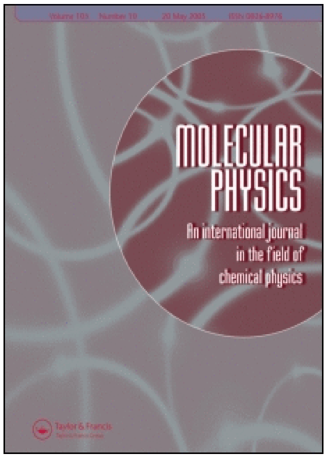

Molecular Physics

An International Journal in the Field of Chemical Physics

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713395160

Excess free energy of different water models computed by Monte Carlo methods

Mihaly Mezei [a]
[a] Chemistry Department, Hunter College of the City University of New York. New York, N.Y.. U.S.A.

Online Publication Date: 20 December 1982
To cite this Article: Mezei, Mihaly , (1982) 'Excess free energy of different water models computed by Monte Carlo methods', Molecular Physics, 47:6, 1307 - 1315
To link to this article: DOI: 10.1080/00268978200100992
URL: http://dx.doi.org/10.1080/00268978200100992

MOLECULAR PHYSICS, 1982, VOL. 47, NO. 6, 1307–1315

Excess free energy of different water models computed by Monte Carlo methods

by MIHALY MEZEI

Chemistry Department, Hunter College of the City University of New York,
695 Park Avenue, New York, N.Y. 10021 U.S.A.

(*Received* 13 *April* 1982 ; *accepted* 3 *August* 1982)

The excess free energy and entropy of three water models (ST2, MCY and SPC) are determined using Monte Carlo thermodynamic integration, with soft spheres as a reference system. The method used is compared with two other methods, the umbrella sampling and the overlap ratio methods. A simple self check for the umbrella sampling method is proposed.

1. INTRODUCTION

Computation of the excess free energy from computer simulations of liquids is a challenging computational task, since the computation of the partition function or an equivalent is required. Several successful calculations have been reported for simple liquids. The problem, however, appears to be more difficult for associated liquids, and the appropriate methodology is not yet well established.

In this paper we present a consideration of three methods for the computation of the excess free energy : thermodynamic integration (in the following : TI) [1], umbrella sampling (in the following : US) [2] and the overlap ratio method (in the following : OR) [3]. These methods have already been used to calculate the free energy of molecular liquids [3, 4, 5]. New calculations are reported here using TI.

Calculations will be presented for three different pairwise additive water models : The *ab initio* MCY model [6], and the empirical ST2 [7] and SPC [8] models.

In the following section the basic difficulty in computing the free energy is reviewed and brief descriptions of the TI, US and OR methods are provided. The calculations are described in § 3. The results are presented and discussed in § 4.

2. BACKGROUND

Monte Carlo computer simulation of molecular liquids has up to this point been focused on the calculation of internal energy and other average properties of the system by the Metropolis method. The success of the Metropolis method for computing ensemble averages of the internal energy and related properties

0026–8976/82/4706 1307 $04·00

is based on two special features of the method : (1) the sampling is successfully reduced to the region of the configuration space where the energy is relatively low, fluctuating around its ensemble average and (2) the need to compute the partition function is eliminated. One finds the computation of heat-capacity to be already more difficult by the Metropolis method, since it requires adequate sampling of a larger region of the configuration space than the computation of the energy. The difficulty increases further in free energy calculations, for several reasons. First of all, the basic equation of statistical mechanics gives the Helmholtz free energy as

$$A = -kT \ln Z, \tag{1}$$

where Z is the partition function, T is the temperature and k is the Boltzmann constant. Direct calculation of Z converges notoriously slowly and the motivation of the Metropolis method was the elimination of the need to calculate Z in the determination of U, C_V, etc. Thus, other routes are needed.

Simple algebraic manipulation shows that

$$\int_V \exp(-U(X)/kT)\, dX = V^N / \langle \exp(+U/kT) \rangle, \tag{2}$$

where $U(X)$ is the internal energy of the configuration X, N is the number of particles in the system, V is the volume of the system and $\langle\ \rangle$ denotes the Boltzman average. The free energy problem can thus be reduced to the computation of an ensemble average, for which the Metropolis method can be used, at least in principle. In practice, however, the Metropolis limitation of the sampling to a small region of the configuration space makes it unsuitable for free energy calculations by (2), as argued very convincingly by Owicki and Scheraga [9] in their critique of the calculation performed by Sarkisov, Dashevsky and Malenkov [10]. In a successful use of (2), it would be necessary to sample the configuration space from energy values that are representative of the system under consideration to energy values that are representative of the reference system configurations, in this case a system with uniform distribution of configurations (that would correspond to infinite temperature). Thus, the key to successful calculation of the free energy is the sampling of a much larger part of the configuration space than the Metropolis method supports.

