

RISM calculation of the structure of liquid acetonitrile†

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The RISM equation is used to study the local structure of acetonitrile. The theoretical calculations predict neutron and X-ray scattering structure factors that are in good agreement with experiment. The following conclusions are drawn from this study. (1) Dipole-dipole interactions play, at most, a minor role in forming the structure of liquid acetonitrile. (2) Even though dipole-dipole interactions are not very significant, there are strong orientational correlations between neighbouring molecules. (3) These pair correlations are similar to those found in liquid carbon disulphide (a non-polar fluid), and are determined primarily by the molecular shape. (4) The accuracy attainable in present neutron diffraction determinations of liquid structure must be improved by an order of magnitude for the effects of dipole-dipole interactions to be discernible in such experiments.

1. INTRODUCTION

Recent scattering experiments performed on liquid acetonitrile [1] and deuterated acetonitrile [2] provide a test of our simple picture of molecular liquids [3, 4]. The CH_3CN molecule has a large electric dipole moment, and we have expressed the belief that dipole-dipole interactions between pairs of molecules are of little consequence in determining the microscopic structure of liquids [5].

The physical basis for this belief is simple. Liquids are very dense fluids (assuming that the thermodynamic state under consideration is outside the critical region). Since the density is high, molecules tend to be very close to their neighbours. Thus, the energetics of displacing a molecule will be dominated by the short-range, quickly varying portions of the intermolecular potential. These short-range interactions should dominate the local arrangements of molecules in a liquid. The effects of slowly varying interactions are those of a mean field, and they play a simple but important role in the thermodynamics. For example, attractive interactions make the liquid densities stable at a pressure of 1 atm, but once the dense fluid is stable, these mean-field interactions should have little effect on the local intermolecular structure of a liquid.

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Dipole-dipole interactions are, by definition, slowly varying interactions. Their functional form becomes quickly varying only at short distances, but at short distances the multipole expansion from which these interactions arise is not valid. It is improper to attribute a physical meaning to dipole-dipole (or quadrupole-quadrupole) potentials that are artificially extrapolated to short distances. Thus, we cannot imagine why multipole moments are directly relevant to the local intermolecular structures of liquids.

'Quickly varying' interactions are reasonably characterized as those portions of the intermolecular potential that change by more than $2k_B T$ when a pair of molecules is moved a distance of one molecular diameter. For most liquids, such forces are usually repulsive, and these repulsions define the shape of a molecule. Thus, unless we anticipate some unusual associative forces, such as hydrogen bonds, it should be possible to interpret the structure of liquids qualitatively from an understanding of the effects caused by the molecular shapes.

This idea is exploited in the RISM theory, in which molecular shapes (i.e. short-range, quickly varying repulsions) are mimicked by imagining that molecules are composed of hard spheres which are fused together. The equilibrium statistical mechanics for this class of models is solved approximately with the RISM integral equation. A comparison of the RISM results with those of computer simulations [4, 6] indicates that the approximations associated with the integral equation introduce errors no larger than about 10 per cent. The RISM theory has been used to interpret scattering experiments on several liquids [3, 4, 7-9]. Most recently, the liquids benzene [7], carbon disulphide [8], and carbon tetrachloride [9] have been examined. In each case, hard spheres with standard van-der-Waals radii could be used to represent the various atoms in the molecules. The RISM equation for these models predicts neutron and X-ray structure factors that are in near-quantitative agreement with the experimental structure factors. Thus, these studies indicate that our simple picture of the structure of non-associated liquids is correct to within 10 per cent—the accuracy of the RISM equation. Of course, C_6H_6 , CS_2 , and CCl_4 possess no dipole moments (although the first two do have large quadrupoles). One might predict the appearance of some qualitative effect when dipoles are present, and this possibility does deserve attention.

For this reason we compare in this paper the predictions of the RISM theory with the results of experiments on liquid acetonitrile.

2. COMPARISON OF RISM THEORY WITH EXPERIMENT

Our RISM picture of a CH_3CN (or CD_3CN) molecule is shown in figure 1. Six overlapping hard spheres are fused together rigidly. The spheres labelled 1, 2 and 3 represent the hydrogen atoms; 4 and 5 are the carbons; and 6 is the nitrogen. The centres of the spheres are located at the average positions of the nuclei. For simplicity, we assume the molecular shape is adequately mimicked by additive sphere diameters. In the absence of a detailed knowledge of intermolecular potentials, these diameters become adjustable parameters in the theory; however, since enough is known about molecules, the adjustability is not very large.

