is invariably desired by physical chemists. This happy circumstance arises because one can prove the remarkable sum rule (see Appendix A)

$$\beta p = -\ln(1-\rho_w),$$
(16)

which is obviously the direct analog of the continuum statement $\beta p = \rho_w$, expressing mechanical equilibrium in a system bounded by a hard wall. Note that, as elsewhere, I have continued to suppress the unit of length, since it is just one lattice spacing. Due to sum rule (16), once T and p are specified, the concentration follows immediately from Eqs. (14) and (15); for all $0 < x_w < 1$. This procedure is just trivial algebra. For completeness, I derive a general expression for the total energy per particle in Appendix B; again, the natural phase space is $[T,p,x_w(x)]$. For all of the results above and below, taking the limit $x_w = x = 1$ reduces to the well-known exact solution of the one-dimensional Ising model [11], provided one translates between Ising and lattice-gas symmetry.

III. CLUSTER DISTRIBUTION AND THE CONCENTRATION DEPENDENCE OF ISODESMIC CHEMICAL EQUILIBRIA

Let us take (as the obvious choice) the definition of a cluster of class $[n]$, to be any continuous chain of n solute particles, whose two ends are separated by at least one lattice spacing from all other solute. The concentration (number

density) of isolated solute, members of cluster type [1], is therefore defined by the probability of finding a solute at a given lattice point ($x\rho$) and the probability of finding a second solute lying directly to (say) the right of the first (which I shall denote Y)

$$[1] = x\rho(1-Y)^2.$$
(17)

Again, the squared factor is exact because in one dimension a fixed particle splits the system into two independent ensembles. The concentration of clusters of size n is obtained by first asking for the probability of finding, say, the left end occupying a given lattice site ($x\rho$), followed by $n-1$ additional solute particles filling sites to the right (Y^{n-1}), plus a solute gap at either end $[(1-Y)^2]$

$$[n] = x\rho Y^{n-1}(1-Y)^2.$$
(18)

The LG system is, therefore, an exact representation of isodesmic chemical equilibria, at all concentrations (regardless of cluster-cluster interactions)

$$[n] = [1]Y^{n-1},$$
(19)

$$K = \frac{Y}{[1]} = \frac{Y}{x\rho(1-Y)^2}.$$
(20)

This is an exponential cluster distribution, defined by a single dimensionless quantity (Y); all the self-assembly properties, therefore, follow from calculating Y. For example, the distribution number average (or aggregation number) is

$$\bar{N} = (1-Y)^{-1}.$$
(21)

Since $Y < 1$, the numbers of large clusters are exponentially damped with respect to isolated solute, which is yet another demonstration of the fact that there can be no phase transition in a one-dimensional short-ranged model. To derive an explicit expression for Y, appropriate to any phase space invoked to express the equation of state (Sec. II), let us again make use of potential distribution theory, this time as a sum rule for the chemical potentials of solute and solvent lying adjacent to a fixed solute particle (or wall). Directly analogous to the derivation of Eq. (13), we can write by inspection,

$$Y e^{-\beta(\mu_A + \epsilon_A)} = (1-\rho_{wA})[1 + a_A x_w \rho_w + a_C(1-x_w)\rho_w],$$
(22)

$$(1-x_{wA})\rho_{wA} e^{-\beta(\mu_B + \epsilon_C)} = (1-\rho_{wA})[1 + a_B(1-x_w)\rho_w + a_C x_w \rho_w],$$
(23)

where the notation subscript wA denotes a property adjacent to a wall of solute. The only slight difference with the hard wall expressions, is that the left sides now contain external field contributions (ϵ_A or ϵ_C). By comparison with Eq. (13) and the corresponding expression for the solvent chemical potential, one immediately eliminates the chemical potentials from expressions (22) and (23) and can, thus, readily solve for ρ_{wA} and $Y \equiv x_{wA}\rho_{wA}$. The key result is that

$$Y = \frac{(1+a_A)x_w\rho_w}{[1+a_Ax_w\rho_w+a_C(1-x_w)\rho_w]} \qquad (24)$$

$$= e^{\beta(\mu_A+\epsilon_A-p)}, \qquad (25)$$

where the second form follows from substitution of Eq. (13) and sum rule (16).

We have therefore obtained an exact physics of isodesmic chemical equilibria and can, thus, directly test the conceptual integrity of the phenomenological approach pioneered by physical chemists [1–3]. For example, combining the results (25), (19), and (20) yields the form

$$n\beta\mu_A = n(-\beta\epsilon_A+\beta p)+\ln K+\ln[n] \qquad (26)$$

$$\equiv n\beta\mu_\infty^0+\ln K+\ln[n], \qquad (27)$$

which is precisely the form that Eqs. (3) and (4) reduce to in the case of strict isodesmic equilibria, provided $\bar{\mu}_n=n\mu_A$, as anticipated on phenomenological grounds. A direct physical meaning to $\bar{\mu}_n$ is pursued in Sec. V below. Interestingly, $\mu_\infty^0(T,p)=-\epsilon_A+p$ is an enthalpy rather than an energy, without entropic contributions, and note also that it is independent of concentration and, thus, is strictly constant at fixed temperature and pressure. In contrast, $\ln K$, the so-called configurational free energy required to create two ends by splitting a chain, is capable of displaying dramatic concentration dependence. To see the physical origin of this behavior, we can substitute Eq. (24) into Eq. (20) and use the results (14), (15) to eliminate $x\rho$, thereby obtaining an explicit expression for $K(T,p,x_w)$

$$\ln K = \beta\epsilon_A$$
$$+\ln\left(\frac{1+[a_Ax_w^2+a_B(1-x_w)^2+2a_Cx_w(1-x_w)]\rho_w^2}{[1-\rho_w+(1+a_C)(1-x_w)\rho_w]^2}\right),$$
$$\qquad (28)$$

and remembering that specifying T defines a_A,a_B,a_C, while $\rho_w=1-e^{-\beta p}$, and Eqs. (14) and (15) define $x(x_w)$ for any given (T,p). At fixed temperature and pressure, K typically varies with concentration in a roughly quadratic manner. The limiting pure-fluid values are

$$\ln K(x=0)=\beta\epsilon_A+\ln\left(\frac{1+a_B\rho_w^2}{(1+a_C\rho_w)^2}\right), \qquad (29)$$

$$\ln K(x=1)=\beta\epsilon_A+\ln\left(\frac{1+a_A\rho_w^2}{(1-\rho_w)^2}\right). \qquad (30)$$

