

0.90 eV. Physically we envision the captured electron staying in the resonance state for only a fraction of the vibrational cycle, and during this short time the modified electronic distribution gives an impulse to the nuclei, which begin to move. A greater impulse to the Cl nucleus occurs when the Cl has greater added electronic charge; this occurs in the (approximately) symmetric π_4 molecular orbital (approximately symmetric because the thermally distorted molecule has, strictly speaking, only unit symmetry; the Σ - Π coupling arguments of Clarke and Coulson⁷ are valid for the ideal geometrical configuration but are relaxed by certain out-of-plane vibrations). Accordingly, we identify the lowest resonance in the electron transmission study of C_6H_5Cl which occurs close to the peak of the dissocia-

tive attachment resonance as being due to electron capture into a symmetric π_4 state. For C_6H_5F , by analogy, we prefer the same assignment.

- ¹J. R. Frazier, L. G. Christophorou, J. G. Carter and H. C. Schweinler, *J. Chem. Phys.* **69**, 3807 (1978).
- ²M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.* **98**, 2053 (1976).
- ³J. A. Sell and A. Kuppermann, *Chem. Phys.* **33**, 367 (1978).
- ⁴L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.* **45**, 536 (1966).
- ⁵D. Mathur and J. B. Hasted, *J. Phys. B* **9**, L31 (1976).
- ⁶R. N. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.* **23**, 656 (1966).
- ⁷D. D. Clarke and C. A. Coulson, *J. Chem. Soc. A* **1969**, 169.

Comment on the role of constraints on the conformational structure of *n*-butane in liquid solvents

David Chandler

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

B. J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

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There are now a number of published computer simulations of the dynamics of flexible chain molecules in condensed phases. Some of these describe true Newtonian trajectories,¹⁻⁶ and others discuss stochastic trajectories⁷⁻¹⁰ (e.g., Brownian dynamics) in which the effects of the solvent surrounding the chain molecule are modeled with stochastic elements. The phenomena investigated in these studies focus on the conformational structures and rates of conformational transitions in the chain molecules. For example, in a *n*-butane molecule, the principal internal degree of freedom is the dihedral angle, ϕ , and one is interested in the effects of the condensed phase on the distribution function for that angle, $s(\phi)$, and on the rates at which transitions occur between the stable *trans* (ϕ near 0) *gauche* (ϕ near $\pm 2\pi/3$) states.

There are other internal degrees of freedom too. But these are less important because so-called⁸ "hard" intramolecular forces nearly constrain those coordinates to particular points in configuration space. For example, in *n*-butane, which can be modeled as four extended atoms (representing two CH_3 groups and two CH_2 groups), the bond lengths between adjacent carbons fluctuate very little from 1.53 Å, and the angles between adjacent C-C bonds remains close to the tetrahedral angle, 109° . Since these degrees of freedom are relatively unimportant, it seems reasonable that the dynamics of the relevant degrees of freedom can be accurately modeled by

assuming that the nearly constrained internal motions are indeed rigid. Then the irrelevant internal degrees of freedom would be eliminated through the introduction of holonomic constraints. This type of procedure can be computationally convenient, especially in light of the SHAKE algorithm^{1,11} that can be used to perform constrained dynamics. But remarkably, the procedure of replacing the actual hard forces with rigid constraints is not altogether insignificant. In a constrained trajectory, the momenta conjugate to the constrained coordinates are set to zero. However, in an unconstrained trajectory, these momenta are not zero *no matter how strong the hard potentials become* which tend to fix the configurations of the coordinates. Indeed, at thermal equilibrium, there is a Boltzmann distribution of these momenta. Thus, it is clear that the constrained dynamical trajectories cover a different region of phase space than trajectories performed with hard forces. Thus, the equilibrium averages associated with the two types of trajectories can be different. This fact has frequently been appreciated and commented upon by others in the recent literature.¹²⁻¹⁵ The purpose of this note is to describe the size of the differences for *n*-butane.

As reviewed by Fixman,¹² one may compute the differences *a priori* by determining how the kinetic energy of the constrained dynamical system depends upon configurations. (The kinetic energy of an unconstrained

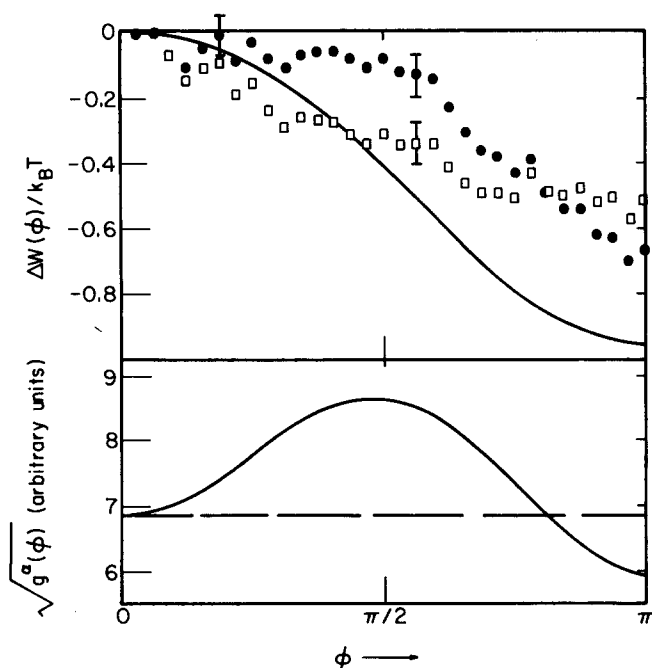


FIG. 1. Solvent contribution to the potential of mean torsion, $\Delta w(\phi)$, for *n*-butane in liquid CCl_4 and the square root of the determinant of the metric tensor $[g^\alpha(\phi)]^{1/2}$. The *trans* $\phi = 0$ conformation is taken as the zero point in the potentials of mean torsion. The open squares are the results obtained from the constrained molecular dynamics simulation of Ref. 6. The closed circles represent the potential of mean torsion appropriate to an unconstrained simulation. The latter is obtained from the former by adding $(\frac{1}{2})\ln[g^\alpha(\phi)/g^\alpha(0)]$ to the former. The error bars show the size of one standard deviation in the simulation. The solid line potential of mean torsion is the approximate two cavity prediction (Refs. 6 and 16).