Let σ_H and σ_N denote the van-der-Waals diameters for hydrogen (or deuterium) and nitrogen, respectively. Various estimates have placed the

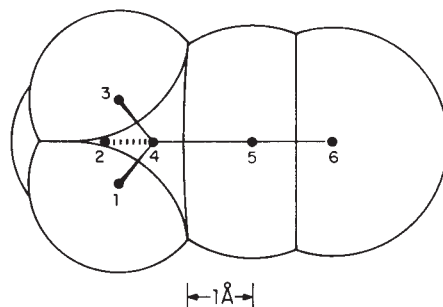


Figure 1. Diagram of the hard-core RISM molecule for acetonitrile. Atoms 1 to 3 are hydrogens, 4 and 5 are carbons, and 6 is the nitrogen. The atom-atom lengths and the hard-core diameters are listed in the text.

van-der-Waals radius of hydrogen atoms at between 1.0 Å and 1.4 Å, 1.1 Å being the most popular. The diameter associated with a nitrogen atom is 3.3 Å when the atom is triply bonded to a neighbouring atom (as occurs, for example, in N_2) [4]. Thus, reasonable values for two of the four RISM parameters for CH_3CN are

$$\sigma_H = 2.2 \text{ \AA}$$

and

$$\sigma_N = 3.3 \text{ \AA}.$$

The remaining two parameters are $\sigma_{C(CH_3)}$ and $\sigma_{C(CN)}$, the van-der-Waals diameters for the carbon atoms associated with the CH_3 and CN groups respectively. In the presence of π bonding, carbon atoms appear to be 3.4 Å in diameter [4, 7, 10]; indeed, the thickness of aromatic rings is 3.4 Å [4, 7, 10], and so $\sigma_{C(CN)}$ should be close to that value. However, $\sigma_{C(CH_3)}$ must be smaller than 3.4 Å, because the carbon atom in the CH_3 group donates all its valence electrons to σ bonds. We believe that $\sigma_{C(CH_3)}$ is probably as small as 3.0 Å because the 1-4 carbon-carbon distance for normal-butane in the stable gauche state is roughly 3.0 Å. Thus, reasonable values for the carbon diameters are

$$\sigma_{C(CN)} = 3.4 \text{ \AA}$$

and

$$\sigma_{C(CH_3)} = 3.0 \text{ \AA}.$$

The above values of σ_H , σ_N , $\sigma_{C(CN)}$ and $\sigma_{C(CH_3)}$ are used in the calculations reported in this paper.

The intramolecular structure of the RISM CH_3CN molecule is determined from the chemical bonding. The molecule is assumed to be rigid, with the following intramolecular atom-atom lengths [1, 2, 10]:

$$L_{14} = L_{24} = L_{34} = 1.10 \text{ \AA},$$

$$L_{15} = L_{25} = L_{35} = 2.11 \text{ \AA},$$

$$L_{16} = L_{26} = L_{36} = 3.16 \text{ \AA},$$

$$L_{45} = 1.47 \text{ \AA},$$

$$L_{46} = 2.62 \text{ \AA},$$

and

$$L_{56} = 1.16 \text{ \AA}.$$

Given this model, the RISM equation provides an approximate method of calculating the atom-atom (i.e. site-site) intermolecular distribution functions

$$g_{\alpha\gamma}(r) = \rho^{-2} \langle N(N-1) \delta(\mathbf{r}_1^{(\alpha)}) \delta(\mathbf{r}_2^{(\gamma)} - \mathbf{r}) \rangle.$$