An alternative approach is the use of the (T, V, μ) ensemble [11, 12] or the closely related particle insertion method [13, 14]. Unfortunately, they require adequate sampling of configurations with large enough cavities to fit in a new molecule and thus break down as the density of the system is increased. A technique is available to make more efficient use of existing cavities in a (T, V, μ) simulation and thereby extending the density range where the method is usable [15], but no way was found yet to increase the occurrence of these larger cavities. The (T, V, μ) ensemble approach, however, may provide efficiently a reference state that is close to the state under investigation [16].

Recent reviews of the several approaches that have been put forward for the calculation of the excess free energy using Monte Carlo methods can be found in Refs. [17, 18]. In the remaining part of this section we limit ourselves to the presentation of the three methods mentioned in the introduction and comment on their relative strength and weaknesses.

2.1. *Thermodynamic integration*

The TI method obtains the excess free energy difference between two states of a system as an integral over a coupling parameter :

$$\begin{aligned}\Delta A' &= A'_1 - A'_0\\ &= -kT\left(\ln \int_V \exp\left(-U_1(X)/kT\right) dX - \ln \int_V \exp\left(-U_0(X)/kT\right) dX\right)\\ &= -kT \int_0^1 d\xi\,(d/d\xi) \ln \int_V \exp\left(-U_\xi(X)/kT\right) dX\\ &= \int_0^1 d\xi \langle \Delta U\rangle_\xi, \end{aligned} \tag{3}$$

$$\Delta U = U_1 - U_0, \tag{4}$$

$$U_\xi = (1-\xi)U_0 + \xi U_1 \tag{5}$$

where the subscripts 0 and 1 refer to the two different states, state 0 being called the ‘ reference state ’ and $\langle\ \rangle_\xi$ denotes a Boltzmann average with potential energy U_ξ. The integration is carried out numerically and each point is a result of a separate Monte Carlo run. It should be stressed that in each calculation only the expectation value of the energy is required, which is known to be the fastest converging quantity [19].

There is little accumulated experience for the determination of the number of quadrature points needed. The minimum number of points is three since $\langle \Delta U\rangle_\xi$ is not a linear function of ξ. A helpful fact is that the integrand $\langle \Delta U\rangle_\xi$ is a monotonous function of ξ since straight differentiation shows that

$$d\langle \Delta U\rangle_\xi / d\xi = -(\langle \Delta U^2\rangle_\xi - \langle \Delta U\rangle_\xi^2)/kT \leqslant 0. \tag{6}$$

In the previous calculation from this laboratory [4] of the excess free energy difference between the MCY water at 25°C and an ideal gas at the liquid density an 8-point gaussian quadrature was used since $\langle \Delta U\rangle_\xi$ was varying strongly near $\xi = 0$. For the problems studied here fewer points should be sufficient since here we are integrating between much more similar states and thus $\langle \Delta U\rangle_\xi$ varies over a relatively narrow range.

2.2. *Umbrella sampling*

The US method is based on the following expression for the excess free energy difference between two states of a system [2, 17] :

$$\begin{aligned}\Delta A' &= -kT \ln \langle \exp(-\Delta U/kT)\rangle_0\\ &= -kT \ln \langle \exp(+\Delta U/kT)\rangle_1. \end{aligned} \tag{7}$$