It is straightforward to see from expanding Eq. (28) about $x_w>0$ and $x_w<1$ that, at fixed temperature and pressure, $\ln K$ is a minimum at some intermediate concentration in all cases, such that

$$a_B\rho_w(1-\rho_w)>1+a_C+a_C\rho_w(1+a_C\rho_w). \qquad (31)$$

When the condition (31) holds, the value of x_w at the minimum in K is given by

$$x_w^{\min}=\frac{a_B\rho_w(1-\rho_w)-(1+a_C)-a_C\rho_w(1+a_C\rho_w)}{\rho_w[a_A(1+a_C\rho_w)+a_B(1-\rho_w)-a_C(1-\rho_w+1+a_C\rho_w)]} \qquad (32)$$

and the corresponding concentration follows from Eqs. (14) and (15):

$$x^{\min}=\frac{x_w^{\min}[1+a_Ax_w^{\min}\rho_w+a_C(1-x_w^{\min})\rho_w]}{1+[a_A(x_w^{\min})^2+a_B(1-x_w^{\min})^2+2a_Cx_w^{\min}(1-x_w^{\min})]\rho_w}. \qquad (33)$$

Finally, to see the significance of the drop in the equilibrium constant, one can combine Eq. (32) with

$$\frac{K(x=0)}{K(x=x^{\min})}=\frac{(1+a_B\rho_w^2)[1-\rho_w+(1+a_C)(1-x_w^{\min})\rho_w]^2}{(1+a_C\rho_w)^2\{1+[a_A(x_w^{\min})^2+a_B(1-x_w^{\min})^2+2a_Cx_w^{\min}(1-x_w^{\min})]\rho_w^2\}}. \qquad (34)$$

Let us now use the above results to explore those physical situations which lead to a strong isobaric concentration dependence to K, associated with a maximum at lowest concentration. This is the somewhat counterintuitive situation encountered in the simulation study of Ref. [7] and explained by Attard [8] in terms of an analogy with colloidal physics. Firstly, note from condition (31) and sum rule (16) that K will be a local maximum at $x=0$ in situations where $a_B>a_C^2$ and the pressure is not too high nor too low. If the latter criteria is not present, then self-assembly is either too low (pressure too small) or saturated at a high value (pressure too high). In the special case considered in Ref. [10],

where $a_C=-1$ but a_A and a_B are positive (as appropriate to attractive interactions), the equilibrium constant is always a maximum at zero concentration. We can regard all such situations as amphiphilic linear self-assembly, since it is driven by significantly reduced solvent-solute attractions in comparison with solvent-solvent attractive energy. At lowest concentration the solute-solute attraction does not contribute to the concentration dependence of the equilibrium constant for solute clustering. Since each a_i depends exponentially on the associated attractive well depth ϵ_i, it is clear from result (34) that if ϵ_B was say an order of magnitude greater than both ϵ_C and ϵ_A, one would find $\ln K$ varying by as much as

ten, as concentration is varied. In these cases, one sees from Eqs. (32) and (33) that $x_w^{\min}$ and $x^{\min}$ lie close to 1 and from Eqs. (14) and (15) that x is a highly reduced function of x_w, so that K drops very rapidly at low concentration, on the scale of x. This, in turn, is associated with an almost constant value of $x_w(x)$ and, hence, also Y from Eq. (24) and the aggregation number (21), until lowest concentration where eventually Y must drop to zero. In terms of the choice of the standard state inherent in physical chemistry Eq. (4), one notes from Eq. (27) and Eqs. (19) and (20) that in this regime the ideal $\ln[n]$ dependence of the chemical potential has been almost entirely canceled by the concentration dependence of $\ln K$; or rather, postponed until low concentration. In Sec. IV, I shall discuss a mapping to three-dimensional systems that implies that such extreme behavior is potentially a common physical situation.

If the solute-solute attraction is the dominant interaction, then the lowest value of K shifts towards or lies at $x=0$, and the equilibrium constant that varies significantly with concentration at fixed pressure is that describing solvent clusters in an excess of solute; alternatively, swap the labels solute and solvent. Finally, if one wanted the concentration dependence at, say, fixed T and μ_B, then although ρ_w is now a function of concentration it is still straightforward to calculate the behavior in any given situation (in the same manner as discussed in Sec. II with regard to equations of state). Given the solvent origin of those cases of dramatic concentration dependence seen at fixed T and p, it is no surprise that switching to a fixed solvent chemical potential tends to suppress such behavior.

IV. MAPPING TO LINEAR SELF-ASSEMBLY WITHIN THREE-DIMENSIONAL SYSTEMS

The simulation study of Ref. [7] chose, for want of any obvious alternative, the same disk-disk attractive well-depth (ϵ) as the solvent-solvent interaction. In terms of repulsive forces, the solute is a disk with a volume seven times that of a solvent particle. This size difference is more than enough to ensure that the system behaves more like a colloidal solution than a molecular mixture. In particular, note that in order to map this three-dimensional model onto the one-dimensional LG analogy, we need to treat any break in a chain as due to intervening disks of solvent. That is, each side of a solute disk interacts with many solvent molecules, which, therefore, need to be summed-up to define an effective solvent disk. The isodesmic chemical equilibria Eq. (1), is concerned with the relocation of entire disks of solvent. For example, when a solute joins the end of a chain, one whole solvent disk is liberated from being stuck between two solutes, so that overall, two disk-solvent contact areas are replaced by a disk-disk and a solvent-solvent contact area. Similarly, when two solvent disks are separated to accommodate a solute, then two surfaces of solvent are created. The loss of attractive solvent-solvent energy is much greater than $k_B T$ unless $T^* \equiv k_B T/\epsilon$ is large. This explains why the low concentration simulation data could not be collected at T^* less than about 1.5, because then the self-assembly was just too strong to be equilibrated. The simulation study measured the partial molecular volumes of disk and solvent, which can be used to define an effective volume of the sol-

