

Chemical Potentials in a Three-Component, 1-Dimensional Liquid

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The chemical potential of a dilute solute in a mixed solvent in a one-dimensional, three-component fluid model is calculated exactly. The results depend on three parameters derived from the interparticle potentials. An explicit formula for the leading deviations from ideality is obtained. For arbitrary cosolvent concentration, but still dilute solute, the chemical potential of the solute is obtained numerically. A lattice model of the same system is also treated exactly. The results depend on three parameters in precisely the same way as do those of the continuum model. However, the parameters have a different physical meaning. In the special case of a hard-core plus-square-well potential, the results of the two models become the same in the high-density limit.

1. Introduction

The thermodynamics of solutions is a very important part of chemical and biochemical thermodynamics. It is a mature field, but one still of great current usefulness. Aside from the utility of macroscopic thermodynamics, the combination of this discipline with statistical thermodynamics provides the opportunity for the molecular interpretation of solution phenomena. It is this aspect of the field which we wish to discuss here.

In any application of statistical thermodynamics, there are two steps (at least). These are, first, adopting a model for the phenomenon under study and, second, solving the mathematical problem posed by statistical mechanics for the evaluation of the properties of the model. These two steps are not independent in practice. A model very faithful to all of the details of the physical situation usually can only be solved in an approximate manner. A model simple enough to be treated exactly often leaves out some of the interesting physics of the system being modeled. There is a kind of inverse relationship between the criteria of accuracy of modeling and accuracy of solution.

For example, in the theory of phase transitions and critical phenomena it is more important to have an accurate solution than to have an accurate model.¹ Approximate theories almost always get the details of the critical region wrong. On the other hand, the details of the short range interactions are largely irrelevant for the critical region; this goes under the code name of “universality”. Another example is the theory of electrolyte solutions, where an accurate treatment of the long-range Coulomb interactions is essential and the details of the short-range interactions between ions are unimportant in dilute solutions. An example where the details of the model are important is the case of liquid water. Molecular dynamics calculations have shown that the properties of models of this important liquid are rather sensitive to the intermolecular potential chosen as part of the model.

The literature is full of work on the experimental thermodynamic properties of binary solutions. Ternary solutions have been less studied but are also important. A major interest of experimentalists is the interaction of B with C in a solvent A. Our interest was drawn to this field by the question of understanding the solution properties of proteins in mixed solvents. Typically, one studies the chemical potential of the protein in aqueous solution to which has been added a third component, which is usually called the cosolvent. The cosolvent might be, for example, urea or guanidinium chloride which destabilize protein structures, or sucrose or alcohols, which stabilize protein structures. The cosolvent may be present in amounts up to about 6 M, but this is still reasonably small on a mole fraction basis. The problem is to interpret the data on such solutions in terms of the interactions between the components in as quantitative a manner as possible.

It would be useful to have an exact solution, even on a model that is not very well motivated physically, to make estimates of the reliability of approximate solutions of more physical models. The only model we know of for a liquid mixture for which there is any hope of obtaining an exact solution is that of a one-dimensional system of interacting particles with hard cores to which there may be adjoined an attractive potential. For the one component case with only hard cores (i.e., hard lines) the equation of state was determined by Tonks.² It is known as the Tonk’s gas. A general method of evaluating the partition function is due to Gürsey.³ The extension of these considerations to the n -component case is discussed by Ben-Naim.⁴ This theory has never been implemented for three-component systems as far as we know. We propose to do so here.

We also propose to treat a lattice version of the same model. Lattice models are often used in solution theory because they are much simpler than continuum models. In fact, lattice models are not exactly soluble in three dimensions either, but there are well studied approximation methods for their application. They

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can be solved exactly in one dimension, and it is worthwhile to see to what degree the predictions of the two classes of models agree.

There are also several existing exact solution theories.^{5,6} These are formal theories, expressing the thermodynamic functions of liquid mixtures in terms of integrals of molecular distribution functions. They provide no prescription for the practical computation of the relevant distribution functions. Important as these theories are, they do not serve our present purpose of providing explicit expressions in terms of intermolecular forces.