Notice that the second expression in (7) is a generalization of (2). For reasons discussed in relation with (2), the application of (7) for Monte Carlo evaluation is limited to rather small differences. Basically, the range of ΔU sampled in a practical realization of the Metropolis Monte Carlo method is much smaller than the range that significantly contributes to the integral in (7). To overcome this, the US method changes the distribution from which the Markov chain is sampled in a direction that ensures the sampling of regions of the configuration space that would have not have been sampled by the conventional Metropolis Monte Carlo method. In this application, the sampling distribution is chosen as $w(\Delta U) \exp(-U_0/kT)$ where $w(\Delta U)$ is a weighting function chosen to selectively give larger weight to configurations with energy that is much different from the average energy of the reference state. Using the weighted distribution, the excess free energy difference can be obtained as

$$\Delta A' = -kT \ln \langle \exp(-\Delta U/kT)/w(\Delta U)\rangle_w / \langle 1/w(\Delta U)\rangle_w, \qquad (8)$$

where the subscript w refers to the change in the distribution sampled by the Markov chain. Torrie and Valleau [2] used $w(\Delta U)$ in a tabular form. A simpler, but not necessarily optimal choice was described recently by Scott and Lee [5]. The presence of $\langle 1/w(\Delta U)\rangle_w$ in (8) points to the limitation of the US method : In order to sample a large enough range for ΔU one needs a w that varies several orders of magnitudes over its range but this in turn will generate progressively larger errors in $\langle 1/w(\Delta U)\rangle_w$.

If the systems 1 and 0 are very different, the above limitations on the choice of w necessitates the computation of $\Delta A'$ in several steps. At each step the excess free energy difference between a system with potential energy U_{ξ_i} and $U_{\xi_{i+1}}$ is computed with the US method. It follows that the multistage US calculation can also provide the quadrature points for the integral in (3) at $\xi_0 = 0$, $\xi_1, \ldots, \xi_k = 1$. Thus, a multistage US calculation can also provide the required quadrature points for TI.

There is an opportunity for a self check in a multistage TI calculation that has not been pointed out before. By simple manipulation of terms and recognizing that $U_{\xi_i + \Delta\xi} - U_{\xi_i} = \Delta U \Delta\xi_i$, it can be shown [20] that

$$\langle U_1\rangle_{\xi_{i+1}} = \langle U_1 \exp(-\Delta U \Delta\xi_i/kT)\rangle_{\xi_i} / \langle \exp(-\Delta U \Delta\xi_i/kT)\rangle_{\xi_i}, \qquad (9)$$

where $\Delta\xi_i = \xi_{i+1} - \xi_i$. Since a TI run with U_{ξ_i} as the reference state should sample adequately configurations with both $U_1 \approx \langle U_1\rangle_{\xi_i}$ and $U_1 \approx \langle U_1\rangle_{\xi_{i+1}}$, (9) can be expected to hold to a good precision and the value of $\langle U_1\rangle_{\xi_{i+1}}$ obtained from the U_{ξ_i} run using (9) should agree with the value obtained from the $U_{\xi_{i+1}}$ run using its definition. If they do not agree the sampling was certainly inadequate and the result is in error.

The above argument shows the relative strengths of the two methods : The US is more efficient than the TI in covering the whole range of the coupling parameter and in fact one US run can be used to obtain more than one quadrature points for the TI by applying (9) to U and arbitrary $\Delta\xi$:

$$\langle \Delta U\rangle_{\xi+\Delta\xi} = \langle \Delta U \exp(-\Delta\xi \Delta U/kT)\rangle_{\xi} / \langle \exp(-\Delta\xi \Delta U/kT)\rangle_{\xi}. \qquad (10)$$

On the other hand, the possibility of interpolation/extrapolation of the integrand in (3) may allow the computation of $\Delta A'$ without sampling the whole range of ΔU. A further advantage of the TI is that relatively short runs are sufficient since only the expectation value of a rapidly converging quantity is needed.

In summary, for systems that do not differ too much from each other, one or two US can provide reliable results as opposed to at least three or more TI calculations and is therefore the better choice. The same is true for systems that are separated by a phase transition, since at quadrature points near the phase transition the convergence of the run would drastically worsen. On the other hand, if the systems are different enough that 3 or more US runs are needed, it is more likely that TI will provide more reliable results with less intermediate states, shorter runs and less human effort as well.

2.3. *The OR method*

The recently developed OR method combines the ideas of the US with those of Bennett [21]. It is based on the following equation that is valid for certain potentials [3] :

$$\exp(\Delta A'/kT) = \exp(u) f_{U_0}(u)/f_{U_1}(u), \tag{11}$$

where u is chosen to be an energy value that is sampled in simulations run by both U_0 and U_1 and $f_{U_i}(u)\,du$ is the fraction of the configurations that have energy $u' \epsilon [u, u+du]$ in the respective simulations. An interesting suggestion is given for a weighting function to extend the energy range covered by a simulation. A recent work [22] presents extensive calculations on liquid nitrogen and provides numerical comparison with Bennett's method.

