

CECAM WORKSHOP ON THE
DYNAMICS OF MOLECULAR LIQUIDS AND OTHER COMPLEX
SYSTEMS UNDER EXTERNAL CONSTRAINTS

(June 20 - July 13, ORSAY, FRANCE)

List of participants:

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SUMMARY OF THE ACTIVITIES DURING THE WORKSHOP

The following topics, related to the general subjects of the workshop, were tackled in small subgroups (two or three people):

- 1) The nature of ensembles corresponding to the dynamic simulation of constrained systems. Case studied: constrained kinetic energy.
- 2) Extension of the Rahman-Parrinello method to molecular crystals made of rigid molecules. Case studied: orthorombic monoclinic transition in solid benzene.
- 3) Solution of the "closest image problem" for molecules in a periodic parallelepiped box of arbitrary shape, using the Wigner-Seitz cell construction.
- 4) Simulation of a Couette flow by the "Doll tensor" perturbation of Hoover and Evans; the perturbation is very weak and the viscosity coefficient is obtained from the difference between perturbed and non-perturbed trajectories in phase space. Case studied: Lennard-Jones molecules.
- 5) Simulation of an oscillating Couette flow for polyatomic systems by means of a strong perturbation (requiring a continuous cooling of the system).
- 6) The evaluation of the free energy of a solid phase along a reversible path, starting from an Einstein solid. Application to hard spheres.

In spite of the rather large number of topics covered, a continuous and fruitful interaction between all participants was maintained during the full duration of the Workshop and various works which were initiated at that time, were carried out further. In the following pages, a certain number of reports concerning some of these topics may be found.

LIST OF REPORTS

- 1) Equilibrium statistical mechanics of constant kinetic energy molecular dynamics: H.C. Andersen.
- 2) Constant temperature - constant pressure molecular dynamics of rigid molecules: M. Ferrario, M. Meyer and J-P. Ryckaert.
- 3) Newton law for simple fluids by non-equilibrium molecular dynamics (NEMD): G. Ciccotti and J-P. Ryckaert.
- 4) Equations of motion for non-equilibrium molecular dynamics, simulations of viscous flow in molecular fluids: A.J.C. Ladd.
- 5) Non-equilibrium molecular dynamics of molecules with bond length constraints: M.P. Allen and G. Maréchal.
- 6) New method to determine the absolute free energy of arbitrary solid phases: D. Frenkel and T. Ladd.

NEW METHOD TO DETERMINE THE ABSOLUTE FREE ENERGY
OF ARBITRARY SOLID PHASES.

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In this publication we present a computer simulation method to determine the domain of thermodynamic stability of solid phases in model systems. The recent development by Parrinello and Rahman (1) of a new Molecular Dynamics simulation technique has greatly stimulated the use of computer simulations to investigate solid-solid phase transitions in model systems. The basic idea upon which the Parrinello-Rahman method is based is that the fixed Periodic Boundary Conditions (PBC's) employed in conventional MD simulations all but exclude the direct observation of solid-solid phase transitions, as boundary conditions chosen to be compatible with one solid phase are in general incompatible with the other. Hence fixed PBC's tend to stabilize one solid phase well beyond its range of thermodynamic stability. Simulations involving fixed PBC's may easily overlook the existence of other, more stable phases altogether. In the Parrinello-Rahman method the shape of the periodic box is no longer fixed; shape and size of the periodic box are expressed in terms of variables which play the role of generalized coordinates in an extended Hamiltonian. The resulting equations of motion describe the "natural" time evolution of the shape and size of the periodic box under constant applied external pressure and zero applied stress. Note that if only the size of the box is treated as a variable the Parrinello-Rahman method reduces to Andersen's constant pressure MD(2). The P-R method provides an easy, "natural" route for a model system to go from one solid phase to the other as the boundary conditions adjust themselves to the favored solid structure. For this reason the P-R method is now widely used for mapping phase diagrams involving several solid phases (3). It should be noted, however, that the P-R method does not provide a reversible route from one phase to the other; the solid-solid phase transformation takes place when the initial solid phase becomes mechanically unstable. The actual thermodynamic phase transition is bracketed by the width of the hysteresis region. In order to locate the thermodynamic phase transition one needs information on the free energy of both solid phases.