Of course, we realize that a one-dimensional model is no doubt a terrible model for real three-dimensional systems, the more so when the components have very different sizes (as would be the case in the protein solutions we mentioned above). Our aim here is methodological, to compare exact solutions of two models of ostensibly the same phenomena, the continuum and the lattice models. However, there is the possibility that our results could be applicable to some real systems in restricted geometries, for example molecules in a nanotube.

2. The Continuum Model

We specify the model for an n -component system, although we shall only implement it for $n = 3$. There are N_i particles of species 1, ..., N_n of species n , lying on a line of length L . A potential function $V_{\alpha\beta}(z)$ describes the interaction potential between a particle of species α and a nearest neighbor of species β and z is the distance between the centers of the two particles. This potential has a hard core of diameter $(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})/2$, where σ_{ii} is the hard core diameter of a particle of type i , in addition to any softer potential which may be present. The hard cores impose the condition that the particles do not interpenetrate; an ordering of the particles, once established, persists forever. This is not a conventional two-body potential because it is limited to nearest neighbors. Note, however, that when the range of the attractive forces is less than the hard core diameter (suitably weighted to take account of the various species) the nearest neighbor restriction is automatically imposed by the potential itself.

The evaluation of the canonical partition function of a single component system of interacting particles in one dimension is well described in the literature.^{3,4,7,8} A very brief outline of the method is the following.

The canonical partition function is given by

$$Q_N(L, T, N) = \frac{1}{\Lambda^N} \int_0^L \cdots \int_0^L e^{-\beta V} dx_1 \dots dx_N \quad (1)$$

Here Λ is the mean thermal de Broglie wavelength of the particles.

One takes the Laplace transform of Q_N with respect to L , the length of the container. This is equivalent to going from the (T, L, N) ensemble to the (T, P, N) ensemble. Using a procedure developed by Gürsey³ that makes use of repeated applications of the convolution theorem of Laplace transforms,⁹ the new partition function (often given the symbol Δ) is of the form

$$\Delta(T, P, N) = \left(\frac{\omega}{\Lambda} \right)^N \quad (2)$$

where

$$\omega(P, T) = \int_0^\infty e^{-\beta P x} e^{-\beta V(x)} dx \quad (3)$$

$$\Lambda = h/(2\pi m k T)^{1/2} \quad (4)$$

P is the Laplace transform variable, and Δ has the thermodynamic meaning of

$$G(P, T, N) = -kT \ln \Delta \quad (5)$$

where G is the Gibbs function. The thermodynamics is now determined.

A multicomponent system requires a more complex formulation, the first part of which is, however, quite analogous to the pure system case. The general case is treated by Ben Naim.⁴ We shall specialize here to the three-component case. The canonical partition function for a system of N_1 particles of species 1, N_2 of species 2, and N_3 of species 3 (with $N_1 + N_2 + N_3 = N$) is

$$Q_N(T, L, N_2, N_3) = \frac{1}{\Pi \Lambda_i^{N_i}} \int_0^L \cdots \int_0^L e^{-\beta V} dx_1 \dots dx_N \quad (6)$$

once a particular ordering of particles on the line is chosen. By ordering, we mean a sequential order of species. For example, ...1122231... is an ordering consisting of two particles of species 1 followed by three of species 2 followed by one of species 3, etc. Notice that Δ depends on only two of the three particle numbers; this is because only three of the four numbers N_1 , N_2 , N_3 , and N are independent. We have chosen to take N_1 as the dependent one.

Going to the (T, P, N_2, N_3, N) ensemble, for any particular fixed ordering one easily finds

$$\Delta_{\text{ordered}} = \prod_{i=1}^N \omega_{\alpha(i), \alpha(i+1)} / \Lambda_i \quad (7)$$

where ω is the same Laplace transform defined in eq 3 except that the potential is that between a particle of species $\alpha(i)$ and $\alpha(i+1)$. The symbol $\alpha(i)$ is the species label for the i th particle in the sequence.