The ensemble average of the weighting function used is not needed, which is an advantage over the US method. However, if the two systems are too different, again intermediate states have to be used. Furthermore, the OR method also requires the calculation to cover fully the intermediate states and in particular overlapping regions of two neighbouring states have to be sampled with rather high precision. In our opinion, this latter is a drawback since in general the uncertainties are the greatest in these regions. However, because of these opposing arguments, actual comparisons are needed before any firm conclusions can be drawn.

3. CALCULATIONS

Liquid water is considered the prototype associated liquid in Monte Carlo methodology as witnessed by the numerous simulations published on this system. Free energy calculations on liquid water have been performed using (2) [10], TI [4], US [5] and even in the (T, V, μ) ensemble using a system of only four water molecules [23]. The present calculation of the excess free energy of the MCY water uses a better choice of reference system as well as a larger cutoff (7·0 Å instead of 6·2 Å) than [4] and is used as the basis for calculating the excess free energy of the other two water models.

3.1. *Thermodynamic integration calculations*

The excess free energy of the MCY water was calculated using soft spheres with $\rho(\epsilon/kT)^{1/4} = 0{\cdot}74$ as the reference state (in the following : SS) [24]. The MCY water then was used as a reference state for the calculation of the excess free energy of both the ST2 and SPC waters. This is a logical choice of intermediate state since the radial distribution functions show that the MCY water is less structured than either the ST2 or SPC waters.

All systems included 64 molecules under face centred cubic periodic boundary conditions, at a density of 0·997 g cm^{-3} and a temperature of 250°C. This system size implies that the distance between a molecule and its periodic image is always greater than 14·0 Å. The potential cutoff is at 7·0 Å.

Table 1. Free energy and entropy results. (*a*) Energy is in kJ mol^{-1}. (*b*) entropy is in JK^{-1} mol^{-1}. (*c*) Experimental results are from [10]. (*d*) SS data includes long range correction. (*e*) The ST2, MCY and SPC results used a 7·0 Å cut-off.

	SS	MCY	ST2	SPC	Exp.
$\Delta A'$		−34·02 ± 0·25	−6·02 ± 0·21	−1·46 ± 0·46	
A'	17·42	−16·57	−22·59	−18·45	−20·02
$\langle U\rangle$	8·89	−35·98	−44·02	−42·59	−41·4
S'	28·6	−65·3	−72·0	−81·2	−58·4

Table 2. The values of $\langle \Delta U\rangle_{\xi_i}$ at the quadrature points of the thermodynamic integration. The integral is approximated by the expression $\sum_{i=1}^{3} c_i\langle \Delta U\rangle_{\xi_i}$.

ξ_i	c_i	$\langle \Delta U\rangle_{\xi_i}$ ST2–MCY	$\langle \Delta U\rangle_{\xi_i}$ SPC–MCY
0·11270160	5/18	−3·47 ± 0·13	7·32 ± 0·63
0·5	4/9	−5·86 ± 0·13	−1·77 ± 0·38
0·88729833	5/18	−8·91 ± 0·21	−9·83 ± 0·38

Table 3. The values of $\langle \Delta U\rangle_{\xi_i}$ at the quadrature points of the thermodynamic integration. The integral is approximated by the expression $\sum_{i=1}^{5} c_i\langle \Delta U\rangle_{\xi_i}$.

ξ_i	c_i	$\langle \Delta U\rangle_{\xi_i}$ MCY–SS
0·046910	0·118463	51·84 ± 0·63
0·230765	0·239314	45·69 ± 0·21
0·5	0·284444	36·69 ± 0·13
0·769235	0·239314	25·06 ± 0·13
0·953089	0·118463	4·06 ± 0·21

All three calculations employed gaussian quadrature [25]. The number of quadrature points was five for the MCY–SS calculation and three for the water–water calculations. We estimate that the relatively small number of quadrature points introduces only an error of 0·4 kJ mol^{-1} or less, since the differences between the water models are relatively small (see tables 2 and 3) and $\langle \Delta U\rangle_\xi$ is a monotonic function of ξ (see (6)). The lengths of the runs were 500–700 K, after 200–300 K equilibration.