vent disk and, hence, the number of solvent particles making up a solvent disk. This is temperature dependent at the fixed simulation pressure, varying from around 6 at $T^*=3$ to about 10 at $T^*=1.5$. If roughly half the solvent molecules of an effective solvent disk interact with a neighboring disk and each such surface molecule looses about two intermolecular bonds when the disks are separated, then the effective solvent-solvent well depth ϵ_B is of order ϵ times the number of molecules in a solvent disk. Typical experimental systems would therefore show strong colloidal effects, since disks synthesized from organic materials are likely to be many times bigger in size than a single water molecule.

The mapping onto a one-dimensional LG model therefore requires an effective solvent-solvent well depth ϵ_B. In the temperature range accessible to the simulations, a reasonable choice of effective LG interaction parameters appropriate to the model of Ref. [7] is

$$\epsilon_A \equiv \epsilon, \quad \epsilon_B = \epsilon\left(1 + \frac{15}{T^*}\right), \quad a_C = -1. \quad (35)$$

This mapping shows that the simulation model lies very much in the strong amphiphilic class discussed in Sec. III; which is a point that was not appreciated in Ref. [10] where only the case $\epsilon_B = \epsilon_A$ was considered. To complete the mapping, we need to consider what the effective one-dimensional pressure should be. Here, I shall treat the thickness of the disks as a single lattice length and take βp to be identical in terms of the appropriate length scales; i.e., in three and one dimensions. In the moderate pressure regime investigated in the simulation study, this choice is not crucial. Rather, it is the interaction set (35) that controls the physical behavior. Figure 1 shows a plot of $\ln K$ versus $1/T^*$, obtained from Eq. (28) with the mapping (35) that I have just described. Note, in particular, the extremely strong concentration dependence at low concentration, in direct qualitative agreement with the simulation study. In fact, the mapping is essentially a semi-quantitative fit, especially with regard to the magnitude of the concentration dependence as a function of temperature and also to the values of the aggregation number that are involved (the latter are relatively low, since simulation cannot readily cope with $\bar{N} > 3$, because this would involve equilibrating a cluster distribution with significant contributions from $n > 20$). The equivalent simulation plot, Fig. 2 of Ref. [7], shows a small upwards shift, as if the repulsive-force length scale does not quite map onto a single lattice spacing, and at highest concentration shows significant downwards curvature. Of course, at such high concentration one would hope that the mapping to an effective one-dimensional model would start to become deficient, since this is where the three-dimensional cluster-cluster interactions should start to effect the physics. For example, in a concentrated three-dimensional model, there will be significant screening of chain ends from solvent, thereby reducing the free-energy cost of breaking a chain. One should also be beware of finite-size effects acting to enhance the aggregation. Notwithstanding these relatively small differences, the remarkable agreement of Fig. 1 with the simulation data strongly supports the colloidal analogy introduced by Attard [8] and, in addition, allows one to use the exactly solvable
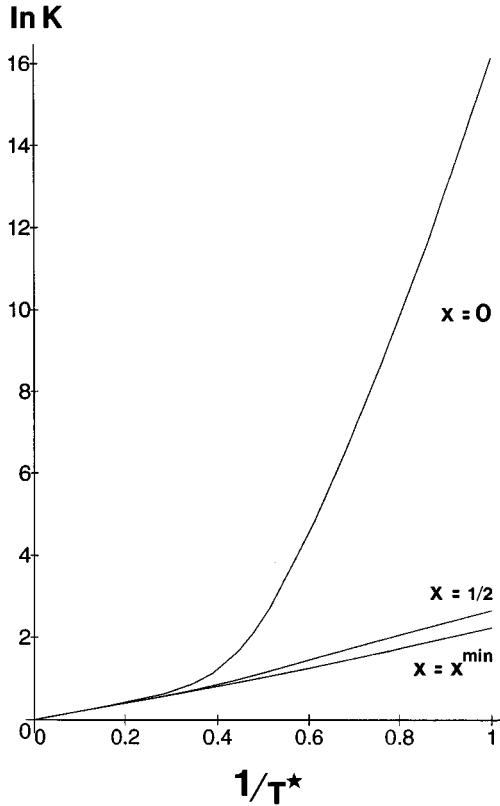
FIG. 1. Isobaric temperature dependence of the isodesmic equilibrium constant, from a one-dimensional lattice-gas mixture Eq. (28), with interaction parameters (35) chosen to map the one-dimensional model onto the three-dimensional system simulated in Ref. [7]; see text. The three curves display the nature of the concentration dependence, which is strong at low concentration. All the plots are at a fixed pressure $p = 0.5\epsilon$, in units that suppress the length scale of one lattice spacing.

one-dimensional LG models to explain or predict the physics of isodesmic chemical equilibria in real systems.

For real systems, such as those described in [5], the set of effective interaction parameters would not usually involve a negative value of a_C nor such a low value of a_A, as in the simulation set (35). However, from Eqs. (32) and (34), one only requires that a_B be significantly larger than a_A and a_C (with the latter positive), in order to be in the strongly amphiphilic or sticky-solvent colloidal regime. Thus the phenomena seen in the simulation model may well be generic whenever the solvent has a high surface tension, such as water. In fact, the Boltzmann factors become very large for typical experimental systems, since solvating a big disk-shaped solute involves the creation of a large amount of water-solute surface area, on the scale of a water molecule. One, therefore, anticipates high values of ln$K$ which itself results from the difference of much larger numbers. Accordingly, it will not be that straightforward to characterize the basic amphiphilic nature of real systems [6]. In short, these systems involve too many molecular contacts to be readily treated microscopically, but are not sufficiently colloidal to allow one to immediately make use of measured surface tension data.