The choice of a given ordering is, of course, arbitrary. The complete Δ is the sum of Δ_{ordered} over all possible orderings. Thus Δ can be written as

$$\Delta = \sum_{\text{orderings}} \prod_i \omega_{\alpha(i), \alpha(i+1)} / \Lambda_i$$

This sum is difficult to carry out because of the restrictions on the numbers N_i . The solution for this difficulty, as in the case of the multicomponent canonical ensemble, is to go to a grand ensemble

$$\Gamma(P, T, \mu) = \sum_{N_1, N_2, N_3=0}^{\infty} \lambda_1^{N_1} \lambda_2^{N_2} \lambda_3^{N_3} \Delta(T, P, N_1, N_2, N_3) \quad (8)$$

where $\lambda_i = \exp(\beta \mu_i)$. The problem with this definition is that the series specified in eq 8 does not converge. This occurs because $P, T, \lambda_1, \lambda_2, \lambda_3$ are not independent variables, their variations being connected by the Gibbs–Duhem equation. Also, the phase rule shows that there are only three independent intensive variables.

This can be understood in the following way. The ordinary grand partition function is $\exp(-\beta P L)$. Its Laplace transform is

$$\Gamma = \int_0^\infty e^{\beta(P-p)L} dL \quad (9)$$

This integral will only converge if $p > P$. The function of p

defined by eq 9 can, however, be analytically continued to the left of P . This analytically continued function has a pole at P .

This problem can be treated by an idea introduced by Sack.¹⁰ Pick one of the variables to have some nonphysical value such that the series converges. The variable picked is usually the pressure, since that is the Laplace transform variable, and for sufficiently large p , the Laplace transform of the ordinary grand partition function will converge. For the questions discussed in this paper, we have found it more convenient to take the chemical potential μ_1 (or the activity λ_1) as the nonphysical variable rather than the pressure. One then looks for the position of the singularity of Γ as the unphysical variable varies. The value of the unphysical variable at the singularity is the physical value of that variable. The partition function Γ differs from more conventional partition functions in the sense that thermodynamic variables are given, not by its logarithm but by the position of its poles, or alternatively by the zeros of Γ^{-1} .

We reserve the symbol λ_1 for the physical value of the activity and introduce the symbol $\bar{\lambda}_1$ for an arbitrary value in eq 8. Then the generalized partition function Γ will converge if $\bar{\lambda}_1$ lies within the radius of convergence of the series. Γ can be evaluated as

$$\Gamma = \sum_{N \geq 0} \sum_{\alpha} M_{\alpha_1 \alpha_2} M_{\alpha_2 \alpha_3} \cdots M_{\alpha_{n-1} \alpha_n} M_{\alpha_n \alpha_1} \quad (10)$$

$$= \text{Tr} \sum_{N \geq 0} \mathbf{M}^N = \text{Tr} (1 - \mathbf{M})^{-1} \quad (11)$$

$$M_{ij} = \left(\frac{\lambda_i \lambda_j}{\Lambda_j \Lambda_i} \right)^{1/2} \omega_{ij} \quad (12)$$

and this is the desired analytic continuation. The α 's are species labels. To get this form, we have closed our linear system into a ring. λ_1 , the physical value of $\bar{\lambda}_1$, comes at the value of $\bar{\lambda}_1$ where $(\mathbf{M} - 1)^{-1}$ does not exist, that is, where $|\mathbf{M} - 1| = 0$. This is because the trace has a pole wherever one of the eigenvalues of \mathbf{M} is unity. However, this is equivalent to $|\mathbf{M} - 1| = 0$.

The equation $|\mathbf{M} - 1| = 0$ determines λ_1 as a function of λ_2 , λ_3 , P , and T ; i.e., it supplies explicitly the relationship between the intensive variables implied by the Gibbs–Duhem equation. (From now on we shall suppress explicit mention of T since we always work at fixed temperature in this paper.) The chemical potentials can then be eliminated in terms of concentrations or mole fractions. This approach is simpler than taking the pressure as the unphysical variable since solving $|\mathbf{M} - 1| = 0$ for P is much more difficult than solving it for λ_1 . The subsequent manipulations to eliminate λ_1 and λ_3 in favor of x_2 and x_3 are also much more complicated.