3.2. *Umbrella sampling calculations*

We attempted the calculation of $\Delta A'$ between the ST2 and MCY waters with the US method as well. The choice of the weighting function, however, proved to be a much more difficult task than that encountered by Torrie and Valleau for the Lennard-Jones fluid. It was found that the effect of the introduction of

$w(\Delta U)$ (used in tabular form with linear interpolation, following Torrie and Valleau) was mostly to shift the range of the ΔUs sampled but it has proven to be very difficult to increase this range. The $\Delta A'$ values obtained using different $w(\Delta U)$s showed large variations, even when a three stage US was attempted. In hindsight, this appears to be reasonable since the topology of the subspace of the configuration space with $\Delta U \epsilon [u, u+du]$ is necessarily more complex than the topology of the subspace with $U' \epsilon [u, u+du]$. It is possible, that the half-US method of Scott and Lee [5] might have proven successful. However, for reasons given in § 2.2 we felt that the number of half-US calculations required would exceed the number of quadrature points necessary for the TI at a given level of accuracy.

4. Results and discussion

The free energy and entropy results are collected in table 1. The entropies are computed from the formula

$$S' = (A' - \langle U \rangle)/T. \tag{12}$$

The $\langle U \rangle_\xi$ values were obtained from previous computer simulations. Since no simulations were performed using the same system size and boundary condition combination, previous results were corrected for the difference in the pair potential cutoff (see table 1.) from calculations run with larger cutoffs.

The $\langle \Delta U \rangle_\xi$ values at the quadrature points are listed in tables 2 and 3. The accompanying error estimates are based on the method of batch means due to Blackman and Tuckey [26] and independently to Wood [27].

The effect of the length of the runs has been studied from two different angles in the ST2–MCY calculation. For one of the runs, the calculation was continued for another 840 K. The value obtained remained well within the error bounds established by the first 700 K. We also examined the results that were obtained by runs of shorter length. The $\Delta A'$ values obtained using 300 K and 500 K long runs were $-5{\cdot}94 \pm 0{\cdot}17$ kJ mol^{-1} and $-5{\cdot}98 \pm 0{\cdot}21$ kJ mol^{-1}, respectively. This shows that the TI calculations can be performed using rather short runs without noticeable loss of precision.

It has been recognized earlier [2, 17] that for the computation of the free energy relatively small systems are sufficient. For example, 32 Lennard-Jones particles were sufficient to compute accurately the free energy of the fluid. Similar behaviour was found recently for liquid nitrogen [22]. Thus it can be expected that the relatively small system size used here is adequate to compute the excess free energy of these water models with a 7·0 Å cutoff.

The adequacy of the 7·0 Å cutoff to represent liquid water is a separate problem and is relevant to the computation of any property, not just the free energy. Most (T, V, N) ensemble calculations reported use cutoffs of 7·5–7·75 Å for the MCY water and 8·46 Å or less for the ST2 water. It is a positive feature of TI that it is based on the computation of energy-type quantities, and thus any technique that estimates the contribution of the long range tail of the potential to the internal energy can be applied independently to each of the quadrature points and thereby provide an estimate of the long range contributions to the excess free energy as well. No correction of this kind was attempted in this work.

The previous TI calculation [4] that used the ideal gas at liquid density as a reference state gave the excess free energy of the MCY water as $-18{\cdot}03 \pm 0{\cdot}29$ kJ mol^{-1} as opposed to $-16{\cdot}57 \pm 0{\cdot}25$ kJ mol^{-1} from the present calculation. The difference between the previous and present result is more than the indicated error-bounds allow. The larger cutoff used in the present work should make the excess free energy more negative, thus it can not account for the difference. The likely sources of this discrepancy are : (1) The extrapolation of the strongly varying $\langle \Delta U \rangle_\xi$ to $\xi \to 0$ in the previous calculation that was implicit in the use of the gaussian quadrature and (2) the extension of the repulsive part of the MCY potential with a simple $1/R_{00}{}^{12}$ term for $R_{00} < 4{\cdot}5$ a.u. For these reasons, the value obtained in the present paper is considered to be the more accurate.

The comparison of the entropies shows that all three water models studied are more structured than real water. The relatively large difference between the ST2 and SPC waters is somewhat surprising since the comparison of the O–O, O–H and H–H radial distribution functions [28, 29] would suggest a similar degree of structure in these water models. The agreement with the experimental value is best for MCY water.

