

To illustrate what L is, consider an ideal gas, for which

$$\eta = \begin{bmatrix} T/C_v & -p/C_v \\ -p/C_v & \gamma p/V \end{bmatrix},$$

the heat capacities are constant, $C_p - C_v = R$ and $C_p/C_v = \gamma$. For convenience, we define $\theta = mC_v/R$, half the number of quadratic degrees of freedom apart from the particle mass scaling factor m . A reversible or endoreversible⁵ process at constant volume gives

$$L^{(v)} = \int_0^1 \left[\frac{T}{C_v} \right]^{1/2} dS \\ = 2\sqrt{C_v} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta}{3}} [v_1^2{}^{1/2} - v_0^2{}^{1/2}].$$

Note that v_1 and v_0 are gas-kinetic velocities at T_1 and T_0 , respectively. A reversible process at constant pressure gives

$$L^{(p)} = \int_0^1 \left[\frac{T}{C_v} \left[\frac{C_p}{V} \right]^2 \left(\frac{\partial V}{\partial \xi} \right)^2 - \frac{2p}{C_v} \frac{C_p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 + \frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi \\ = \int_0^1 \left(\frac{\gamma}{\gamma-1} \right)^{1/2} \sqrt{\frac{p}{V}} dV \\ = 2\sqrt{C_p} [\sqrt{T_1} - \sqrt{T_0}] = 2\sqrt{\frac{\theta+1}{3}} [v_1^2{}^{1/2} - v_0^2{}^{1/2}],$$

where we assume $C_p = (\theta+1)R/m$.

A reversible process at constant temperature gives $L=0$, as expected because U is a function only of T .

A reversible adiabatic process gives

$$L^{(s)} = \int_0^1 \left[\frac{\gamma p}{V} \left(\frac{\partial V}{\partial \xi} \right)^2 \right]^{1/2} d\xi = \frac{2}{\gamma-1} \sqrt{\gamma p_0 V_0} \left[1 - \left(\frac{p_1}{p_0} \right)^{(\gamma-1)/2\gamma} \right],$$

which is the change in flow velocity of a gas undergoing

an isentropic expansion, e.g., in a rarefaction wave.⁶ In general, L is a change in a mean velocity, but characteristic of the constraints defining the path of the integral along which the length is measured. Incidentally for a solid whose equation of state is $V = V_0[1 + \alpha(T - T_0) - kp]$, $\eta_{11} = T/C_v$ as for the ideal gas, $\eta_{12} = \alpha T/kC_v$, and $\eta_{22} = (\alpha^2 T/kC_v) + 1/V_0 k$. The length L for an isochoric process is the same as for the gas; the length L for an isentropic process is of the form $L = \int [At + B]^{1/2} dV$.

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¹(a) F. Weinhold, *J. Chem. Phys.* **63**, 2479 (1975); (b) *ibid.* **65**, 559 (1976).

²P. Salamon, Doctoral Dissertation, The University of Chicago (1978) discusses this point specifically; standard texts on differential geometry, such as M. M. Lipschutz, *Differential Geometry* (McGraw-Hill, New York, 1969) or W. C. Graustein, *Differential Geometry* (Dover, New York, 1966), give general discussions of first and second fundamental forms. L. Tisza, *Generalized Thermodynamics* (MIT, Cambridge, Mass., 1966) discusses the subject and designates η_{ij} as the "stiffness" form.

³J. W. Gibbs, *Collected Works*, Vol. 1 (Yale Univ., New Haven, 1948); J. H. Keenan, *Thermodynamics* (MIT, Cambridge, Mass., 1970).

⁴The positivity of η fails at phase transitions; where these occur, there are lines along which η vanishes, which correspond to transformation of material from one phase to another without disrupting the equilibrium between system and environment. For further discussion see Ref. 1(b).

⁵"Endoreversible" is a term introduced by M. Rubin, *Phys. Rev. A* **19**, 1272 (1979) to characterize a thermodynamic system whose working substance undergoes reversible transformations, independent of whether the system is in equilibrium with its surroundings.

⁶E. F. Greene and J. P. Toennies, *Chemical Reactions in Shock Waves* (Edward Arnold, London, 1969), p. 109.