3. Algebraic Solution

In principle, the carrying out of the program sketched above is straightforward. In practice, for a three-component system it is rather complicated. We carried out the algebra with the aid of the program *Mathematica* and outline the steps in the solution procedure here.

In this paper, we consider the case of a ternary solution. In accord with standard convention, we denote the solvent as component 1, the solute as component 2, and the cosolvent as component 3. The overall object of the calculation is to evaluate μ_2 as a function of the mole fractions of the components 2 and 3. The steps to accomplish this aim are as follows.

(1) Solve the equation $|\mathbf{M} - 1| = 0$ for λ_1 as a function of λ_2 , λ_3 , and P . The equation for λ_1 is a linear equation, easy to solve. Introducing the notational shorthand

$$D_{\alpha\beta} = \frac{\omega_{\alpha\beta} \omega_{\beta\alpha}}{\omega_{\alpha\alpha} \omega_{\beta\beta}} \quad (13)$$

the solution can be written

$$\lambda_1 \omega_{11} = \frac{1 - \lambda_2 \omega_{22} - \lambda_3 \omega_{33} + (1 - D_{23}^2) \lambda_2 \omega_{22} \lambda_3 \omega_{33}}{Z} \quad (14)$$

$$Z = 1 - \lambda_2 \omega_{22} (1 - D_{12}^2) - \lambda_3 \omega_{33} (1 - D_{13}^2) + \lambda_2 \omega_{22} \lambda_3 \omega_{33} (1 + 2D_{23} D_{13} D_{12} - D_{23}^2 - D_{13}^2 - D_{12}^2)$$

(2) Using the Gibbs–Duhem equation $\sum x_i d\mu_i = 0$ (fixed T and P), we compute

$$x_2 = - (1 - x_2 - x_3) \left(\frac{\partial \mu_1}{\partial \mu_2} \right)_{\mu_3} \quad (15)$$

$$x_3 = - (1 - x_2 - x_3) \left(\frac{\partial \mu_1}{\partial \mu_3} \right)_{\mu_2} \quad (16)$$

Since μ_1 is known as a function of μ_2 and μ_3 from step 1 (since $\lambda_i = \exp \beta \mu_i$), these equations can be solved for x_2 and x_3 as a function of μ_2 and μ_3 .

(3) Fix x_2 at some low value. (We have usually used 10^{-3} and checked that 10^{-5} gives the same results.) Then, choosing μ_3 (or equivalently λ_3) yields μ_2 and x_3 , which are what we want. This solution was carried out numerically by *Mathematica*.

The limiting slopes, $\lim_{x_2, x_3 \rightarrow 0} (\partial \mu_2^{\text{ex}} / \partial x_2)_{x_3}$ and $\lim_{x_2, x_3 \rightarrow 0} (\partial \mu_2^{\text{ex}} / \partial x_3)_{x_2}$ are of interest. μ_i^{ex} is the excess chemical potential of species i , the actual chemical potential less its ideal value. Evaluated at infinite dilution, they are the coefficients of the linear terms of an expansion of μ_2 in powers of x_2 and x_3 . In fact, for real protein solutions, the protein concentration is kept low, so the term linear in x_2 is not detectable. These limiting slopes can be obtained analytically from the equations produced in the steps outlined above. Again, the analytical work was done by *Mathematica*.

The result is

$$\frac{\mu_2}{kT} = \frac{\mu_2^*}{kT} + \ln x_2 - \frac{2}{D_{12}} (1 - D_{12}) x_2 - \left(1 - \left(\frac{D_{23}}{D_{12} D_{13}} \right)^{1/2} \right) x_3 + \cdots \quad (17)$$

In the above, we have only computed analytically the linear terms in the expansion of μ_2 in the x 's.