V. AGGREGATE CHEMICAL POTENTIALS

In the phenomenology of self-assembly, the left side of Eq. (26) is β times the chemical potential of aggregates of size n. This interpretation arises because the form (4) can be derived by treating each cluster size as a separate species and then minimizing the grand potential with respect to fluctuations in the number of species of type n, as if the ensemble was defined by an entire set of chemical potentials rather than just one solute and one solvent chemical potential. I have already noted that the exact LG results are consistent with this picture provided $\bar{\mu}_n = n\mu_A$; see Eqs. (26) and (27). This raises the question as to whether $\bar{\mu}_n$ has any physical meaning at all, or is just a tautological partitioning of the Gibbs free energy of solute amongst the various (typically ill-defined) environments that a solute molecule can inhabit. We can answer this question precisely within the one-dimensional LG models for two reasons; firstly, because we can chose a completely unambiguous partitioning into clusters (as in Sec. III), and secondly, because we can evaluate exactly the chemical potential of any well-defined species, from potential distribution theory.

Let us then apply sum rule (5) to a species of size n. The hard-core insertion factor is just $(1-\rho)(1-\rho_w)^{n-1}$; i.e., the probability of finding a cavity of length n whose left end (say) sits on a chosen lattice site. The Boltzmann factor average in the presence of the cavity consists of a sum of three terms, arising from the probability that both ends of the cavity are separated from solvent as well solute, the probability that one end is in contact with solvent but the other is not, and finally, the probability that solvent is in contact with both ends, respectively. The potential distribution theorem can, therefore, be evaluated as

$$[n]e^{-\beta\bar{\mu}_n} = (1-\rho)(1-\rho_w)^{n-1}[(1-\rho_w)^2 + 2(1+a_C)$$
$$\times (1-\rho_w)(1-x_w)\rho_w + (1+a_C)^2(1-x_w)^2\rho_w^2]$$
$$= (1-\rho)(1-\rho_w)^{n-1}[1-\rho_w+(1+a_C)(1-x_w)\rho_w]^2$$
$$= (1-\rho)(1-\rho_w)^{n-1}(1-Y)^2$$
$$\times [1+a_Ax_w\rho_w+a_C(1-x_w)\rho_w]^2, \qquad (36)$$

where the last line has been obtained using Eq. (24). So when Eq. (18) is substituted, one finds that

$$e^{\beta\bar{\mu}_n} = \frac{x\rho}{1-\rho}\left(\frac{Y}{1-\rho_w}\right)^{n-1}\frac{1}{[1+a_Ax_w\rho_w+a_C(1-x_w)\rho_w]^2}. \qquad (37)$$

All the factors on the right side of Eq. (37) can be rewritten in terms of μ_A and ϵ_A, using Eq. (25) with sum rule (16) and the standard potential distribution theorem Eqs. (10)–(12)

$$e^{\beta\bar{\mu}_n} = e^{\beta\mu_A}[e^{\beta(\mu_A+\epsilon_A)}]^{n-1}, \qquad (38)$$

or finally

$$n\mu_A = \bar{\mu}_n - (n-1)\epsilon_A. \qquad (39)$$

This exact result differs from the expected phenomenology ($n\mu_A = \bar{\mu}_n$) by a term that is clearly the internal contribution to the Gibbs free energy per particle within a cluster of size

n. In hindsight, this is obvious. Namely, the potential distribution theorem treats a given species as a true particle species and, thus, is only concerned with configurational and entropic contributions that arise from interactions with other species. To describe chemical equilibria we need the total Gibbs free energy, but nevertheless, it is interesting that one can rigorously define a cluster chemical potential using potential distribution theory.

A particularly interesting case is the limit $n=1$, where there is no longer an internal contribution. Although $\bar{\mu}_1=\mu_A$, this does *not* hold because a cluster of size one is equivalent to a molecular species. Rather, objects that belong to class [1] must always be separated from all other solute by at least one lattice spacing, unlike real molecules. Accordingly, in the special case $n=1$ of the proof given above, the statistical mechanics is not simply reducing to an identity, but instead is proving the important result that at chemical equilibrium the chemical potential of a molecule does not distinguish between the instantaneous environments it may find itself in.

At this point, it is worthwhile to consider how the mapping of a LG model to a real system is affected by the choice of length scale, inherent in the dimensions of ρ and, hence, K, and the related issue of the incorporation of de Broglie wavelengths. Let us denote with a superscript prime, any quantity that is redefined when the length scale is altered from one lattice spacing to any other microscopic length σ. From the definition of an ideal gas limit and the isodesmic equilibrium constant, in terms of number densities, we have the following relationships:

$$\beta\mu_A'=\beta\mu_A+\ln\sigma, \quad \beta\mu_\infty^{0'}=\beta\mu_\infty^0+\ln\sigma, \quad K'=K/\sigma, \tag{40}$$

where in a three-dimensional model σ becomes σ^3. The fact that the equilibrium constant varies with the choice of unit of length indicates that there is a natural length scale involved in the process of self-assembly. This is the microscopic length at which ρ and $[n]$ can be treated as probabilities, i.e., their maximum physical value is unity. On this scale, the classical scale, the ideal gas limit reduces to the law of mass action in the form $[n]=[1]^n$, i.e., $K_{ideal}=1$. Now consider, in the real world, how the quantum ideal degrees of freedom should be incorporated. If the clusters were real species, then one would be tempted to give each cluster its own de Broglie wavelength defined in terms of the total mass of the cluster (proportional to n). Rotational quantum factors would then also be required. This approach would alter the n dependence of the chemical equilibria, so that, for example, the exponential form for isodesmic chemical equilibria (19) would no longer hold [12]. However, this is inappropriate to chemical equilibria, where the clusters are composed of molecules that carry their own quantal degrees of freedom with them. For example, consider all the vibrational modes present in a self-assembled chain of molecules. The correct approach is to include a factor of Λ^{3n}, where Λ is the de Broglie wavelength of a single molecule in units of the classical length scale, into the ideal term [13]. Thus, denoting this new definition of a standard state by subscript double prime, we have the mapping (in three dimensions)