Two methods have traditionally been used to obtain such information. Both methods rely on constructing a reversible path from a state of known free energy to the solid phase under consideration. The first method is the so-called Single Occupancy Cell (SOC) method introduced by Hoover&Rea(4). In this method one starts with a lattice gas with one particle per lattice cell. At high densities the centers of the lattice cells coincide with the average atomic positions in the unconstrained solid. Expanding this lattice uniformly one approaches a dilute gas which has the same pressure as an ideal

gas at the same density, and a free energy that can be evaluated exactly. The free energy of the lattice gas at high densities coincides with the free energy of the corresponding unconstrained solid (if the density is sufficiently high to ensure that the artificial cell walls have negligible effect on the particle displacements). The free energy of the solid is then obtained by computing:

$$F_{\text{solid}}(V_2) - F_{\text{lattice gas}}(V_1) = - \int_{V_1}^{V_2} P(v) dv \quad (1)$$

This method was used by Hoover & Ree to obtain the free energy of the hard-sphere (and 2D hard-disk) solid (5,4). The actual numerical integration of eqn. 1 may require evaluating the pressure at quite a few state points because the P-V relation of a lattice gas exhibits a cusp at the point where nearest-neighbor interactions take over from the cell walls in constraining the particles. There is even some evidence that a weak first order transition takes place at this point (6), in which case the supposedly reversible path linking the solid to the dilute lattice gas may, after all, be not quite reversible.

A second method to compute the free energy of a solid phase is to start from the low-temperature harmonic solid, the free energy of which can be computed exactly. This method was first used by Hoover, Gray & Johnson (7). There are two factors limiting the applicability of the latter method. The first is that it only works for solids that are harmonic at low temperatures (and/or high densities). This excludes all systems with discontinuous intermolecular forces, e.g. the hard-sphere solid. Moreover, solid phases that are mechanically unstable at low temperatures cannot be investigated by this method. A practical problem with the harmonic-lattice method is that for anything but the simplest solids, and in particular for molecular solids, evaluating the harmonic lattice free energy involves some non-trivial computation.

Below we present a method to compute the free energy of an arbitrary solid in a way that we believe is easy, reliable and efficient. Our approach is once again based on the construction of a reversible path to a state of known free energy. In this case the reference state is an Einstein crystal with the same structure as the solid under consideration. This reference state can be reached from the real solid by slowly switching on harmonic springs which bind the atoms to their lattice sites. As the Einstein solid is very similar to the initial solid, it is very likely that such a path will be free of phase transitions and hence reversible. The simplest way to transform a solid to an Einstein crystal is to add a term λV to the unperturbed Hamiltonian H_0 , such that

$$H(\lambda) = H_0 + \lambda V = H_0 + \lambda \sum_{i=1}^N (\vec{x}_i - \vec{x}_i^0)^2 \quad , \quad (2)$$

where \vec{r}_i^0 is the lattice position of particle i . The derivative of the free energy of this system with respect to the coupling constant λ is given by:

$$\frac{\partial F}{\partial \lambda} = -kT \frac{\partial}{\partial \lambda} \ln \left(\int \int \exp(-\beta(H_0 + \lambda V)) d\vec{q}^n \right) = \langle v \rangle_\lambda , \quad (3)$$

from which it follows that the free energy of the real crystal is related to the free energy of a crystal with spring constant λ by:

$$F(\lambda=0) = F(\lambda) - \int_0^\lambda \langle v \rangle_{\lambda'} d\lambda' . \quad (4)$$

At sufficiently high λ the free energy of the system reduces to that of an Einstein crystal:

$$F(\lambda) = \phi_0 - kT \ln \left(\frac{\pi kT}{\lambda} \right)^{\frac{3N}{2}} + C(T) + O(\lambda) , \quad (5)$$

where ϕ_0 is the potential energy of a system with all atoms at their lattice sites. $C(T)$ is the kinetic contribution to the free energy which depends only on the temperature. Of course, a rather high value of λ may be required before the terms of order $O(1/\lambda)$ in eqn.5 become negligible. In practice there is no need to go to very high values of λ as it is rather simple to evaluate the leading corrections to the free energy at finite λ . In some cases these corrections can be evaluated analytically (as in the case of hard spheres, to be discussed below), but in the most general case the free energy difference between the ideal Einstein crystal and the Einstein crystal with intermolecular interactions can be found numerically by performing a Monte Carlo simulation on the ideal Einstein crystal, and deriving the free energy of the interacting Einstein crystal by umbrella sampling (3).