If more than the limiting slopes of μ_2 is desired, then the equations for x_2 and x_3 in terms of λ_2 and λ_3 can be solved numerically. These solutions as well as the analytical slopes of eq 17 will be presented and discussed after the lattice case is treated

4. The Lattice Model

We imagine N_1 particles of type 1, etc. arranged along a line (actually, in a circle, because end effects are of no interest here). There is an interaction energy w_{ij} between two nearest neighbor particles of types i and j respectively. The N_i and N are fixed. The canonical partition function is

$$Q_N(N_2, N_3) = \Pi_{N_i!} \sum \exp - \beta w_{i_1 i_2} \exp - \beta w_{i_2 i_3} \cdots \exp - \beta w_{i_{N-1} i_N} \quad (18)$$

The sum in this equation is extended over all arrangements of the particles with the restriction that $\sum N_j = N$. This partition function may be evaluated in several ways, the matrix method^{11,12} and the sequence generating function method^{13,14} being perhaps the most common. We shall use a method that brings out the similarities to the continuum model more clearly.

Multiply eq 18 by $\bar{\lambda}_1^{N_1} \bar{\lambda}_2^{N_2} \bar{\lambda}_3^{N_3}$ and sum over all N_1, N_2, N_3 . $\bar{\lambda}_1$ is not the activity of component 1, but is an arbitrary number at the moment; it will evolve into λ_1 at the pole of F

$$F(\bar{\lambda}_1, \bar{\lambda}_2, \bar{\lambda}_3) = \sum_{N_1, N_2, N_3} \bar{\lambda}_1^{N_1} \bar{\lambda}_2^{N_2} \bar{\lambda}_3^{N_3} Q_N \quad (19)$$

This sum will not converge if $\bar{\lambda}_1 \geq \lambda_1$. Hill has shown¹⁵ this for the two component case and the three-component case is completely analogous. Nevertheless, for sufficiently small $\bar{\lambda}_1$, the sum exists. Given the form of Q_N eq 18, F can be put in the form of the trace of a matrix, just as in the continuum case. In fact

$$F(\bar{\lambda}_1, \bar{\lambda}_2, \bar{\lambda}_3) = \text{Tr}(1 - \mathbf{K})^{-1} \quad (20)$$

where the matrix elements K_{ij} are given by

$$K_{ij} = (\lambda_i \lambda_j)^{1/2} e^{-\beta w_{ij}} \quad (21)$$

The matrix $1 - \mathbf{K}$ is singular, and hence does not possess an inverse, when $|1 - \mathbf{K}| = 0$. This will occur when $\bar{\lambda}_1 = \lambda_1$. Thus, the equation $|1 - \mathbf{K}| = 0$ determines λ_1 as a function of λ_2 and λ_3 . Furthermore, the matrix elements K_{ij} have precisely the same structure as the matrix elements M_{ij} of the matrix \mathbf{M} that occurred in the continuum case, eq 12. The mole fractions can be found similarly as functions of the activities.

It is therefore not necessary to solve these equations for the properties of the lattice model. The solution for the continuum model can be taken over in toto, merely replacing D_{ij} by $\exp[-\beta(2w_{ij} - w_{ii} - w_{jj})]$.

In this section, the pressure plays no role since we are here considering a lattice model. The chemical potential of one of the components (here chosen to be the solvent) plays the role of the variable determining the position of the singularity from the beginning. The equations determining the singularities in the lattice and continuum cases are structurally the same. The difference between the two models is that the Boltzmann factors in the matrix \mathbf{K} for the lattice model take the place of the Laplace transforms in the matrix \mathbf{M} for the continuum case. There is, of course, the trivial difference that there is no translational energy contribution in the lattice case (the Λ factors).

We emphasize that, even though \mathbf{M} and \mathbf{K} have the same formal structure as ratios of binary interaction parameters, they are not identical. The elements of \mathbf{M} are ratios of Laplace transforms of Boltzmann factors; they depend on the pressure, P . The elements of \mathbf{K} are just ratios of "raw" Boltzmann factors. In the next section we shall discuss a specific potential for which \mathbf{M} and \mathbf{K} are the same in the high-density limit.