$$\beta\mu_A''=\beta\mu_A+3\ln\Lambda, \quad \beta\mu_\infty^{0''}=\beta\mu_\infty^0; \quad K''=K, \tag{41}$$

and therefore the equilibrium constant is unaffected by the inclusion of quantal degrees of freedom into the ideal terms. The isodesmic aggregation number is not affected by either Eq. (40) or Eq. (41), since the cluster distribution remains exponential and is therefore defined in terms of a dimensionless quantity $[n]/[n-1]$, independent of the choice of length scales. In the second case, this arose only because the consistent method of including quantal degrees of freedom contributed a term strictly proportional to n in $\bar{\mu}_n$. Namely, to preserve the condition for chemical equilibria ($\bar{\mu}_n=n\bar{\mu}_1$) in the limit of ideality, we require $\ln([n]\Lambda_n^3)=n\ln([1]\Lambda^3)$ together with the law of mass action in the classical length scale ($[n]=[1]^n$) and, hence, $\Lambda_n=\Lambda^n$ as used above.

VI. HARD-BODY AMPHIPHILES

For LG mixtures in which the repulsive interactions have identical range, we see from Eq. (34) that the strongest concentration dependence, or colloidal behavior, is the limit where only the solvent-solvent interactions are attractive

$$\frac{K(x=0)}{K(x=x^{\min})}=(1+a_B\rho_w^2)[(1-\rho_w)^2+a_B^{-1}], \tag{42}$$

provided of course the pressure is consistent with condition (31) at $a_C=0$. At temperatures such that $\beta\epsilon_B$ is large, this ratio is exponentially large, for pressures that are neither very low nor very high (ρ_w not too close to zero or one). This dramatic self-assembly of hard solute particles at low concentration, is driven by what in colloid science is referred to as solvent pressure, i.e., sticky solvent-solvent interactions.

It is also of interest to consider cases where there are no attractive interactions between any species, but the solute-solvent repulsive range is greater than that of the solvent-solvent and solute-solute repulsions. In such a model, self-assembly is driven by free-volume considerations alone. It might conceivably be possible to find approximate realizations of this physics in nature, if for example the solute molecules contained flexible tails that coiled up when confined with like tails, but regardless of such speculations it is still of academic interest to investigate the role of entropy in situations where self-assembly is dominated by free-volume effects. The lattice-gas model of Sec. II can be used to realize this phenomena, by taking the special case where the unlike repulsive range is two lattice spacings ($a_C=-1$, $a_A=a_B=0$). Here, the condition (31) is always satisfied, and Eq. (34) reduces to the result

$$\frac{K(x=0)}{K(x=x^{\min})}=\frac{2}{2-\rho_w^2}, \tag{43}$$

with $x^{\min}=1/2$, as follows from the symmetry of the special model under consideration. This shows that free-volume considerations alone lead to a much more restricted concentration dependence to self-assembly. Even at infinite pressure, the equilibrium constant only doubles as concentration is reduced to the low concentration limit. Nevertheless, the effect clearly belongs to the same phenomena that I have defined as amphiphilic, and it is at least of conceptual inter-

est that self-assembly could be studied entirely within the context of hard-body models [14]. At the maximum value of the equilibrium constant, the special hard-body model reduces to the simple result, see Eq. (28),

$$\ln K(x=0,1)=2\beta p. \tag{44}$$

At constant pressure, this implies that the maximum driving force for self-assembly arises entirely from enthalpy; $\Delta H^0(x=0,1)=-2p$, $\Delta S^0(x=0,1)=0$. In the ordinary amphiphilic case, Fig. 1 of Sec. IV, one finds an even stronger dominance of enthalpy; namely, that entropy actually acts against the self-assembly. Before jumping to completely the wrong conclusion that free-volume considerations are not responsible for the hard-body self-assembly, it must be remembered that in statistical thermodynamics when one switches from a constant volume ensemble to a constant pressure ensemble then free volume entropy is transformed into enthalpy. For example, although the hard-sphere fluid to crystal phase transition is almost universally referred to as an entropy driven phase transition, at constant pressure (which could easily be argued to be the most physically correct approach), the phase transition is driven by enthalpy to the extent that configurational entropy not only works against the transition but does so to an extent of around 12 times the ideal entropy cost

$$0=\frac{\Delta G}{Nk_BT}=-\frac{\beta p}{\rho_L}\left(\frac{\rho_S-\rho_L}{\rho_S}\right)-\frac{\Delta S}{Nk_B}, \tag{45}$$

where G denotes the Gibbs free energy and subscripts L, S denote liquid and solid, respectively. Since the compressibility factor $\beta p/\rho_L$ is roughly 13 at the phase transition, the enthalpy and the entropy changes are both large and negative. The ideal entropy cost corresponds to a compressibility factor of unity and so is only 1/13 of the total entropy cost. This is, of course, only stating the result that in order to maintain a fixed pressure, when hard sphere liquid freezes the volume must shrink substantially; as one knows from the increase in density of around 10%. Nevertheless, at constant pressure it is clearly completely incorrect to describe hard sphere crystallization as an entropy driven phase transition. I have belabored this point because it highlights the care with which one must use the terms entropy driven and enthalpy driven, especially in chemical equilibria phenomena, when one is invariably working at fixed pressure and, thus, has transformed free-volume effects, from entropy (ΔS) into enthalpy ($p\Delta V$). The exact LG mixture results given in Secs. II and III are readily evaluated to yield the enthalpic and entropic contributions to the isodesmic chemical equilibria (for example, one can read off Fig. 1 the standard enthalpy and entropy as a function of temperature, from slopes and intercepts, respectively) but interpreting the results in terms of molecular physics demands full attention to the issue that I have just stressed.