Comment on the structure of a simple liquid solvent near a n -butane solute molecule^{a)}

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The purpose of this comment is to discuss the distribution of solvent molecules around two different conformations of an n -butane solute molecule. In a recent pair of publications,^{1,2} we have reported computer sim-

ulation results for a fluid containing one model n -butane solute species and 123 Lennard-Jones solvent particles chosen to mimic liquid CCl_4 . The work presented here extends those studies by examining the distribution of

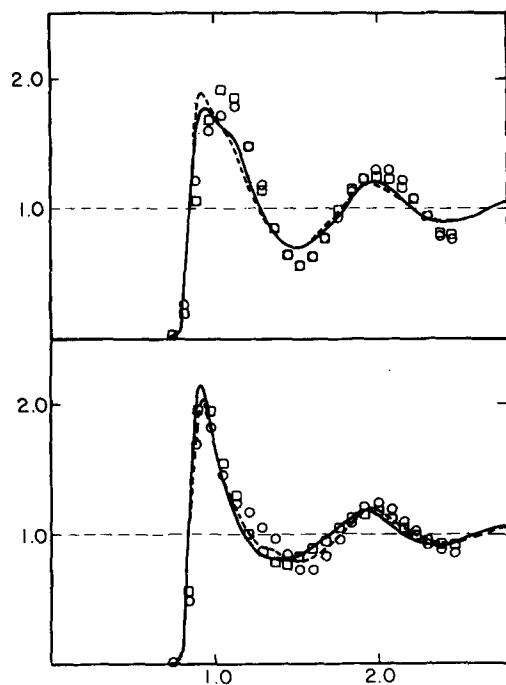


FIG. 1. The methylene to solvent radial distributions $g^E(r|trans)$ and $g^E(r|gauche)$, below, and the radial distributions of $g^I(r|trans)$ and $g^I(r|gauche)$, above. The superscripts *E* or *I* describe whether we are referring to an exterior or interior methylene group. The labels *gauche* and *trans* refer to the conformational state of the *n*-butane molecule. The solid and dashed lines are the RISM theory results for *trans* and *gauche* *n*-butane conformers, respectively. The squares and circles are the Force-Bias Monte Carlo results for the *trans* and *gauche* *n*-butane conformers, respectively. The length scaled is reduced by $\sigma_S = 5.27 \text{ \AA}$.

solvent molecules around the exterior methyl and interior methylene groups of the *n*-butane molecule in its *trans* and *gauche* conformations. Preliminary results for these distributions obtained from a Force-Bias Monte Carlo calculation were reported in Fig. 3 of Ref. 1. After publication of Ref. 1, we discovered a coding error in part of those calculations. We report here the results of a Force-Bias Monte Carlo calculation in which the program error was corrected and the sampling was increased several fold to obtain improved statistics. In addition, we report the theoretical results obtained from the solutions of the RISM integral equation.³

The theoretical results were computed by summation of the interaction site cluster diagrams which contribute⁴ to the solutions of the RISM integral equation. The summation was accomplished by a chain recursion method analogous to the scheme discussed by Dale and Friedman.⁵ The diagrammatic summation procedure is particularly convenient for obtaining the solutions of the

RISM equation for continuous force systems as opposed to hard core systems. The results reported here are computed with the continuous repulsive force system formed by truncating the Lennard-Jones potentials specified in Ref. 1 in the standard WCA fashion.⁶ Thus, the theoretical calculations are based on two approximations: 1. attractive interactions are consistently neglected; 2. the statistical mechanics of the repulsive forces are treated by summing only those classes of graphs contained in the RISM integral equation.

Both theoretical and Monte Carlo results are shown and compared in Fig. 1. The source of errors in the computer simulation are different from those of the theory. First, there are statistical uncertainties due to insufficient sampling of configuration space. Second, the simulation is performed on a system of finite size. We estimate the statistical uncertainties to be no larger than ± 0.09 in the region of the first peak of these distributions, and less than ± 0.05 at larger distances. From experience with simple liquids, we believe the possible errors due to finite size are even smaller. Based on this belief, it appears that the theoretical results are systematically in error in that the predicted distributions are slightly out of phase with those computed from the Force-Bias Monte Carlo simulation. We suspect that the primary source for this error is the neglect of attractive forces by the theory since the attractive forces in this system will favor contacts between solvent pairs as opposed to solvent-solute pairs.

Despite these differences, which provide an interesting subject for future investigation, the qualitative results of the RISM theory and the simulation are in general agreement. From this agreement it seems safe to conclude that the distribution of solvent around the interior methylene groups is fairly insensitive to the conformational state, whereas the distribution of solvent around the exterior groups is sensitive to the conformation. This latter difference is due to the screening of one exterior group from the solvent due to the presence of the other group.

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²B. J. Berne, D. Chandler, and D. W. Rebertus, *Chem. Phys. Lett.* (in press).

³See D. Chandler, *Ann. Rev. Phys. Chem.* **29**, 441 (1978) and references cited therein.

⁴D. Chandler, *Mol. Phys.* **31**, 1213 (1976).

⁵W. D. T. Dale and H. L. Friedman, *J. Chem. Phys.* **68**, 3391 (1978).

⁶J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).