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LA-UR 89-3060

TITLE    A NEW SIMULATION METHOD FOR THE EFFICIENT CALCULATION OF
BENCHMARKS FOR DETONATION PRODUCTS EQUATIONS OF STATE

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A NEW SIMULATION METHOD FOR THE EFFICIENT CALCULATION OF BENCHMARKS
FOR DETONATION PRODUCTS EQUATIONS OF STATE

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A new variation on the Monte Carlo method is presented here in the
context of its potential impact on the development of detonation
products equations of state (EOS). The configurational density of
states and other quantities are determined for a nonstandard reference
simulation. Then the EOS for a linear combinations of potentials is
evaluated through a density of states transformation at arbitrary
densities and temperatures in the fluid range. The computer time
required for the EOS calculation (including free energies) is negligible
once the reference simulation is made. The EOS over the entire fluid
regime for a Lennard-Jones fluid (including the location of the
gas/liquid equilibrium phase line) is calculated. Preliminary results
on the extension of the method to the exponential-six potential are
presented. The efficient calculation of benchmarks over the very large
parameter space of relevance to detonation products EOS may now be
possible.

# INTRODUCTION

In the last two decades, a great deal of progress has been made in the area of theoretical equations of state for fluids. Of particular interest to the explosives community has been the work of the last decade in applying these methods to the construction of physically meaningful detonation products equations of state. The goal for thermodynamic theory is to be able to take a given set of interaction potentials for an arbitrary mixture of product molecules and calculate accurately and quickly the equilibrium EOS under the extreme conditions of pressure and temperature characteristic of detonation products. Then the potentials could be determined from quantum mechanics or normalization to data (typically the quantum calculations are qualitative and are useful for the determination of functional forms to be used in fitting data). Until the thermodynamic theory is tied down, there will be too many free parameters to assure a predictive EOS in which all of the constants are physically meaningful.

Although much progress has been made, we are not yet at this goal for thermodynamic theory. Fast quantitative methods[1] are available for the EOS of single species with spherically symmetric interaction potentials. Methods exist for spherical mixtures[2], but their accuracy has only been tested against a limited set of simulations in the regions of interest. An accurate method[3] for treating single species nonpolar, nonspherical interactions (e.g. $N_2$ and $CO_2$) as an effective spherical interaction has been developed. The mixture problem for molecules with shape and the problem of the large dipole moment in $H_2O$ are largely unsolved. Of course, there are benchmark type methods such as molecular dynamics (MD) and Monte Carlo (MC) which provide accurate thermodynamics at the cost of around 10 minutes of CRAY time per EOS point. The parameter space is too large to use these methods directly for a practical explosives EOS. They are used to test the accuracy of much faster approximate methods that are then used to model explosives.

This paper gives results for a new[4] variation on the Monte Carlo method that retains the accuracy of the standard MC methods, but dramatically increases the speed with which the parameter space can be mapped out. Starting from a non standard reference simulation which samples essentially all of the phase space relevant to fluids, a remapping is made to determine the EOS for different values of density and temperature throughout the fluid regime. Since the reference

simulation is only calculated once and the remapping is very fast, the cost per EOS point is small.

In the remainder of the paper, we will begin with a discussion of the evaluation of the configurational density of states for a reference potential using a nonstandard Monte Carlo method. Then the transformation of the reference density of states into that for a linear combination of the reference potential and other potentials is presented. Next is given the method for evaluation of thermodynamic quantities from the transformed density of states. Results for the Lennard-Jones potential are then illustrated. This is followed by a preliminary version of the treatment of the exponential-six potential fluid. Finally, the implications for the development of a predictive, accurate EOS for detonation products is discussed.

## DENSITY OF STATES FROM MONTE CARLO

The usual NVT ensemble Monte Carlo (MC) method uses importance sampling to evaluate integrals of the form

$$\langle f \rangle = \frac{\int f(r_1, \ldots, r_n) \exp(-\beta U(r_1, \ldots, r_n)) dr_1 \cdots dr_n}{Z(\beta)} . \quad (1)$$

where $Z(\beta) = \int \exp(-\beta U(r_1, \ldots, r_n)) dr_1 \cdots dr_n$ is the configuration integral, U is the total potential energy, and $\beta = 1/kT$. The MC steps are taken with a probability density $P_r(r_1, \cdots, r_n)$ which is proportional to $e^{-\beta U}$. The approximation to $\langle f \rangle$ from the MC sample is given by

$$\langle f \rangle = \sum_{i=1}^{N} f_i e^{-\beta U} P_r(i)^{-1} / \sum_{i=1}^{N} e^{-\beta U} P_r(i)^{-1} = \sum_{i=1}^{N} f_i / \sum_{i=1}^{N} 1 = N^{-1} \sum_{i=1}^{N} f_i , \quad (2)$$

where only ratios of integrals are evaluated since the overall normalization is not defined by the method. Here i designates the coordinates $r_1, \cdots, r_n$ at the ith step of the simulation.