VII. SOLVENT-EXCLUDED CLUSTER DEFINITION

Since the choice of cluster definition is not unique, one should sensibly enquire as to the significance of the choice. Attard [8] has pointed out that for amphiphilic systems, involving significant solvent exclusion from in between solute,

there is an obvious alternative class of solute cluster definitions. Namely, one could define a solute cluster as any cluster that actively excludes solvent, regardless of the absence of some solute-solute contacts. In terms of the LG models discussed in this paper, taking the limit $a_C=-1$ offers a well-defined way of exploring this issue, i.e., since solvent is now completely excluded from a lattice site lying either side of a solute, it makes sense in this case to ignore any isolated break of one lattice unit in a chain of solute. At first sight, this could allow for a dramatic change in the self-assembly, since solute clusters as defined previously can now break up without altering the redefined chain length. Thus, our new cluster definition allows for a significant amount of entropy to be accommodated within a single chain. On the other hand, the absence of phase transitions in short-ranged one-dimensional models implies that the new cluster definition cannot involve a qualitative change in the isodesmic chemical equilibria.

Adopting the new cluster definition, for the purposes of this section only, let us now redo the analysis of Sec. III, to obtain the solvent-excluded cluster distribution. In place of Eq. (17), the concentration of isolated solute becomes

$$[1]=x\rho(1-Y)^2(1-x_w\rho_w)^2, \tag{46}$$

where the additional squared factor arises because the solute would not now be regarded as isolated if there was a solute lying two squares away (since solvent could not get in between when $a_C=-1$). Note that I am continuing to denote the probability of finding a solute next to another solute as Y, without of course assuming that Y remains the fundamental quantity defining self-assembly. I shall also continue to use K as defined by the old cluster definition, Eqs. (19) and (20), although it is no longer the equilibrium constant that we desire to calculate. In place of Eq. (19), the new cluster distribution is

$$[n]=[1][Y+(1-Y)x_w\rho_w]^{n-1}. \tag{47}$$

The factor multiplied to the power of $n-1$ has been modified in this particular way, because when expanded, as in the binomial theorem, each term expresses the number of ways of introducing $n-m$ single unit breaks in a chain of length n under the previous definition. So, the new cluster properties are readily expressed in terms of the previous cluster distribution

$$\hat{Y}=Y\left(1+\frac{(1-Y)x_w\rho_w}{Y}\right), \tag{48}$$

$$=Y[1+e^{-\beta(p+\epsilon_A)}], \tag{49}$$

$$\hat{K}=K\left(\frac{1+\dfrac{(1-Y)x_w\rho_w}{Y}}{(1-x_w\rho_w)^2}\right), \tag{50}$$

$$=\frac{K[1+e^{-\beta(p+\epsilon_A)}]}{(1-x_w\rho_w)^2}, \tag{51}$$

where the quantities with a hat belong to the new cluster distribution and the second version of each result follows

from inserting Eq. (24) in the limit $a_C = -1$. Note that the concentration dependence of the equilibrium constant is reduced and the aggregation number is increased, by switching to the solvent excluded definition. The effects are not large in the sticky solvent case however, because the solvent-solvent attractions do not contribute directly to the renormalization. Notwithstanding this conclusion, it is possible that the above analysis is of significance to computer simulation studies [7]. This is because one can envisage situations in which the solvent excluded distribution was not equilibrated, for example if all the solutes became trapped in a single renormalized cluster, but that by using the ordinary cluster distribution one might observe many apparent breaks in the chain, i.e., breaks of one spacing that do not let in solvent. Here, the ordinary cluster distribution would look equilibrated, with an isodesmic exponential form appropriate to the quasi-one-dimensional subsystem, whereas the solvent excluded distribution would show that the full three-dimensional simulation is not equilibrated [8].

VIII. LINEAR SELF-ASSEMBLY AT SURFACES

As a final application of the exact physics of isodesmic equilibria, let us consider inhomogeneous systems in which the ends of the chains are able to adsorb onto a surface (or wall). There are now two cluster distributions present; namely, clusters in bulk and clusters with one end attached to the wall. Of course, in a three-dimensional system, there are other possibilities, such as clusters growing along the surface and chains that attach twice or more to the surface (loops). The one-dimensional LG model can only apply if the three-dimensional nature plays no role. This situation is plausible for discotic solutions in cases where the solute disks assemble into relatively stiff chains and are highly disfavored from lying edge onto the wall. Then, at moderate to low concentration, one envisages a situation where aggregates sometimes terminate on the surface. The question that can then be answered is, how is the cluster distribution of attached chains related to the cluster distribution in bulk?

Consider a semi-infinite LG mixture in one dimension, where the left side of the system ends in a wall and the wall-fluid interactions are limited to one lattice spacing. Far from the wall, the cluster distribution is that calculated in Sec. III. Using *superscript w* to denote a chain whose left end lies next to a general wall (with *subscript w* continuing to label a hard wall quantity), one sees immediately that the form of the wall cluster distribution remains exponential,

with the only difference being that arising from the termination at the wall

$$[1]^w = x^w \rho^w (1 - Y),$$ (52)

$$[n]^w = [1]^w Y^{n-1}.$$ (53)

Thus the wall cluster distribution is identical to the bulk cluster distribution, apart from an amplitude factor, and the aggregation number is again given by Eq. (21). The probability of adding another monomer to the far end of a chain adsorbed at the wall is obviously no different to that for joining a bulk cluster, i.e., K is also the equilibrium constant for the equilibria

$$[1] + [n-1]^w \rightleftharpoons [n]^w.$$ (54)

However, when modeling a three-dimensional system of sufficiently large surface area, the ratio of wall clusters to bulk clusters is controlled by the process of attaching a chain to the wall ($[n] \rightleftharpoons [n]^w$)

$$K^w \equiv \frac{[n]^w}{[n]} = \frac{[1]^w}{[1]}.$$ (55)

It is therefore of some interest to inquire under what circumstances K^w differs greatly from unity.