system is independent of coordinates.) The integration over momenta in a canonical average then yields a non uniform metric for configurational averages of the constrained system. The degree with which the metric depends upon the relevant coordinates (e.g., the dihedral angle) determines the importance of the differences between averages computed for constrained and unconstrained trajectories. Fixman has provided a general theorem with which the metric can be computed,¹² and we have applied the theorem to evaluate the metric for a *n*-butane molecule in which the adjacent C–C bond lengths are fixed at 1.53 Å and the angles between adjacent C–C bonds are constrained to be 109° 28'. The square root of the determinant of the metric tensor, $[g^\alpha(\phi)]^{1/2}$ in Fixman's notation, is graphed in Fig. 1. Its variation is appreciable, though most of it occurs in the region between the stable *trans* and *gauche* states. Thus, for *n*-butane, constraints will have a larger effect on the population of the transition state than on *trans*–*gauche* equilibrium.

To discuss the role of the metric on the dihedral angle distribution, let $s_c(\phi)$ denote this distribution for a constrained *n*-butane molecule, and let $s(\phi)$ denote the distribution for the unconstrained species. In the limit of infinitely strong hard forces, the two distributions are related by¹²

$$s(\phi) = c s_c(\phi) / [g^\alpha(\phi)]^{1/2},$$

where c is a normalization constant. It is readily shown that this result is correct whether the *n*-butane molecules are isolated in the gas phase or as a solute in a condensed phase at infinite solute dilution. In Ref. 6 we presented a molecular dynamics computation the solvent contribution to $s_c(\phi)$ for carbon tetrachloride solvent. Its logarithm gives the solvent contribution to the potential of mean torsion, $\Delta w_c(\phi)$. If a simulation had been performed with flexible *n*-butane, the potential of mean torsion obtained would be $\Delta w(\phi) = \Delta w_c(\phi) + \frac{1}{2}k_B T \ln g^\alpha(\phi) + \text{constant}$. These potentials of mean torsion are graphed in Fig. 1 along with the approximate two-cavity theoretical prediction.¹⁶ The theoretical model is based on statistical mechanics which does not artificially couple coordinates to momenta by introducing holonomic constraints. Thus, the approximate model should be compared with $\Delta w(\phi)$ and not $\Delta w_c(\phi)$.

For this particular system, whether or not the irrelevant degrees of freedom in the *n*-butane molecule are taken to be constrained, we find the solvent shift of the *trans*–*gauche* equilibrium to be $K/K^{(0)} \approx 1.5$. However, the constraints increase the likelihood of molecules in the vicinity *trans*–*gauche* transition state (ϕ near $\frac{1}{3}\pi$) by 20% to 30%. Thus, the constraints may be of greatest significance for transition rates in this system.

This note owes its existence to a conversation with Eugene Helfand during which Dr. Helfand alerted us to the fundamental differences in the intramolecular distribution functions for flexible and nonflexible molecules and pointed out the discussions of the differences in Refs. 12–15.

- ¹J. P. Ryckaert, G. Ciccoliti, and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 329 (1977).
- ²J. P. Ryckaert and A. Bellemans, *Chem. Phys. Lett.* **30**, 23 (1975).
- ³J. P. Ryckaert and A. Bellemans, *Faraday Discuss. Chem. Soc.* **66**, 95 (1978).
- ⁴T. A. Weber, *J. Chem. Phys.* **69**, 2347 (1978).
- ⁵T. A. Weber, *J. Chem. Phys.* **70**, 4277 (1979).
- ⁶D. W. Rebertus, B. J. Berne, and D. Chandler, *J. Chem. Phys.* **70**, 3395 (1979).
- ⁷E. Helfand, Z. R. Wasserman, and T. A. Weber, *J. Chem. Phys.* **70**, 2016 (1979).
- ⁸M. Fixman, *J. Chem. Phys.* **69**, 1527 (1978).
- ⁹M. Fixman, *J. Chem. Phys.* **69**, 1538 (1978).
- ¹⁰R. M. Levy, M. Karplus, and J. A. McCammon, *Chem. Phys. Lett.* **65**, 4 (1979).
- ¹¹The proof that the SHAKE procedure is a numerical algorithm for implementing Lagrange's equations with holonomic constraints is given by J. P. Ryckaert, G. Ciccoliti, and H. J. C. Berendsen, *J. Comp. Phys.* **23**, 327 (1977). A discussion of the numerical advantages is given by W. F. van Gunsterin and H. J. C. Berendsen, *Mol. Phys.* **34**, 1311 (1977).
- ¹²M. Fixman, *Proc. Nat. Acad. Sci. U.S.A.* **71**, 3050 (1974).
- ¹³N. Gó and H. A. Scheraga, *Macromolecule* **9**, 535 (1976).
- ¹⁴M. Gottleib and R. B. Bird, *J. Chem. Phys.* **65**, 2467 (1976).
- ¹⁵M. R. Pear and J. H. Weiner, *J. Chem. Phys.* **71**, 212 (1979).
- ¹⁶L. R. Pratt, C. S. Hsu, and D. Chandler, *J. Chem. Phys.* **68**, 4202 (1978).