We can transform the complications of the many-body integration to that of finding the configurational density of states. Laying the foundation for a whole class of methods, McDonald and Singer[5,6] evaluated relative values for the configurational density of states $\gamma(U)$ over a limited range by reweighting the results of a standard MC simulation. That is, Equation (1) can be rewritten as

$$\langle f \rangle = \frac{\int f(U) \gamma(U) \exp(-\beta U) dU}{Z(\beta)} , \quad (3)$$

where $Z(\beta) = \int \gamma(U)\exp(-\beta U)dU$, $\gamma(U)$ is the number of configurations between U and U+dU, and f(U) is the average of f over those configurations. Then $\gamma(U)$ is proportional to $e^{+\beta U}$ times the number of counts in the range U to U+dU. With further reweighting, thermodynamic quantities can be evaluated for different values of density, $\rho$, and temperature, T, over a limited range. For example, Equation (3) can be evaluated for any value of $\beta$ provided $\gamma(U)$ and f(U) are known over the range of importance to the integrals. This idea was made more efficient by Torrie and Valleau's umbrella sampling[7] in which a non-Boltzmann distribution is used to cover a wider range in a single sample. A number of applications of these and related methods have been made.

In this paper, we develop a variation on the types of methods mentioned above with the advantage of spanning a very large range in U in a straightforward manner. In addition, a reasonable number of particles can be used in the simulation (in this example N=122) in contrast to many of the other methods which are typically implemented with N=32. The evaluation of thermodynamic quantities from the simulation is different from the above methods although there is some overlap. In addition to the usual steps in configuration space, a step in $\ln\beta$ is made after a given number of steps in U. This combined algorithm samples with probability density $P(\beta, r_1, \cdots, r_N) = \exp(-\beta U(r_1, \cdots, r_N))/Z(\beta)$ in the limit of slow motion in $\beta$ relative to motion in U. A uniform distribution over $\ln\beta$ could be made with random steps. For numerical convenience, however, we have chosen to make constant size steps in $\ln\beta$ moving alternately up and then down a given range of $\ln\beta$.

Consider each value of $\beta$ to designate a separate NVT ensemble simulation. Provided the initial condition of the $\beta$ simulation is from a configuration that is typical of a simulation at that value of $\beta$, then the usual equilibration part of the run can be eliminated. (Note that there is no preference inherent in the simulation for any given configuration with energy U over any other with the same U. So, a change in $\beta$ only changes the overall probibility of sampling a state with energy U and not the relative probabilities of particular configurations with the same U.) Given 1) a small enough step in $\beta$ to yield a small change in the distribution of U's sampled and 2) a long enough sub-simulation at each $\beta$ to eliminate any significant correlation in U between the initial and final state of the sub-simulation, then the neglect of the equilibration stage is valid. In addition, a repeated entry of the $\beta$ sub-simulation at several stages in the full simulation is qualitatively the same as taking

uncorrelated sub-simulations from a very long NVT MC run.

Given this reference simulation, how can we evaluate $\gamma(U)$? Now $\gamma(U)$ is a very rapidly rising function and $\exp(-\beta U)$ is a very rapidly decreasing function such that the product is sharply peaked. This peak occurs where $\partial[\ln\gamma(U)-\beta U]/\partial U=0$. Because of the very sharp peak, we also know that it occurs at $U=\langle U\rangle$. This gives a simple relation from which to determine $\gamma(U)$,

$$\beta = \left.\frac{\partial\ln\gamma(U)}{\partial U}\right|_{U=\langle U\rangle_\beta} , \qquad\qquad (4)$$

where the $\beta$ subscript is a reminder that $\langle U\rangle$ is a function of $\beta$. Then by integration,

$$\ln\gamma(U) = -\int_U^\infty \beta(U)\,dU. \qquad\qquad (5)$$

From the reference simulation, we obtain approximate values for $U(\beta)$ for as many values of $\beta$ as were sampled. The scatter in this data can be reduced by fitting to a reasonable functional form. Since the reference simulation used throughout this paper is for the $r^{-12}$ potential, we will restrict the discussion to that particular case. In reference 4, we fit $\ln\beta$ vs. $\ln U$ which is fine for a relatively large but finite range in U. For this study, however, we have extended the range of the simulation from the virial region to the melt line. By choosing a functional form consistent with the virial EOS, the range is further extended from the ideal gas regime to the melt line.

The soft sphere fluid has scaling properties that allow the "excess" or non-ideal properties to be expressed in terms of a single scaled variable, $x=\beta^k\rho$. (The reference simulation of the soft sphere fluid was made with parameters $\rho=\epsilon=\sigma=1$.) In the virial region (i.e. ideal gas plus second virial coefficient terms only), the compressability factor $Z=PV/NkT$ is given by $Z=1+Bx$ where $B=\pi 2^{3/2}\Gamma(^3/_4)/3=3.62958864$ is the reduced second virial coefficient. Similarly, the excess energy is given by $U/N=kBx^{-3}$. Since we have chosen $\rho=1$, this expression can be inverted to give $x=\beta^k=(4U/NB)^{-1/3}$. The simulation results are then fit to the form,

$$x=\beta^k = \sum_{i=1}^{n} a_i U^{-1/3} . \qquad\qquad (6)$$

The fit and the simulation data are compared in Figure 1. Note that Equation (5) can now be integrated analytically for the functional form, Equation (6).