5. Discussion

The main conclusion of this paper so far is that just stated above: The concentration dependence of the chemical potential

of the solute in a three-component one-dimensional mixture depends on concentration in the same way for a continuum model and for a lattice model of the solution. One need only reinterpret the parameters that determine the coefficients.

The reader whose primary acquaintance with one-dimensional models comes from the study of helix-coil transitions in polymers will have noticed that the transition matrix, \mathbf{M} , which we have used is different from that conventionally used in polymer studies. Our \mathbf{M} is symmetric, whereas the conventional matrix for units with three possible states has the structure

$$\mathbf{M}_{\text{pol}} = \begin{pmatrix} u & av & cw \\ ua & v & bw \\ cu & bv & w \end{pmatrix}$$

where u , v , and w are statistical weights for segments of the polymer and a , b , and c are weights for starting a new sequence of a different type.

\mathbf{M}_{pol} and \mathbf{M} are similar in the matrix algebra sense of the word. That is, there exists a matrix \mathbf{P} such that $\mathbf{M}_{\text{pol}} = \mathbf{PMP}^{-1}$. The matrix \mathbf{P} is just $\text{diag}(u^{1/2}, v^{1/2}, w^{1/2})$. Since the matrices are similar, it does not matter which is used in evaluating the trace. For the lattice version of the fluid problem, we have found the symmetric form more convenient. The difference between the two formulations is solely a matter of how the bookkeeping is arranged. Different physical interpretations of the one-dimensional model may suggest different ways of expressing the transfer matrix, but the basic underlying mathematics is not altered by these (unless new physical interactions are introduced).

To understand the implication of these formal results, it is useful to pick a potential energy function to represent the interaction of the particles. The simplest useful potential is the square well

$$V(x) = \begin{cases} \infty & 0 \leq x < \sigma \\ -\epsilon & \sigma \leq x \leq \sigma + \tau \\ 0 & x > \sigma + \tau \end{cases} \quad (22)$$

We have omitted the subscripts on V , σ , τ , and ϵ for the sake of economy of writing. We further assume that the hard cores are additive, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$. If we were to consider additive hard cores alone, without the attractive bowls, the problem would be trivial, for additive hard rods mix ideally in one dimension. Their entropy of mixing is the ideal value and their enthalpy of mixing is zero.

For this potential, ω_{ij} can easily be evaluated from its definition eq 3. Using eq 22 the ω integrals can be written

$$\omega_{ij} = \frac{e^{-\beta P \sigma_{ij}}}{\beta P} [e^{-\beta P \tau_{ij}} + e^{\beta \epsilon_{ij}} (1 - e^{-\beta P \tau_{ij}})] \quad (23)$$

We need only concern ourselves with the quantities inside the square brackets in eq 23 since the factors outside the brackets will cancel out when the D 's are formed from the ω 's. If we want our one-dimensional system to simulate liquid densities, then $\beta P \sigma \gg 1$. Furthermore, the width of the attractive bowls will be of the same order of magnitude as the hard cores, so $\beta P \tau \gg 1$. So it will be a very good approximation to set $\omega_{ij} = \exp(\beta \epsilon_{ij})$. Remember that $-\epsilon$ is the depth of the potential well, so ϵ is positive.

Even if one does not make this approximation, it is clear from the foregoing that the chemical potential of the solute does not depend on the hard core diameters of the particles but only on the depth and breadth of the potential well. This property will certainly not carry over to three-dimensional models. It is a