In order to investigate the usefulness of the method described above, we used it to compute the free energy of the hard sphere solid. We chose this particular system because reliable numerical results on the Hard-Sphere (HS) solid are available (5), yet the calculations on which these results are based are by no means trivial (it involves computing a complete isotherm of the single-occupancy cell system). Of course, for hard spheres the harmonic approximation cannot be used. In the present study we computed the free energy of the hard sphere solid at the fluid-solid coexistence point ($\rho_0 = 0.736$, $P_0/kT = 8.27$). The actual simulation consisted of 10 runs, each of 10^4 sweeps (i.e. 10^4 attempted moves/particle) excluding equilibration (typically 10^3 sweeps). Each run was carried out for a different value of the spring constant λ . The values of λ at which the different runs were performed were chosen as follows. For $\lambda > 600$ the free energy of the interacting Einstein crystal

could be accurately approximated by an analytical expression based on a "virial" expansion to be described below. Hence the numerical simulations were limited to the interval $0 \leq \lambda < 600$. At high values of λ , $\langle r^2 \rangle \sim 1/\lambda$ whereas $\langle r^2 \rangle \rightarrow c$ as $\lambda \rightarrow 0$, where c is the mean-square displacement of an atom around its lattice site in the normal hard-sphere solid (note that in the simulation we have kept the center of mass of the system fixed; we correct for the effect of this constraint on the free energy). Clearly then the function $(\lambda+c)\langle r^2 \rangle_\lambda$ varies little over the interval $0 \leq \lambda < 600$. Hence to compute the desired free energy difference we evaluated the integral:

$$\Delta F = - \int_0^{\lambda_{MAX}} \langle r^2 \rangle_{\lambda} (\lambda+c) \frac{d\lambda}{(\lambda+c)} = - \int_{\ln c}^{\ln(\lambda_{MAX}+c)} \langle r^2 \rangle_{\lambda} (\lambda+c) d \ln(\lambda+c) . \quad (6)$$

Here the integrand is a very smooth function of λ , and the integral could be evaluated using a 10-point Gauss-Legendre quadrature. Later tests indicated that no significant loss of accuracy resulted if a 5-point quadrature was used. Each simulation took about 2 minutes on an IBM 192 computer.

The free energy of the interacting Einstein crystal at λ_{MAX} was evaluated in the following way. The configurational part of the partition function of the interacting Einstein crystal is of the following form:

$$Q(\tau; \lambda) = \int \dots \int \exp(-\beta \lambda \sum_i (\Delta \vec{r}_i)^2) \exp(-\beta \sum_{i,j} U(r_{ij})) dr^N , \quad (7)$$

where $\Delta \vec{r}_i = \vec{r}_i - \vec{r}_i^0$ (\vec{r}_i^0 is the lattice site of particle i), $\beta = 1/kT$ and $U(r_{ij})$ is the value of the pair potential of particles i and j . Eqn. 7 can be rewritten as:

$$Q(\tau; \lambda) = Q_E(\tau; \lambda) \left(\int \dots \int \exp(-\beta \lambda \sum_i (\Delta \vec{r}_i)^2) \exp(-\beta \sum_{i,j} U(r_{ij})) dr^N / Q_E(\tau; \lambda) \right) , \quad (8)$$

where $Q_E(\tau)$ is the partition function of the non-interacting Einstein crystal. Hence:

$$Q(\tau; \lambda) = Q_E(\tau; \lambda) \langle \exp(-\beta \sum_{i,j} U(r_{ij})) \rangle_E . \quad (9)$$