Periodic boundary conditions were used with a potential cutoff radius $r_c$ chosen at half the box size. Corrections were made with the usual approximation that $g(r)=1$ outside $r_c$ and

integrating the appropriate expressions to get the long range contribution to the quantities of interest. The intial configuration was determined by choosing each coordinate from a uniform random distribution within the box and then ignoring steps in an equilibration period.

As a check on whether $\delta\beta$ is small enough and the number of steps in U between steps in $\beta_0$ is large enough, two sub-averages of U are made for each value of $\beta$. One average is made from segments of the simulation where $\beta$ is increasing and the other for $\beta$ decreasing. The lack of a systematic difference between the two types of averages indicates that the simulation is satisfactory.

DENSITY OF STATES TRANSFORMATION

The real advantage of the method comes from the transformation of the reference density of states to that for an arbitrary linear combination of potentials. Then the EOS over a large parameter space may be sampled from one reference simulation, as demonstrated below.

Consider the following functional form for W the total potential energy per particle,

$$W = \sum_i a_i W_i, \tag{7}$$

where

$$W_i = \frac{1}{2N} \sum_{k=1}^{N} \sum_{l=1}^{N} \varphi_i(r_{kl}), \tag{8}$$

$\varphi_i$ is the ith pair potential for particles k and l separated by distance $r_{kl}$.

For a fixed reference energy U, the probability distribution of configurations with potential energy W, denoted $P(W,U)$, can be sampled from the reference simulation. Then the configurational density of states for the potential W is given by

$$\Gamma(W) = \int \gamma(U) P(W,U) dU. \tag{9}$$

The evaluation of $P(W,U)$ is greatly simplified because its functional form in the variable W is that of a normal distribution to a very good approximation. (This is essentially a consequence of the central limit theorem.) Then $P(W,U)$ is determined by the evaluation of moments

$$\langle W \rangle_U = \sum_i a_i \langle W_i \rangle_U, \tag{10}$$

and

$$\sigma(U)^2 = <W^2>_U - (<W>_U)^2 - \sum_i \sum_j a_i a_j (<W_i W_j>_U - <W_i>_U <W_j>_U). \quad (11)$$

where $< >_U$ denotes the average over all configurations with the reference energy between U and U+dU. For a given value of U, the normal distribution form is

$$P(W,U) = \exp(-\tfrac{1}{2}((W-<W>_U)^2/\sigma(U)^2))/\sigma(U)\sqrt{2\pi}. \quad (12)$$

Note that the linear coefficients $a_i$ enter in a trivial fashion and Equation (12) can be evaluated for an arbitrary set of $a_i$'s once the set of $<W_i>$'s and $<W_i W_j>$'s are sampled from the reference simulation as a function of U. In practice, the moments are sampled over bins in U and fit to algebraic functions of U over the region of U sampled by the reference simulation. Then $<W>_U$ and $\sigma(U)^2$ are evaluated using Equations (10) and (11) for the given set of $a_i$'s. For a given value of W, we can evaluate $\beta(W) = \Gamma'(W)/\Gamma(W)$ (i.e. Equation (4)) from the integral

$$\Gamma'(W) = \int ((<W>_U - W)/\sigma^2(U))\gamma(U)P(W,U)dU \quad (13)$$

and Equation (9).

In order to get the pressure, we also need the average over configurations in the range U to U+dU of that part of the virial due to interparticle forces. For spherical potentials, the relevant functions are $-\tfrac{1}{3}r\varphi_i'(r)$ rather than $\varphi_i(r)$ in Equation (8). For the special case of inverse power law potentials, these two quantities only differ by a constant multiplier. It is a straightforward generalization of the derivation above to obtain an expression for pressure involving the ratio of one dimensional integrals. The Gibbs free energy can also be obtained since the excess entropy is equal to the logarithm of the configurational density of states.

A further simplification can be made, however. Again using the sharpness of the distributions, the integral in Equation (8) can be approximated as

$$\ln \Gamma(W) = \ln [\gamma(U)P(W,U)]_{U@peak} + O(N^{-1}). \quad (14)$$

The other thermodynamic averages then become the values of quantities evaluated at the peak of the sharp distribution. For example, we now have

$$\beta(W) = \Gamma'(W)/\Gamma(W) = (<W>_U - W)/\sigma^2(U) \quad (U@peak). \quad (15)$$

The details are beyond the scope of the present discussion and will be presented in a subsequent paper[8]. The important point is that the thermodynamic quantities are evaluated from algebraic expressions.

We now turn to the calculation of thermodynamics for a system of interest in order to test the precision of this method. Because of its widespread use and available simulation data from other methods, we have chosen the Lennard-Jones fluid as the test case with the soft sphere fluid for the reference simulation.

