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FUNDAMENTAL INFORMATION FOR TIGER CODE CALCULATIONS (2)

DETERMINATION OF POTENTIAL ENERGY FUNCTION PARAMETERS

D.E.G. Jones and R. Triebe

Canadian Explosives Research Laboratory

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D.E.G. Jones* and R. Triebe**

ABSTRACT

In all computer codes, using the hydrodynamic conservation conditions and equilibrium thermodynamics to calculate detonation parameters and detonation product composition, an equation of state (EOS) which adequately describes the products is required. This EOS is based on a particular potential energy function with potential parameters specific to that function. These parameters are used in the computer code and must therefore be representative of the EOS used. This report describes two methods for determining these parameters for a variety of potential energy functions, using second virial coefficient data, and demonstrates the effect of these parameters on the results of calculations using the TIGER code.

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INFORMATION DE BASE POUR LE CALCUL DU CODE MACHINE "TIGER" (2)
DÉTERMINATION DES PARAMÈTRES D'ÉNERGIE POTENTIELLE

par

D.E.G. Jones* et R. Triebe**

RÉSUMÉ

Une équation d'état (EOS) décrivant adéquatement les produits est
requise dans le cas de tous les codes machine qui utilisent des équations
de conservation hydrodynamique et d'équilibre thermodynamique pour le calcul
des paramètres relatifs à la détonation et la composition du produit de
détonation. Cette équation d'état (EOS) est basée sur une fonction d'énergie
potentielle particulière qui possède ses propres paramètres. Ces paramètres
sont utilisés dans le code machine et doivent, par conséquent, être
représentatifs de l'équation d'état (EOS) utilisée. Le rapport fait état de
deux méthodes employées pour déterminer ces paramètres pour une gamme de
fonctions d'énergie potentielle qui utilisent le deuxième coefficient virial
et démontre l'effet de ces paramètres sur les résultats des calculs réalisés
au moyen du code machine "Tiger".

Mots-clé :.

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INTRODUCTION

In the estimation of detonation parameters of explosives using hydrodynamic equilibrium computer codes, it is necessary to have available or be readily able to obtain fundamental molecular parameters of the expected gaseous detonation products. These molecular parameters are inherent in the equation of state (EOS) used both to represent the gases in the code and to calculate the thermodynamic properties of these gases. The JC3 EOS appears to be a useful EOS for this purpose (1). Selection of the EOS determines the required intermolecular parameters since the EOS is based on a particular intermolecular potential function. Unfortunately, these parameters are often unavailable in the literature and one is then forced to use the values obtained from the Lennard-Jones (L-J) potential function (2) as estimates.

It is the purpose of this report to describe methods by which the intermolecular parameters can be obtained for any potential function and hence any EOS. More particularly, these parameters are determined for the JC3 EOS and their use is illustrated in the TIGER code for calculating detonation parameters (3).

RELATION OF THE INTERMOLECULAR POTENTIAL
FUNCTION TO SECOND VIRIAL COEFFICIENT

The link between the forces of intermolecular interaction and macroscopic experimental quantities is the relation between the second virial coefficient at temperature T, B(T) and the intermolecular potential energy function, U(r) (4)

$$B(T) = (2\pi N_A/3kT) \int r^3 [d\ U(r)/dr]\ exp(-U(r)/kT)dr \qquad [1]$$

where N_A and k are, respectively, Avogadro's and Boltzmann's constants and r is the distance of intermolecular separation. This equation is valid for angle independent U(r) and for substances independent of quantum effect. Experimental values for B(T) (5) are obtained from pVT

measurements and use of the virial EOS. For any potential function of the form (see Appendix A)

$$U(r) = f(n,m) \; \varepsilon \; [(\sigma/r)^n - (\sigma/r)^m] \qquad [2]$$

where ε is the maximum energy of interaction (depth of the potential well) and σ is the value of r for which $U(r) = 0$ (other than $r = \infty$), an analytical expression for B(T) can be obtained. (Figures 1 and 2 show the dependence of $U(r^*)$ on r^* and the effect of variations of T^* and the exponent n on the form of this function). This method has been outlined (4) for the L-J potential function (n = 12, m = 6 and f(n,m) = 4) and can be generalized as follows:

Substitution of [2] into [1] gives

$$B^*(T^*) = -[f(n,m)/T^*] \int (m/r^{*m}-n/r^{*n})r^{*2} \; \exp\{-[f(n,m)/T^*] \qquad [3]$$
$$(1/r^{*n}-1/r^{*m})\}dr^*$$

where $B^*(T^*) = 3 \; B(T) \; / \; 2\pi N_A \sigma^3$, a dimensionless quantity.