Substituting Eqs. (52) and (17), we have $K^w = x^w \rho^w / x \rho (1 - Y)$ and so there are three obvious cases we can consider without introducing any further energies: (i) a solute wall, where $x^w \rho^w = Y$ and thus K^w follows immediately from the results of Sec. III; (ii) a solvent wall, where $x^w \rho^w$ is the probability of finding a solute next to a solvent and can thus be obtained in direct analogy to the calculation used to derive Eq. (24); and (iii) a hard wall, where $x^w \rho^w = x_w \rho_w$. The first two cases are directly related to experimental procedures that use self-assembled monolayer chemistry to generate surfaces that are either solutelike or solventlike; for example, by bonding a monolayer of solute to a mica or gold substrate in a particular orientation such as discotic molecules lying flat. Inserting results from Sec. III and carrying out the recalculation needed for case (ii), the exact LG solutions for these three situations are (i) solute wall

$$\ln K^w = \beta \epsilon_A + \ln \left(\frac{1 + [a_A x_w^2 + a_B (1-x_w)^2 + 2 a_C x_w (1-x_w)] \rho_w^2}{[1 - \rho_w + (1+a_C)(1-x_w)\rho_w][1 - \rho_w + (1+a_A)x_w\rho_w + (1+a_C)(1-x_w)\rho_w]} \right),$$ (56)

(ii) solvent wall

$$\ln K^w = \beta \epsilon_C + \ln \left(\frac{1 + [a_A x_w^2 + a_B (1-x_w)^2 + 2 a_C x_w (1-x_w)] \rho_w^2}{[1 - \rho_w + (1+a_C)(1-x_w)\rho_w][1 - \rho_w + (1+a_B)(1-x_w)\rho_w + (1+a_C)x_w\rho_w]} \right),$$ (57)

and (iii) hard wall

$$\ln K^w = \ln\left(\frac{1 + [a_A x_w^2 + a_B(1-x_w)^2 + 2a_C x_w(1-x_w)]\rho_w^2}{1 - \rho_w + (1+a_C)(1-x_w)\rho_w}\right).$$
(58)

At low temperature, when all the interaction parameters a_A, a_B, a_C are exponentially large, the above results reduce to a simple balance of energies in the low concentration limit; provided the pressure is not extremely low

$$\text{solute wall:} \quad k_B T \ln K^w(x=0) = \epsilon_A + \epsilon_B - 2\epsilon_C, \quad (59)$$

$$\text{solvent wall:} \quad k_B T \ln K^w(x=0) = 0, \quad (60)$$

$$\text{hard wall:} \quad k_B T \ln K^w(x=0) = \epsilon_B - \epsilon_C + k_B T \ln(1 - e^{-\beta p}). \quad (61)$$

The most interesting class of behavior is therefore the sticky-solvent case discussed in Sec. IV, i.e., $a_B \gg a_A, a_C$. Here, when the wall-solvent interaction is not sticky (such as a solute wall or a hard wall), the value of K^w is exponentially greater than unity in the low concentration regime. Accordingly, in this situation, the probability of finding a chain end adsorbed to the surface is very much greater than finding the left end of an identical length chain at any specified bulk lattice site. When mapped onto three-dimensional systems, this implies that the low concentration regime of isodesmic chemical equilibria in a sticky solvent in the presence of a solute surface, involves a strong tendency for chain ends to anchor to the wall. However, the form and aggregation number of the wall clusters will be identical to the bulk cluster distribution, provided the clusters are not interacting side by side, so that one envisages this regime as a random forest of floating anchored chains, generated entirely by the colloidal effect known as solvent pressure. In contrast, if the solvent wall case mapped to three-dimensional systems in which the chains adsorbed along the wall, strong solvent-induced self-assembly parallel to the wall would be consistent with layer-by-layer growth.

IX. SUMMARY

I have explained in detail how potential distribution theory is able to solve lattice-gas mixture problems in one-dimensional systems exactly, with an absolute minimum of mathematical effort. In particular, this approach leads directly to the full equation of state, in any desired phase space, together with the cluster properties of aggregated states. Section III proved that LG mixture models are exact representations of isodesmic chemical equilibria, at all concentrations. Thus, the cluster distribution (19) and the phenomenological form (27) are not just ideal approximations, but instead hold everywhere throughout phase space. A highly successful interpretation of recent surprising simulation data followed from a simple mapping of three-dimensional discotic amphiphilic solutions to one-dimensional models. The key point here is that such systems are colloidal

in nature, rather than molecular, i.e., a break in a chain involves the insertion of many solvent molecules. Thus, the mapping is based on imagining solvent to be divided, at any instant, into solvent disks. This in turn implies that the sticky solvent limit, where the one-dimensional solvent-solvent attractions outway all other effects, is potentially a common physical situation. At fixed total pressure, this latter case is associated with a dramatic increase of the isodesmic equilibrium constant in the limit of low concentration; driven by what colloidal scientists would recognize as solvent pressure.