The soft sphere pair potential is given by

$$u_{12}(r) = 4\epsilon (r/\sigma)^{-12} , \tag{16}$$

and the Lennard-Jones potential is

$$u_{LJ}(r) = 4\epsilon [ (r/\sigma)^{-12} - (r/\sigma)^{-6} ] , \tag{17}$$

where $\epsilon$ is the well depth and $\sigma$ is the point where the LJ potential crosses 0. The same parameters are used in the soft sphere potential to simplify the connection between the two even though a single constant would be sufficient. The scaling properties of the LJ potential make it convenient to use reduced quantities with the following relations: $T^* = kT/\epsilon$, $\rho^* = \rho\sigma^3$, $u^* = u/\epsilon = U^*/N$, and $P^* = P\sigma^3/\epsilon$, where T is the temperature, $\rho$ is the number density, u is the potential energy per particle U/N, and P is the pressure. The simulation was made with $\rho = 1$ and we have chosen $\epsilon = 1$ for convenience. Then we have $\rho^* = \sigma^3$, $a_1 = \sigma^{12}$, $a_2 = -\sigma^{-6}$, $\varphi_1 = 4r^{-12}$, and $\varphi_2 = -4r^{-6}$. With $\rho^*$ and $U^*$ as the independent variables, $T^*$, $P^*$, and $G^*$ are calculated as outlined in the previous section. In this example, the one dimensional integral forms were evaluated using a 20 point Gauss-Hermite quadrature.

In Figure 2 we show how well the simulation fits the functional form Equation (12) for several values of $U_{12}$. The data are scaled such that the data would then lie on a single curve if the fuctional form were exact. We see that this form does fit quite well. In Figures 3 and 4, the analytic fits to scaled values of $<W>$ and $\sigma^2$ are compared with those directly evaluated from the reference simulation. The results for $P^*$ are compared with MC[9,10] and molecular dynamics[11,12] (MD) simulation values in Figure 5. Similar comparisons for a different range of $\rho^*$ and $T^*$ are shown in Figure 6. Note that differences are smaller than the inherent scatter in the usual MD/MC methods. The gas/liquid phase equilibrium line calculation is compared with standard simulation[10,13] and perturbation methods[14] in Figure 7.

The most commonly used pair potential for
detonation products EOS is the exponential-six
form given by

$$\varphi(r) = \epsilon[6\exp(\alpha(1-r/r\ast)) - \alpha(r/r\ast)^{-6}]/(\alpha-6). \qquad (18)$$

Preliminary results are presented here for a fit
(to an accuracy of better than 1%) of the exp-6 as
a linear combination of inverse power law
potentials given by $\varphi_i = 4r^{-i}$ over a range of i=6 to
15. The $a_i$'s are chosen for a given value of $\alpha$
with $\epsilon = r\ast = 1$. The scaling properties in the
Lennard-Jones section are the same here with the
additional relation $\sigma^6 = 2r\ast^6$. Then the $a_i$'s are
scaled to give results for different values of $\rho\ast$.
The algebraic forms for evaluation of
thermodynamic quantities are used. The reference
simulation needs to be run longer to improve the
statistics. but the preliminary results are
accurate to about 2% in comparison with standard
MC simulations[15] for $\alpha = 13.5$. The analytic
representation for the moments are compared with
the direct evaluation from the simulation in
Figures 8, 9, and 10 for a typical case. Results
for 5 values of $\alpha$, 30 values of $\rho\ast$, and 3 values
of T* are shown in Figures 11 and 12. Since the
final expressions are algebraic, as many EOS
points as are desired may be generated with a
negligible amount of computer time once the single
long reference simulation is made.

IMPLICATIONS

We have demonstrated a very efficient method
to generate EOS simulation benchmarks for the
Lennard-Jones and exponential-six potentials.
Indeed the final analytic representations could
compete with perturbation theories for speed and
accuracy. The extension of the method to
mixtures, polar fluids, nonspherical interactions,
and combinations of these appears to be
straightforward. For example, mixtures could be
studied by choosing the $W_i$'s to include the
interactions within and between subgroups of
particles rather than all of the particles in a
simulation. Then the cross potential could be
varied as easily as the density. The phase
segregation line could then be explored as a
function of cross potential parameters using the
free energy results for pure species and mixtures.
These types of studies would be extremely
expensive in both computer time and man-time for
any systematic study with standard methods. With
the new method, these studies become tractable and
the remaining parameter space for detonation

products EOS can be explored. The net goal is to
fill in the gap of missing benchmarks for the
development of thermodynamic theories that will
lead to a detonation products EOS that is
accurate, predictive, and physically meaningful.

FIGURE CAPTIONS

FIGURE 1.   COMPARISON OF SIMULATION DATA (+) AND
EQUATION (6) (LINE).

FIGURE 2.   COMPARISON OF THE NORMAL DISTRIBUTION
(LINE) AND SAMPLES OF THE ACTUAL DISTRIBUTION FROM
THE SIMULATION (SYMBOLS).

FIGURE 3.   COMPARISON OF THE FIT TO <W> (LINE) AND
VALUES FROM THE SIMULATION (+).   VALUES ARE
SCALED.

FIGURE 4. COMPARISON OF THE FIT TO $\sigma^2$ (LINE) AND
VALUES FROM THE SIMULATION (+).   VALUES ARE
SCALED.