Here, the pointed brackets denote the equilibrium ensemble average, $\mathbf{r}_i^{(\alpha)}$ is the location of the α th site (i.e. atom) in molecule i , and ρ is the average number of molecules per unit volume, $\langle N/V \rangle$. The RISM equation is the Ornstein-Zernike-like equation

$$\mathbf{h} = \boldsymbol{\omega} * \mathbf{c} * \boldsymbol{\omega} + \rho \boldsymbol{\omega} * \mathbf{c} * \mathbf{h},$$

with the closure relations

$$g_{\alpha\gamma}(r) = 0, \quad r < d_{\alpha\gamma}$$

and

$$c_{\alpha\gamma}(r) = 0, \quad r > d_{\alpha\gamma}.$$

The asterisks in the Ornstein-Zernike-like equation denote convolutions. The matrices \mathbf{h} and \mathbf{c} have elements $g_{\alpha\gamma}(r) - 1$ and $c_{\alpha\gamma}(r)$ respectively. The

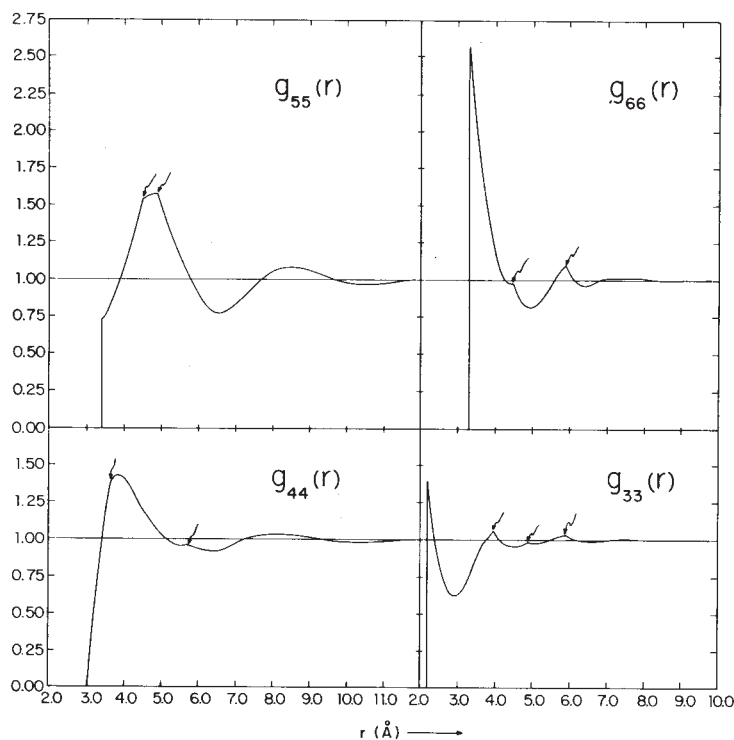


Figure 2. Intermolecular atom-atom distribution functions for liquid acetonitrile, $g_{\alpha\alpha}(r)$, obtained from the RISM equation for the hard-core model depicted in figure 1. The molecular density is 1.15×10^{-2} molecules/ \AA^3 , which corresponds to a pressure of 1 atm and a temperature of 20°C. Note the cusps in the distribution functions, identified by arrows. These are produced by interference between intramolecular and intermolecular lengths [11].

diagonal elements of ω are unity, while the off-diagonal elements are the intramolecular distribution functions (the 'spring' bonds in the interaction site cluster series [11]). Thus, in Fourier transform space,

$$\hat{\omega}_{\alpha\gamma}(k) = (kL_{\alpha\gamma})^{-1} \sin(kL_{\alpha\gamma}).$$

The site-site diameter $d_{\alpha\gamma}$ is the distances of closest approach between atom α in one molecule and atom γ in another. Since we assume that the diameters are additive, these distances are fixed with the assignment of σ_H, σ_N and the two σ_C 's.

We have solved the RISM equation for the model depicted in figure 1. The variational procedure [3] was used with Lowden's FORTRAN programmes [12]. In the calculations, the molecular density was taken to be $\rho = 1.1527 \times 10^{-2} \text{ \AA}^{-3}$, the density of liquid acetonitrile at a pressure of 1 atm and a temperature of 20°C [13]. The atom-atom distribution functions obtained in this way are shown in figures 2 and 3.