Here the subscript E stands for averaging over all configurations of the non-interacting Einstein crystal. This average can of course be carried out by Monte Carlo (umbrella sampling) but in the present case we an expansion in cluster functions $f_{ij} = \exp(-\beta u(r_{ij})) - 1$,

$$\langle \exp(-\beta \sum_{i,j} U(r_{ij})) \rangle_E = \langle 1 + \sum_{i,j} f_{ij} + \sum_{i,j} \sum_{k,l} f_{ij} f_{kl} + \dots \rangle_E . \quad (10)$$

Note that $-\langle f_{ij} \rangle_E = \langle p_{ij}^{overlap} \rangle_{overlap}$, the probability that particles i and j in the non-interacting Einstein crystal are separated by a distance $|r_{ij}| < \sigma$. At high values of λ all $\langle f_{ij} \rangle$ for i and j not nearest neighbors become negligible, while $|\langle f_{ij} \rangle|_{n.n.} \ll 1$ (n.n. stands for "nearest neighbor"). In this limit we may approximate eqn. 7 by:

$$\langle \exp(-\beta \sum_{ij} U(r_{ij})) \rangle_E \approx (1 + \langle f_{ij} \rangle^{n,n})^{\frac{Nn}{2}} \quad . \quad (11)$$

In eqn. 11 n stands for the number of nearest neighbors of a particle i (in the present case : n=12). To the same level of approximation, $\langle f_{ij} \rangle^{n,n}$ can be evaluated by computing the probability of overlap of 2 isolated, harmonically bound penetrating spheres at an average separation $a = |\vec{r}_i^0 - \vec{r}_j^0|$. This probability can be evaluated analytically; the result is:

$$\langle P_{\text{OVERLAP}}^{n,n} \rangle = \frac{1}{2} \left[erf\left(\frac{\beta \lambda}{2} (\sigma-a)\right) + erf\left(\frac{\beta \lambda}{2} (\sigma+a)\right) \right] - \left(e^{-\frac{\beta \lambda}{2} (\sigma-a)^2} - e^{-\frac{\beta \lambda}{2} (\sigma+a)^2} \right) / ((2\pi\beta\lambda)^{1/2} a) \quad . \quad (12)$$

The expression for the free energy of the interacting Einstein crystal then becomes:

$$F(T; \lambda) = F_E(T; \lambda) - \frac{Nn}{2} kT \ln(1 - \langle P_{\text{OVERLAP}}^{n,n} \rangle_\lambda) \quad . \quad (13)$$

From this expression for $F(T, \lambda)$ we can obtain an estimate for $\langle r^2 \rangle_\lambda = \frac{1}{N} \sum_i \langle r_i^2 \rangle_\lambda$, viz.:

$$\langle r^2 \rangle_\lambda = - \frac{\partial \ln Q_E}{\partial \beta \lambda} - \frac{1}{2} \frac{\left[\frac{\beta \lambda}{2} (\sigma-a)^2 (erf(\frac{\beta \lambda}{2} (\sigma-a)) + erf(\frac{\beta \lambda}{2} (\sigma+a))) + \frac{\beta \lambda}{2} (\sigma+a)^2 (erf(\frac{\beta \lambda}{2} (\sigma+a)) - erf(\frac{\beta \lambda}{2} (\sigma-a))) \right]}{2a (2\pi\beta\lambda)^{1/2} (1 - \langle P_{\text{OVERLAP}}^{n,n} \rangle)} \quad . \quad (14)$$

This expression can be compared with the Monte Carlo results for the interacting Einstein crystal at high values of λ . Fig. 1 shows such a comparison. Actually we found a very small difference between the Monte Carlo $\langle r^2 \rangle_\lambda$ and the corresponding virial result. This difference decreased rapidly with increasing λ ; we observed that it fitted well to an expression of the form: $\Delta = \alpha \exp(-\lambda/\delta)$ with $\alpha \approx 10^3$ and $\delta \approx 130$. We took this correction into account in evaluating the free energy but it had no significant effect on the final result. Finally, as mentioned above, we corrected for the fact that we were constraining the center of mass of the system to be fixed. The partition function of an Einstein crystal with fixed center of mass is given by:

$$Q'_E(T; \lambda) = N^{3/2} \left(\frac{\pi}{\beta \lambda} \right)^{\frac{3}{2}(N-1)} \quad . \quad (15)$$