FIGURE 5.   P* VERSUS T* FOR A RANGE OF REDUCED
DENSITIES FROM 0.6 TO 1.2.   MC/MD SIMULATIONS
(SYMBOLS), THIS WORK (LINE), . D LOCATION OF THE
MELT LINE (DASH).

FIGURE 6.   PV/NKT VERSUS T* FOR A RANGE OF REDUCED
DENSITIES FROM 0.1 TO C.9.   MC/MD SIMULATIONS
(SYMBOLS) AND THIS WORK (LINE).

FIGURE 7.   GAS/LIQUID EQUILIBRIUM PHASE LINE FOR
THE LENNARD-JONES FLUID.   THIS WORK (LINE),
STANDARD MC SIMULATION (BOX, +), AND PERTURBATION
THEORY FOR THE CRITICAL POINT (LARGE +).

FIGURE 8.   <W> VERSUS $U^{-1/3}$ FOR A TYPICAL EXP-6
CASE.   ANALYTIC FIT (LINE) AND VALUES FROM THE
SIMULATION (DASH).

FIGURE 9.   SAME AS FIGURE 8.

FIGURE 10.   $\sigma^2$ VERSUS $U^{-1/3}$ FOR A TYPICAL EXP-6
CASE.   ANALYTIC FIT (LINE) AND VALUES FROM THE
SIMULATION (DASH).

FIGURE 11.   PV/NKT VERSUS $\gamma$* FOR $\alpha$=12, 12.5, 13,
13.5, AND 14, T*=5, 20, AND 100, AND $\gamma$*=0.1 TO
3.0.   THIS WORK $\alpha$=13.5 (LINE) AND OTHER $\alpha$'S
(DASH), STANDARD MC SIMULATIONS FOR $\alpha$=13.5 (BOX).

FIGURE 12.   SAME AS FIGURE 12 EXCEPT $\beta$U VERSUS $\gamma$*.