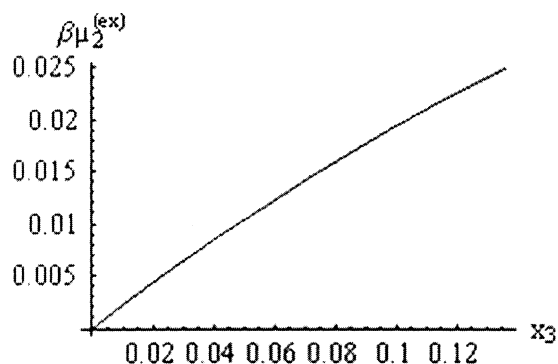


Figure 1. Excess chemical potential of solute versus mole fraction of cosolvent. The potential between particles is the square well potential specified in the text. The parameters used are $\beta P\sigma_{11} = 10$, $x_3 = 0.001$, $D_{12} = 1.28$, $D_{13} = 1.28$, $D_{23} = 1.29$. This figure depicts the numerical solution of the equations of section 3, not just the linear terms.

deficiency of the one-dimensional model as a proxy for a three-dimensional solution.

It is known that a one-dimensional system of hard rods of varying core lengths (with additive core lengths) forms an ideal solution.⁴ Of course, the system is not ideal from the point of view of the equation of state, but that is not relevant to its mixing properties. This result holds independently of the relative core lengths of the components and is a topological peculiarity of one dimension; such a conclusion does not hold for hard spheres in three dimensions. This is an additional reason that the one-dimensional model is not completely satisfactory as a proxy for a real three-dimensional system.

Another feature of the one-dimensional model is that there are only two parts of the solute particle (component 2) that can interact with the solvent or cosolvent, those at the ends of the molecule. This is independent of the size of the solute. For a three-dimensional model, however, the interactions of a large solute with the solvent ought to be roughly proportional to the surface area of the solute, i.e., roughly to the 2/3 power of its radius. This is another deficiency of the one-dimensional model.

Of course, one-dimensional systems with forces of finite range do not undergo a liquid–gas transition as do three-dimensional systems. Since we are working well away from any phase transition region, it is not likely that this discrepancy is of importance for our purposes.

Experimentally it is observed that μ_2 depends linearly on x_3 over a very wide concentration range of component 3. As stated in the Introduction, this can be as much as 6 molar in cosolvent for proteins in water with various cosolvents. It is therefore of interest to see if our computations predict a linear dependence. Equation 17 certainly does, but this does not demonstrate anything. This equation only gives the linear terms in a series expansion and does not tell us how large the higher order terms are. We must carry out the program of section 3 numerically.

We have done this for a typical value of the D parameters. The result is shown in Figure 1. It can be seen that μ_2 is quite

linear in x_3 at least up to $x_3 = 0.1$ though there is a slight curvature to the plot. This corresponds to a solution with $c_3 \approx 5.5$ M in water if the system were three-dimensional. So, in this respect, the one-dimensional model mimics experiment on three-dimensional systems quite well.

The model makes a definite and simple prediction about how the initial slope of the chemical potential versus x_3 plot depends on the intermolecular potentials. The interesting thing about this prediction is that all of the parameters on which it depends are obtainable from calculations on the three possible two-component systems available from the three species. Of course, it is not possible to test this prediction experimentally, since one-dimensional fluids do not exist. On the other hand, it would be worthwhile testing eq 17 for real three-dimensional solutions. The formula would have to be regarded as an empirical formula; we certainly do not claim to have derived it for three-dimensions, nor even to have provided a plausibility argument. It is merely a suggestion.

On the other hand, eq 17 predicts that the limiting slope of μ_2^{ex} versus x_2 curve as $x_2 \rightarrow 0$ in a binary system with component 1 should be the same as the limiting slope of μ_1^{ex} versus x_1 in the same binary system as $x_1 \rightarrow 0$. This occurs because $D_{12} = D_{21}$. Analogous relations hold for the other two possible binary systems. This is not true in three dimensions in general, so that our suggestion can have only limited usefulness at best.

The main conclusion of this paper is that the chemical potential of a solute in a three-component one-dimensional continuum system and a one-dimensional lattice system depend on composition in precisely the same way. It is only necessary to reinterpret the parameters occurring in the two cases. In the high-density limit for the fluid system, the parameters even have the same physical meaning in terms of intermolecular interactions in the two cases.

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