The partition function of the unconstrained hard sphere solid differs from the partition function of the constrained solid by a factor V . In table I we have collected all different contributions to the free energy of the hard-sphere solid, referred to the ideal gas at the same density. The table contains the results obtained for a 32, 108 and 256 particle system. Fig. 2 shows the N-dependence of the computed free energy (or actually, the entropy). To obtain the result at $N = \infty$, two different extrapolation methods were employed. In one it was assumed that the leading N-dependence of the free energy is of the form $A(N)/N$, in the second we assumed a simple $1/N$ dependence. In the present case the latter assumption is more realistic as the explicit $A(N)/N$ dependence both on the ideal gas side and

on the Einstein crystal side were taken into account (see table I). In fact we find that the MC data fit a $1/N$ dependence far better than $\ln(N)/N$. The entropy difference between the hard-sphere solid at $\rho\sigma^3 = 1.041$ and an ideal gas at the same density was thus estimated to be:

$$\Delta S = -5.932 \pm .006$$

($1/N$ extrapolation)

$$\Delta S = -5.940 \pm .006$$

($\ln N/N$ extrapolation)

The error bars quoted correspond to 2 standard deviations. For the sake of comparison we give the Hoover-Ree results using the single occupancy cell method:

$$\Delta S = 5.924 \pm 0.015$$

Clearly, our results agree very well with the Hoover&Ree result. In fact, the present results may even be marginally more accurate.

In summary, we have developed a simple, efficient and accurate method to obtain absolute free energies of arbitrary solid phases. For hard spheres our results agree well with the results obtained by Hoover&Ree using a different approach. We are currently applying the present technique to a number of unsolved problems concerning the thermodynamic stability of solid phases in model systems.

ACKNOWLEDGEMENTS.

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TABLE CAPTIONS.

Table I.

Contributions to the free energy difference (= -(entropy difference)) between hard-sphere solid and ideal gas at same density. N: number of particles, $F_E(\lambda_{\max})$: estimated free energy of interacting Einstein crystal (eqn.13) , F_{CM} : free energy difference between "floating" and fixed center of mass Einstein crystals, ΔF :free energy difference along reversible path (eqn.6), $\Delta F_{corr.}$: estimated correction to $F_E(\lambda_{\max})$ (see below eqn.14). F_{IG} : free energy of N-particle ideal gas. ΔS_{tot} :estimated entropy difference between N-particle hard-sphere solid and ideal gas at the same density. The bottom rows show the estimated results for $N=\infty$. Our best estimate for the free energy difference is $F=5.932$. All free energies quoted are per particle; $\lambda_{\max}=632.026$.

TABLE I

N	$F_E(\lambda_{\max})$	F_{CM}	ΔF	ΔF_{corr}	F_{IG}	ΔS_{tot}
32	7.8885	-0.1071	-2.7933	-0.0008	-0.87707	-5.8643
108	7.9660	-0.0430	-2.9403	-0.0007	-0.9289	-5.9118
256	7.9761	-0.0215	-2.9776	-0.0018	-0.9455	-5.9234
∞	1/N extrapolation					-5.932(6)
∞	$\ln(N)/N$ extrapolation					-5.940(6)

FIGURE CAPTIONS.

Fig. 1.

Mean square displacement of atoms in an interacting Einstein crystal as a function of the "spring" constant λ . \square : MC data, $- - -$: "virial" approximation (eqn. 14), $- - - -$: Einstein crystal ($N \rightarrow \infty$) , $- - - -$: Einstein crystal (fixed center of mass: $N=108$). All results apply to the case: $\lambda_{\max} = 632.026$ and, unless stated otherwise, $N=108$. To improve the legibility of this figure, all mean square displacements have been multiplied by $(\lambda+c)$, with $c=33.115$.

Fig. 2.