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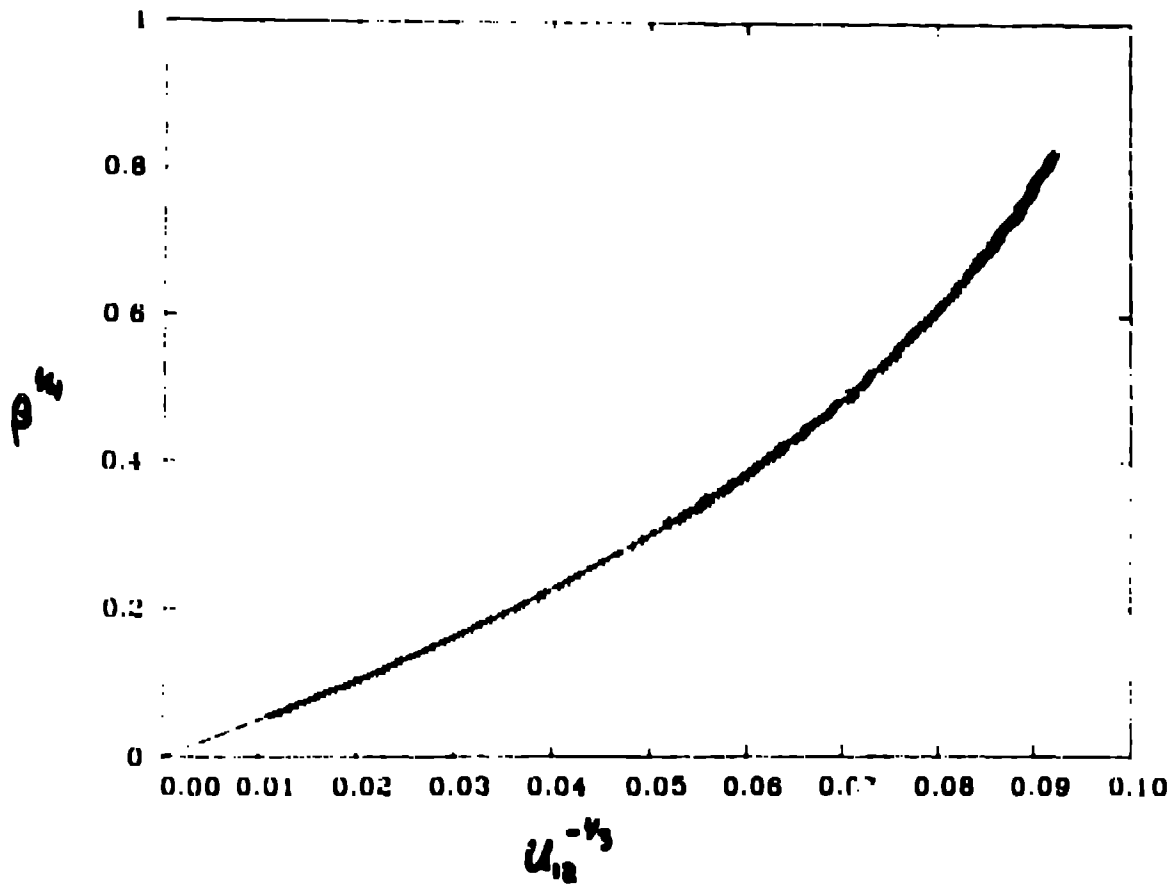
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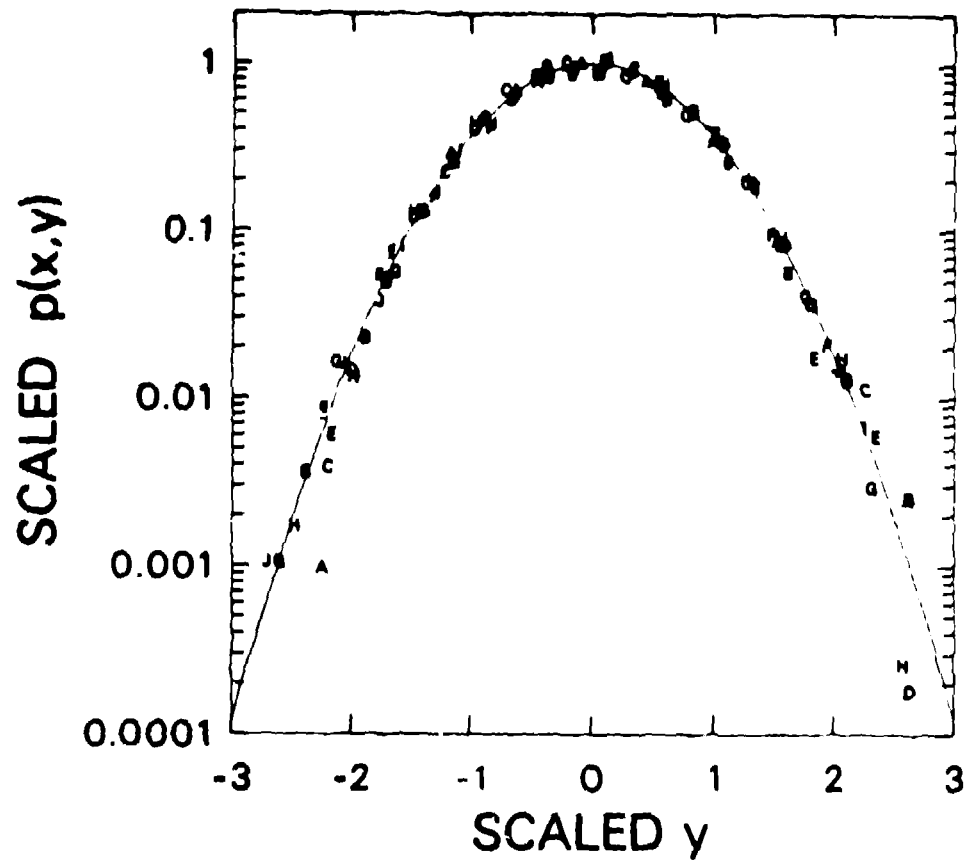