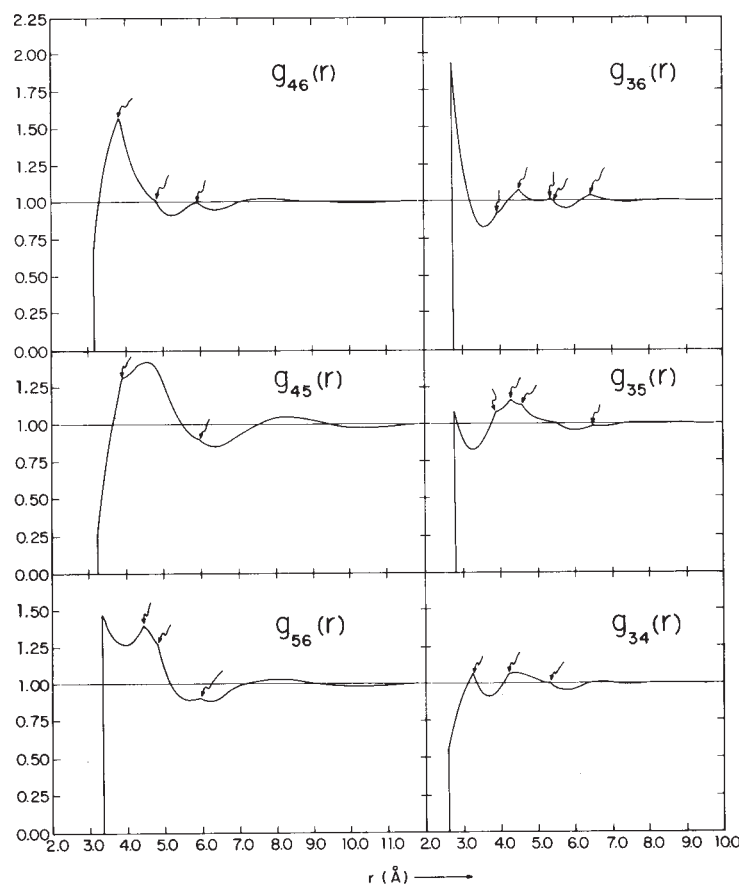


Figure 3. Intermolecular atom-atom distribution functions for liquid acetonitrile, $g_{\alpha\gamma}(r)$, obtained from the RISM equation for the hard-core model depicted in figure 1. The molecular density is $1.15 \times 10^{-2} \text{ molecules/\AA}^3$, which corresponds to a pressure of 1 atm and a temperature of 20°C. Note the cusps in the distribution functions, identified by arrows. These are produced by interference between intramolecular and intermolecular lengths [11].

Scattering experiments can probe the linear combinations of the Fourier transforms of these pair distributions, and can be used to determine the structure factor

$$S(k) = \left[\sum_{\alpha=1}^6 a_{\alpha}^2(k) \right]^{-1} \sum_{\alpha, \gamma=1}^6 a_{\alpha}(k) a_{\gamma}(k) [\hat{\omega}_{\alpha\gamma}(k) + \rho \hat{h}_{\alpha\gamma}(k)],$$

where, for neutron scattering, $a_{\alpha}(k) = b_{\alpha}$ is the coherent neutron scattering length for the nucleus of atom α [14], and for X-ray scattering, $a_{\alpha}(k) = f_{\alpha}(k)$ is the X-ray atomic form factor [15]. Our results for $S(k)$ are plotted in figure 4 along with the experimental results. Also shown for comparison is the ideal gas result,

$$S_{\text{ideal}}(k) = \left[\sum_{\alpha=1}^6 a_{\alpha}^2(k) \right]^{-1} \sum_{\alpha, \gamma=1}^6 a_{\alpha}(k) a_{\gamma}(k) \hat{\omega}_{\alpha\gamma}(k),$$

which arises from intramolecular scattering. The theory attempts to explain the difference between $S_{\text{ideal}}(k)$ and $S(k)$.