N -dependence of the free energy difference between a hard sphere solid at $p\sigma^3 = 1.041$ and an ideal gas at the same density. As can be seen from the figure, the relation between ΔF and $1/N$ is very nearly linear. The intercept at $1/N=0$ yields an estimate for ΔF at $N=\infty$: $\Delta F=5.932$. For the sake of comparison, the Hoover&Ree value $\Delta F=5.924$ is also shown (●). In the upper right hand side of the figure the present value for ΔF and the Hoover & Ree result are shown with their respective error bars.

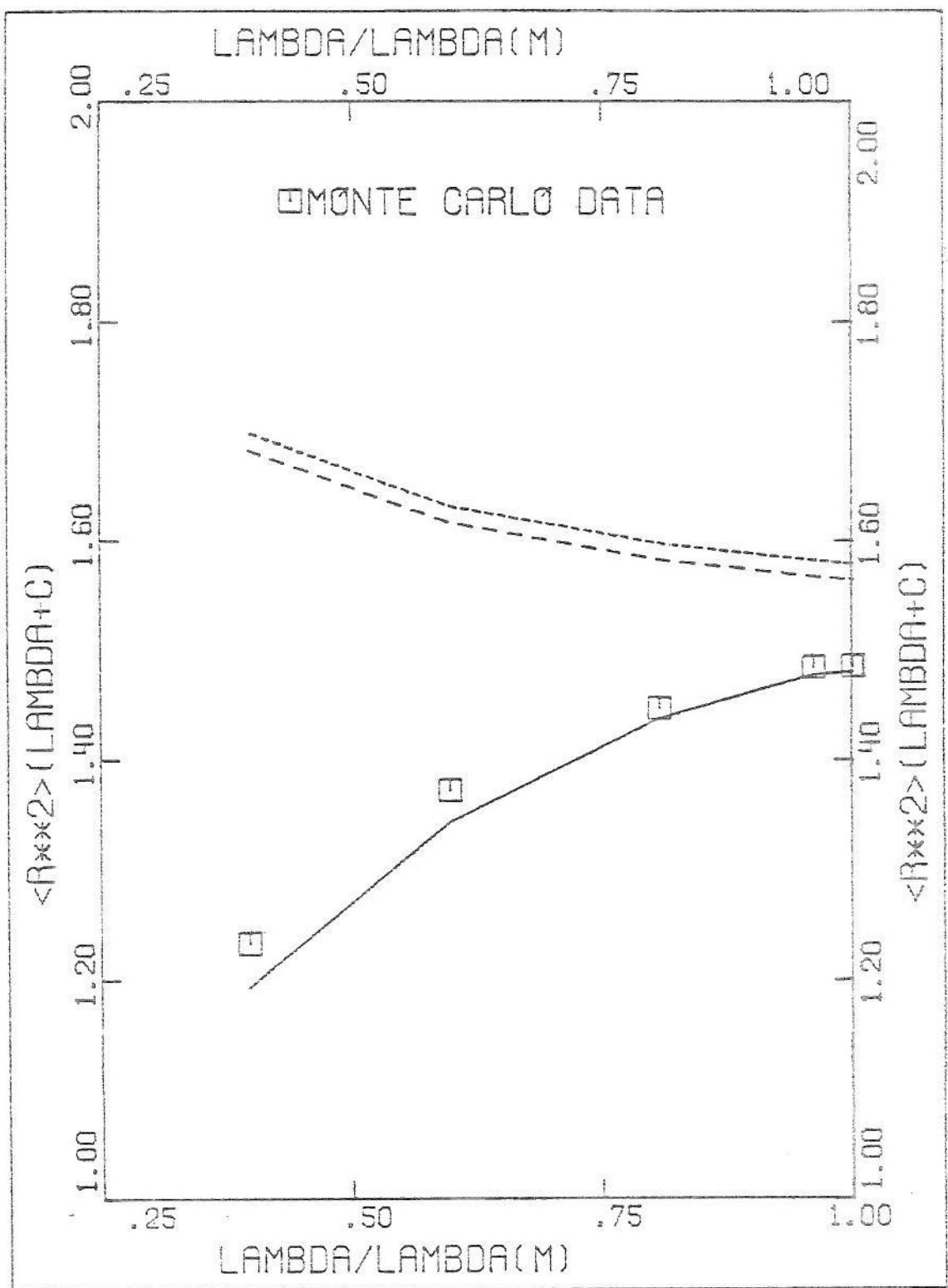


FIGURE 1

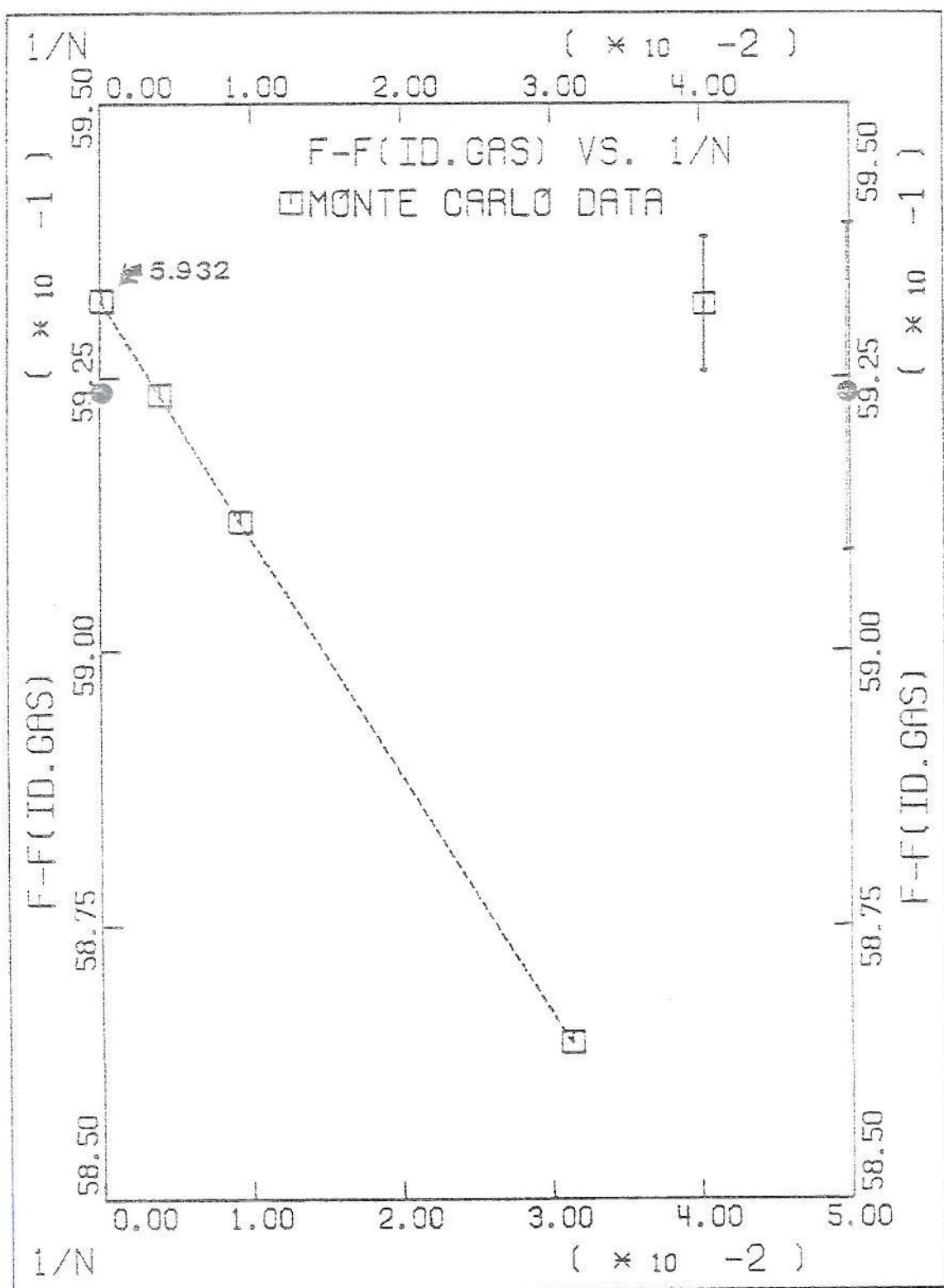


FIGURE 2