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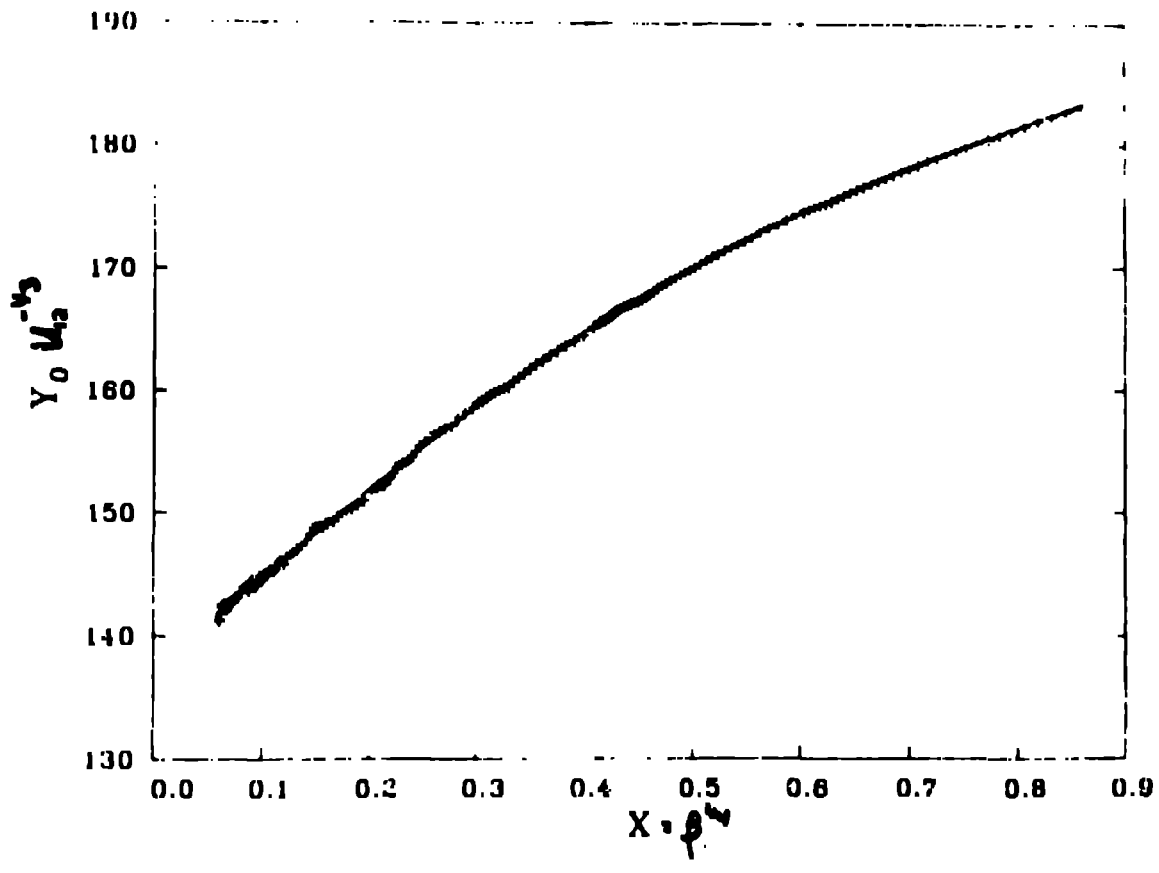
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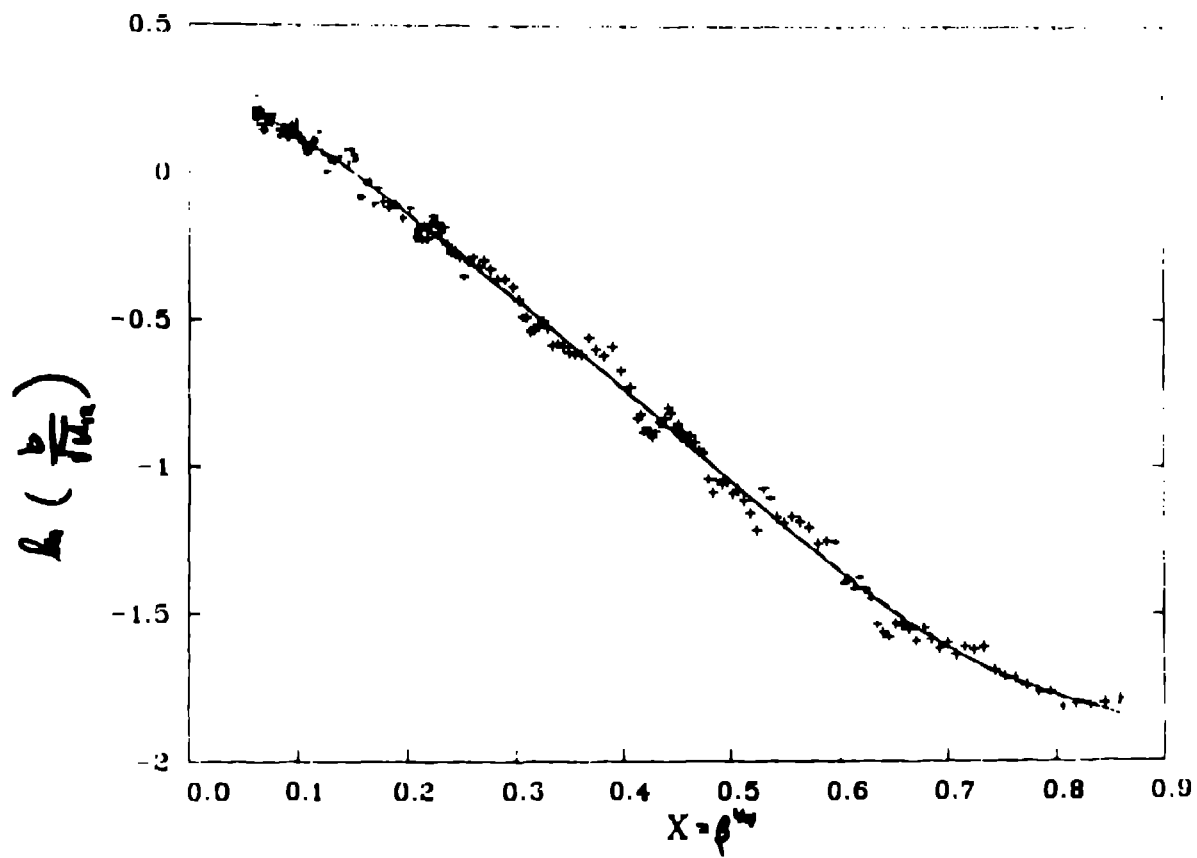
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