From figure 4, we conclude that the simple RISM theory describes the experimental results within the uncertainty of the latter. The agreement between theory and experiment changes quantitatively, but not qualitatively if the

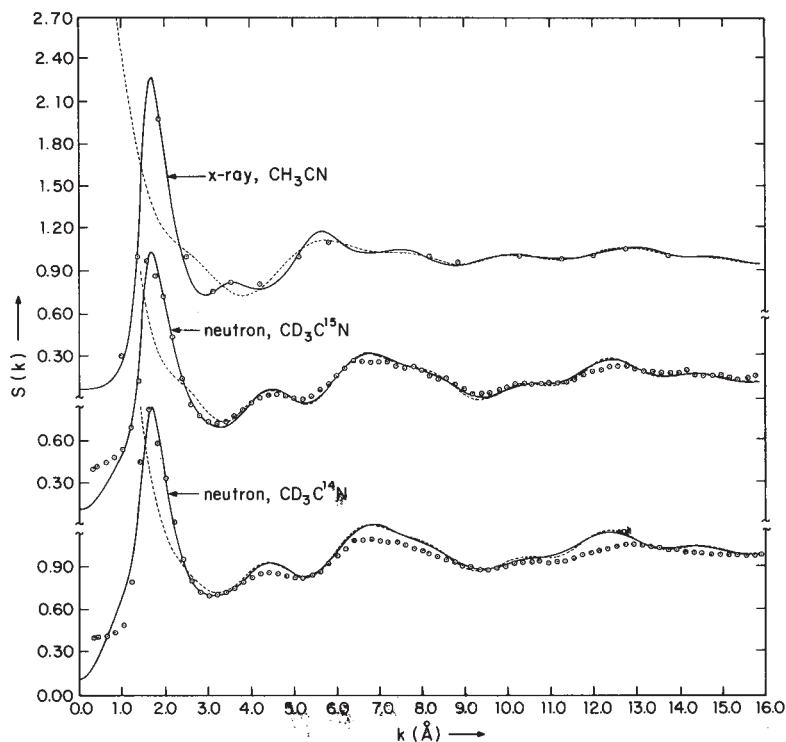


Figure 4. The neutron and X-ray diffraction structure factor for liquid acetonitrile. The solid lines are the $S(k)$ s obtained from the RISM theory, employing the model shown in figure 1. The circles represent the experimentally determined values of $S(k)$ [1, 2]. The dashed line is $S_{\text{ideal}}(k)$. (See the text for definitions.)

values of σ_H , σ_N and the σ_C s are altered by $\pm 0.1 \text{ \AA}$ or $\pm 0.2 \text{ \AA}$ from those listed above. The theoretical results are most sensitive to the choice of σ_H : a shift of 0.2 \AA from 2.2 \AA changes the value of $S(k)$ at the main peak by 8 per cent.

The typical size of the differences between the neutron diffraction determinations of $S(k)$ obtained with different incident wavelengths is roughly 0.05. The actual experimental errors are at least this big and possibly larger. Indeed, the experimental neutron results do not even converge to $S_{\text{ideal}}(k)$ at large k . It is clear that the constant energy approximation introduces serious errors into the data interpretation. Blum and Narten [16] have developed a procedure by which this approximation can be avoided for molecules containing heavy elements, but at present no generally accepted method is available for hydrogenous species.

3. DISCUSSION

Except for when very small wave-vectors are involved, the RISM theory agrees with experiment within the possible uncertainty of the latter. There is no doubt that dipole-dipole potentials and other slowly varying interactions do affect the local structures of liquids. However, as is known from work on simple liquids [5], the effects are relatively small compared to those produced by the short-range repulsions. If one is interested in such details, experimental determinations of $S(k)$ must be performed that are more accurate than those cited in this paper.

The similarity in shape of the CH_3CN molecule pictured in figure 1 and models for CS_2 used in [3] and [8] should imply that the local structures of the liquids CH_3CN and CS_2 resemble one another. Indeed, this expectation is qualitatively correct, as can be verified by comparing the radial distribution function pictured in figures 2 and 3 for sites 5 and 6 with those found for liquid CS_2 [3, 8]. The differences between the two systems is due to the non-sphericity of the CH_3 group in acetonitrile. The additional complexity makes $g_{44}(r)$ more diffuse than $g_{66}(r)$ for CH_3CN , or than $g_{SS}(r)$ for CS_2 . Furthermore, the two peaks and pronounced minimum in $g_{33}(r)$ show that when two CH_3 groups come into contact, the hydrogen atoms must interlock, as is evidenced by the second peak lying at the location of a cusp. Hence, there are two well-resolved intermolecular H-H lengths associated with the same pair of neighbouring molecules. These features in $g_{33}(r)$ are reminiscent of (but not as dramatic as) those in $g_{\text{ClCl}}(r)$ for liquid carbon tetrachloride [3, 9] which indicated an interlocking structure.