This paper also makes use of exact results of one-dimensional LG mixtures to explore the physics that lies behind the well known phenomenology of chemical equilibria of self-assembly; Secs. V to VIII. Section V shows that it is possible to give a precise meaning to the chemical potential of an aggregate, via potential distribution theory, provided the chosen cluster definition is well defined (no ambiguity about which cluster a given molecule belongs to in any particular configuration). It is also of interest to note from Eq. (27) that $\bar{\mu}_n = n\mu_A$ is an exact consequence of statistical mechanics, and that $\bar{\mu}_1 = \mu_A$ is not just an identity (see Sec. V) but rather the same statement that the chemical potential of a solute cannot distinguish the cluster environment that we chose to assign it to for any particular configuration. Section VI discussed self-assembly in hard-body systems, showing that amphiphilic behavior can continue to hold even in the absence of attractive interactions. This somewhat esoteric exercise highlighted the significance to free volume arguments of choosing to work at constant pressure (the standard choice in chemical equilibria), i.e., enthalpy now plays the role that entropy would have at fixed volume. The nonuniqueness of the choice of cluster definition was tackled in Sec. VII by explicitly recalculating the cluster distribution for a particular example of a solvent-exclusion definition. As expected, qualitative changes (such as the appearance of a phase transition) cannot be altered by changing the cluster definition, but significant quantitative and conceptual consequences can arise in amphiphilic systems. Finally, Sec. VIII discusses a potentially useful mapping of three-dimensional inhomogeneous systems to semi-infinite one-dimensional LG models. This could only hold when the most favored adsorption of chains is via attachment end on to a surface; as with disks that lie flat on the surface. The LG results imply that the sticky-solvent regime of this class involves an overwhelming driving force for chains to attach by one end to a solute wall (or a hard wall).

In everyone of the above topics, the results obtained from the one-dimensional LG models are exact. That is, there exists an exact physics of isodesmic chemical equilibria. This physics allows important conceptual conclusions concerning the physical chemistry of self-assembly, as well as yielding quantitative predictions of linear self-assembly phenomena. In general, the physical chemists appear to have been remarkably successful in developing what is in fact an exact phenomenology of self-assembly, with the exception that the significance of concentration dependence has not been fully appreciated. Thus, the main additional point to add to the physical chemistry of self-assembly is to be beware that in many amphiphilic systems the physics will be more closely related to colloidal science than that of typical molecular solutions.

ACKNOWLEDGMENT

APPENDIX A: PRESSURE SUM RULE

The pressure is defined by the Gibbs-Duhem equation, which we can write as

$$-\frac{\partial \beta p}{\partial \rho_w} = \rho e^{\beta \mu_A} \frac{\partial (x e^{-\beta \mu_A})}{\partial \rho_w} + \rho e^{\beta \mu_B} \frac{\partial [(1-x) e^{-\beta \mu_B}]}{\partial \rho_w},$$

(A1)

and then use potential distribution theory to eliminate the chemical potentials from the right side

$$-\frac{\partial \beta p}{\partial \rho_w} = \rho e^{\beta \mu_A} \frac{\partial}{\partial \rho_w} \left[\left(\frac{1-\rho}{\rho} \right) [1 + a_A x_w \rho_w \right.$$

$$+ a_C (1-x_w) \rho_w]^2 \right] + \rho e^{\beta \mu_B} \frac{\partial}{\partial \rho_w} \left[\left(\frac{1-\rho}{\rho} \right) \right.$$

$$\times [1 + a_B (1-x_w) \rho_w + a_C x_w \rho_w]^2 \right]$$

$$= \rho \frac{\partial \ln[(1-\rho)/\rho]}{\partial \rho_w} + \frac{2(1-\rho) \rho_w}{1-\rho_w}$$

$$\times \left[a_A x_w^2 + a_B (1-x_w)^2 + 2 a_C x_w (1-x_w) \right.$$

$$+ [a_A x_w - a_B (1-x_w) + a_C (1-2x_w)] \rho_w \frac{\partial x_w}{\partial \rho_w} \right].$$

(A2)

If one then evaluates the quantity $\partial \ln(1-\rho_w)/\partial \rho_w$, via repeated use of Eq. (15), beginning with

$$\frac{\partial \ln(1-\rho_w)}{\partial \rho_w}$$

$$= \frac{\partial \ln\left(\frac{1-\rho}{\rho} \right)}{\partial \rho_w} + \frac{\partial}{\partial \rho_w} \ln\{\rho_w + [a_A x_w^2 + a_B (1-x_w)^2$$

$$+ 2 a_C x_w (1-x_w)] \rho_w^2 \},$$

(A3)

one eventually proves equivalence, i.e., sum rule (16). To complete this derivation, note in particular that after rewriting

$$\frac{\partial \ln\left(\frac{1-\rho}{\rho} \right)}{\partial \rho_w} = \rho \frac{\partial \ln\left(\frac{1-\rho}{\rho} \right)}{\partial \rho_w} + \rho \frac{\partial \left(\frac{1-\rho}{\rho} \right)}{\partial \rho_w}$$

(A4)

one can eliminate ρ entirely from the final derivative, using Eq. (15).

APPENDIX B: LATTICE-GAS ENERGY

For a one-dimensional binary LG mixture, the total energy per particle (U/N) is, by inspection,

$$\frac{U}{N} = -x(\epsilon_A \rho_{AwA} + \epsilon_C \rho_{BwA})$$

$$- (1-x)(\epsilon_B \rho_{BwB} + \epsilon_C \rho_{AwB}),$$

(B1)

where I have introduced a notation such that a subscript IwJ denotes a density of type I next to a wall of type J. In terms of the notation of Sec. III, we have $\rho_{AwA} = Y$ and $\rho_{BwA} = (1-x_{wA}) \rho_{wA}$, which were evaluated via potential distribution theory, i.e., Eqs. (22) and (23). The other two analogous wall densities follow from the same analysis, but applied to measuring the chemical potentials next to a wall of type B; as discussed in Sec. VIII. One can check these derivations against the symmetry requirement $x \rho_{BwA} = (1-x) \rho_{AwB}$, i.e., the second and last terms of Eq. (B1), the cross interaction energies, are equal. Collecting all these expressions together and inserting into Eq. (B1) yields the desired result

$$\frac{U}{N} = -\frac{\rho_w [\epsilon_A (1+a_A) x_w^2 + \epsilon_B (1+a_B)(1-x_w)^2 + 2\epsilon_C (1+a_C) x_w (1-x_w)]}{1 + [a_A x_w^2 + a_B (1-x_w)^2 + 2 a_C x_w (1-x_w)] \rho_w}.$$

(B2)

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