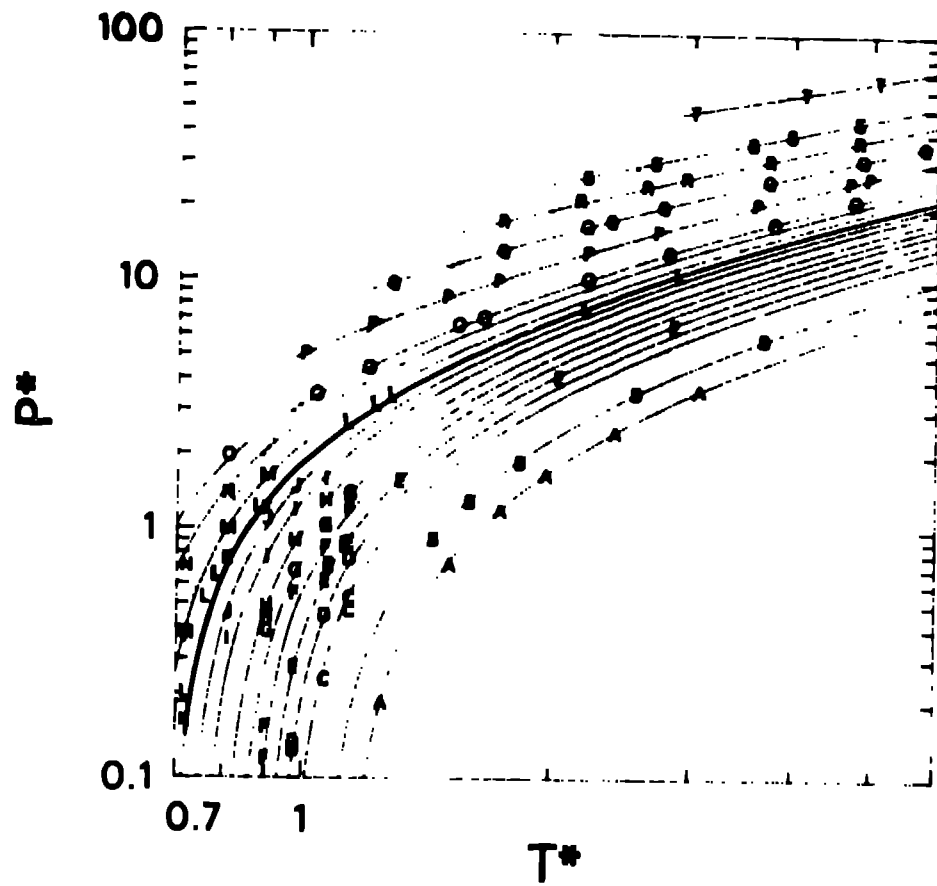
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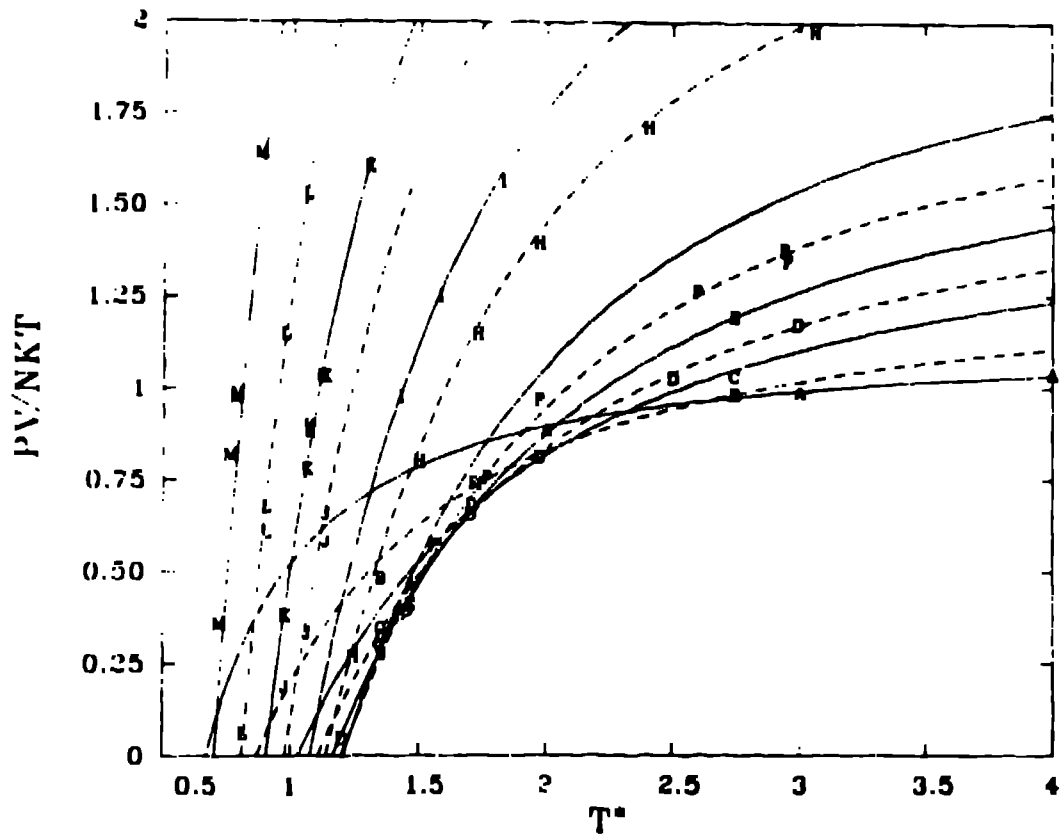
Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12