One way of interpreting the nature of the correlations between CH_3CN molecules is to form the functions $G_1(R, \theta_R)$ and $G_2(R, \theta)$ described in an earlier paper [4]. In particular, consider the coordinate system shown in figure 5. We neglect the slight deviations from linearity associated with sites 1, 2, and 3 (the hydrogen atoms). Let

$$|\mathbf{r}_1^{(\alpha)} - \mathbf{r}_2^{(\gamma)}| = r_{12}^{(\alpha\gamma)}(R, \theta_R, \theta, \phi), \quad 4 \leq \alpha, \gamma \leq 6,$$

where R , θ_R , θ and ϕ are defined in figure 5. Following the method of [4], let

$$G(R, \theta_R, \theta, \phi) = C(R) \sum_{\alpha, \gamma=4}^6 g_{\alpha\gamma}(r_{12}^{(\alpha\gamma)}),$$

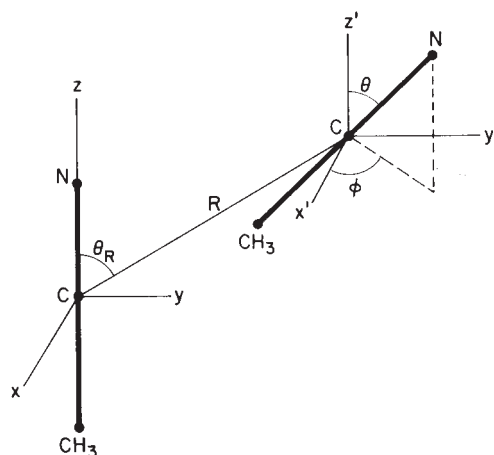


Figure 5. The coordinate system used to describe the relative arrangement of a pair of acetonitrile molecules.

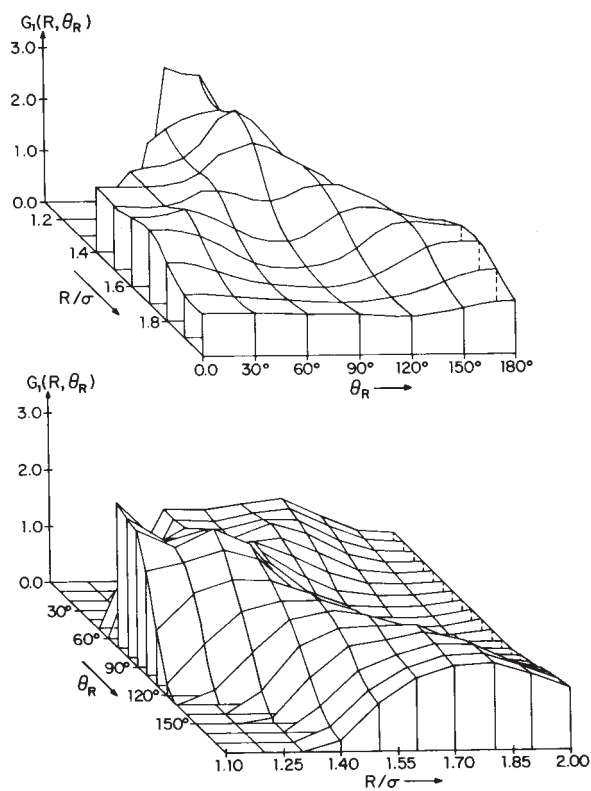


Figure 6. Two views of the function $G_1(R, \theta_R)$. (See the text for definitions.) The unit of length is $\sigma = 3.4 \text{ \AA}$.

where $C(R)$ is a normalization constant chosen to satisfy the equation

$$g_{55}(R) = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) \int_{-1}^1 d(\cos \theta_R) G(R, \theta_R, \theta, \phi).$$

The function $(R, \theta_R, \theta, \phi)$ is a superposition approximation to the full two-molecule distribution function. It should provide an estimate of the density of molecules around a central molecule as a function of the relative coordinates R , θ_R , θ and ϕ . The functions $G_1(R, \theta_R)$ and $G_2(R, \theta)$ are contractions of the

$$G_1(R, \theta_R) = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) G(R, \theta_R, \theta, \phi)$$

and

$$G_2(R, \theta) = \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta_R) G(R, \theta_R, \theta, \phi).$$