This research was supported by NIH Grant No. 5-R01-GM-24914 and a CUNY Faculty Research Award. Fruitful discussions with Professor D. L. Beveridge are greatly acknowledged.

REFERENCES

[1] KIRKWOOD, J. G., 1968, *Theory of Liquids*, edited by B. J. Alder (Gordon & Breach).
[2] TORRIE, G., and VALLEAU, J. P., 1977, *J. comput. Phys.*, **23,** 187.
[3] JACUCCI, G., and QUIRKE, N., 1980, *Molec. Phys.*, **40,** 1005.
[4] MEZEI, M., SWAMINATHAN, S., and BEVERIDGE, D. L., 1978, *J. Am. chem. Soc.*, **100,** 3255.
[5] SCOTT, H. L., and LEE, C. Y., 1980, *J. chem. Phys.*, **73,** 4591.
[6] MATSUOKA, O., CLEMENTI, E., and YOSHIMINE, M., 1976, *J. chem. Phys.*, **64,** 1351.
[7] STILLINGER, F. H., and RAHMAN, A., 1974, *J. chem. Phys.*, **60,** 1545.
[8] BERENDSEN, H. J. C., POSTMA, J. P. M., VAN GUNSTEREN, W. F., and HERMANS, J., 1981, *Jerusalem Symposia on Quantum Chemistry and Biochemistry*, edited by B. Pullman, (Reidel). A potential with the same functional form was developed earlier by JORGENSEN, W. L., 1981, *J. Am. chem. Soc.*, **103,** 335.
[9] OWICKI, J. C., and SCHERAGA, H. A., 1977, *J. Am. chem. Soc.*, **99,** 7403.
[10] SARKISOV, G. N., DASHEVSKY, V. G., and MALENKOV, G. G., 1974, *Molec. Phys.*, **27,** 1249.
[11] ADAMS, D. J., 1975, *Molec. Phys.*, **29,** 311.
[12] NORMAN, G. E., and FILINOV, V. S., 1969, *High Temp. USSR*, **7,** 216.
[13] WIDOM, B., 1963, *J. chem. Phys.*, **39,** 2808.
[14] ROMANO, S., and SINGER, K., 1979, *Molec. Phys.*, **37,** 1765.
[15] MEZEI, M., 1980, *Molec. Phys.*, **40,** 901.
[16] Referee's comment.
[17] VALLEAU, J. P., and TORRIE, G. M., 1977, *Modern Theoretical Chemistry: Statistical Mechanics*, Part A, edited by B. J. Berne (Plenum Press).
[18] QUIRKE, N., 1980, *Proceedings of the NATO Summer School on Superionic Conductors*, Odessa, Denmark.
[19] MEZEI, M., SWAMINATHAN, S., and BEVERIDGE, D. L., 1979, *J. chem. Phys.*, **71,** 3366.
[20] BARKER, J. A., and HENDERSON, D., 1975, *Rev. mod. Phys.*, **48,** 587.
[21] BENNETT, C. H., 1976, *J. comput. Phys.*, **22,** 245.
[22] QUIRKE, N., and JACUCCI, G., 1982, *Molec. Phys.*, **45,** 823.

[23] Makovskij, N. N., 1978, Preprint No. ITF-78-33P, Institute of Theoretical Physics, Kiev, U.S.S.R.

[24] Hoover, W. G., Ross, M., Johnson, K. W., Henderson, D., Barker, J. A., and Brown, B. C., 1970, *J. chem. Phys.*, **52**, 4931.

[25] Margenau, H., and Murphy, G. M., 1956, *The Mathematics of Physics and Chemistry*, Vol. I (Van Nostrand).

[26] Blackman, R. B., and Tuckey, J. W., 1958, *The Measurement of Power Spectra* (Dover). Blackman, R. B., 1965, *Data Smoothing and Prediction* (Addison-Wesley).

[27] Wood, W. W., 1968, *Physics of Simple Liquids*, edited by H. N. V. Temperley, F. S. Rowlinson and G. S. Rushbrooke (North-Holland).

[28] Mezei, M., and Beveridge, D. L. (to be published).

[29] Beveridge, D. L., Mezei, M., Mehrotra, P. K., Marchese, F. T., Ravishanker, G., Thirumalai, V., and Swaminathan, S., 1982, *Advances in Chemistry*, edited by J. M. Haile and G. A. Mansoori (American Chemical Society, Washington D.C.).