We have used the RISM $g_{\alpha\gamma}(r)$ s for acetonitrile to compute $G_1(R, \theta_R)$ and $G_2(R, \theta)$; the results are shown in figures 6 and 7. Notice that a great deal of structure is present. Even though dipolar interactions are apparently of little

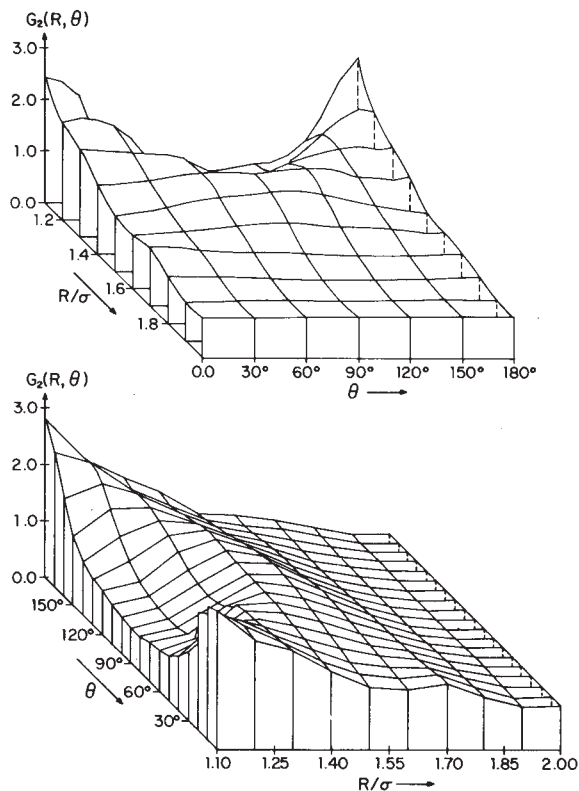


Figure 7. Two views of the function $G_2(R, \theta)$. (See the text for definitions.) The unit of length is $\sigma = 3.4 \text{ \AA}$.

importance, there are strong pair correlations between neighbouring acetonitrile molecules. According to figure 6, the most probable location of a neighbouring CH_3CN molecule is between 3.5 Å and 4.5 Å, with θ_R near 90° . However, the most probable separation of a neighbouring pair is obtained from $g_{55}(R)$, which is the integral of $G_1(R, \theta_R)$ with respect to $\cos \theta_R$. In view of figure 2 it is seen that the most probable separation is between 4.5 Å and 5.0 Å. At those distances (corresponding to roughly 1.35σ to 1.45σ), $G_2(R, \theta)$ reveals a mild tendency for θ (the angle between the principle axes) to lie between 60° and 120° . Stronger orientational pair correlations exist at closer pair separations. For $R < 4.5$ Å, the most preferred orientation is near either $\theta = 0^\circ$ or $\theta = 180^\circ$, which correspond to parallel alignments, but relatively few pairs of CH_3CN molecules are that close. The integration of $R^2 g_{55}(R)$ out to the first minimum in $g_{55}(R)$ indicates that, on average, there are slightly more than 12 neighbours in a first coordination shell. Integration out to $R = 4.5$ Å shows that fewer than 3 of these 12 neighbours lie within $R < 4.5$ Å. Beyond $R = 6$ Å, $G_2(R, \theta)$ is essentially independent of θ , and $G_1(R, \theta_R)$ is nearly independent of θ_R for $R > 6.5$ Å. Thus, the orientational pair correlations and the coupling of orientational and translational coordinates are negligible outside of the first coordination shell. Inside, however, they are fairly strong. The short-range nature of these correlations are undoubtedly a consequence of the fact that neighbours which are very close, $R < 4.5$ Å, tend to be parallel, while neighbours that are still within the first coordination shell, but have $R > 4.5$ Å, tend to be perpendicular or skewed, with θ_R near 60° or 120° and θ between 60° and 120° . This variety of arrangements will wash out noticeable orientational pair correlations in a short distance.

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