Equation [3] can be integrated analytically and the details can be found in Appendix B. The result is:

$$B^*(T^*) = \sum_{i=1}^{\infty} \{a^{i-f_1} \; \Gamma(f_1)m/n - a^{i-f_2} \; \Gamma(f_2)\}/(i-1)! \qquad [4]$$

where $a = f(n,m)/T^*$, $f_1 = (im-3)/n$, and $f_2 = [n+(i-1)m-3]/n$ and $\Gamma(x)$ is the gamma function (6).

In practice, as T^* increases from 0.3 to 1.5, the number of terms required in the summation of expression [4] decreases from 50 to 25, in order that $B^*(T^*)$ be determined to at least 10 significant figures.

For more complex potential functions, $U(r)$, where the integration

cannot be carried out analytically, a numerical technique can be used to determine B*. The Gauss-Aitken method has been described (7) and has been found effective here, with due regard for singularities in the integrand function.

Both methods have been used to calculate B* for the L-J potential function and for the potential function for which n = 13.5 and m = 6, i.e. that function on which the JC3 EOS is based (1). Additionally, B* has been calculated numerically, using the modified Buckingham-Corner potential function (4)

$$U(r) = \varepsilon[6 \exp \{\alpha(1-r/r_m)\}/\alpha -(r_m/r)^6]/(1-6/\alpha) \qquad [5]$$

for $r \geq r_{max}$, and U(r) = ∞ for $r < r_{max}$, where r_{max} is the value of r for which U(r) given by [7] has a spurious maximum. The parameters, r_m and α in [7] are, respectively, the value of r when U(r) is a minimum, and the number of nearest neighbour contacts in the crystalline structure of the substance.

Figures 3.1 and 3.2 show the dependence of U(r*) on r* = r/r_m and the effect of variations of T* and the parameter α on the form of this function.

Equation [1] cannot be integrated analytically, when [7] is substituted therein. For the purpose of carrying out the numerical integration, the following expression for B* is used

$$B*(T*) = -6/X \int (1/r*^4-r*^3f(r*))\exp\{[1/r*^6-6f(r*)/\alpha]/X\}dr* \qquad [6]$$

where r* = r/r_m, X = T*(1-6/\alpha) and f(r*) = $\exp[\alpha(1-r*)]$.

In equation [6] the integrand is singular when r* = 1. Singularities in equation [3] occur at values of r* given by

$$r* = (n/m)^{1/(n-m)}.$$

These points of singularity represent limits in the integration. It is usually practical to carry out the numerical integration in four parts and establish the lower and upper limits by trial and error, using plots of the integrand functions (see Figs. 4.1 and 4.2) as a guide. Generally, the integrand function is negligibly small in the range $5.0 < r* < 0.5$, the exact range being dependent on $T*$ and exponents n and m.

DETERMINATION OF ε/k AND σ (4)

The experimental data for B(T)(5) can be used to calculate k_B given by

$$k_B = B(T_1)/B(T_2).$$ [7]

This value of k_B is compared with that determined from

$$k_B* = B*(kT_1/\varepsilon)/B*(kT_2/\varepsilon)$$ [8]

using the values of B* for a particular potential function and an estimated ε/k as a starting point. The parameter ε/k is then adjusted so that k_B and k_B* correspond within the limits of the uncertainty in k_B (usually approximately ±5%) and σ can then be calculated from (4),

$$1.2615 \ \sigma^3 = B(T_j)/B*(kT_j/\varepsilon).$$ [9]

DETERMINATION OF "BEST" POTENTIAL FUNCTION

Smith et al (8) (9) have described a method for determining the form of U(r) from reasonably accurate experimental B(T) values over a wide range of T. This method starts with an initial approximate potential function, such as the Lennard-Jones function, to obtain an inversion function G(T*) by determining $B + T$ (dB/dT) for the approximate potential function. From G(T*) a new potential function is determined and used to calculate a new inversion function and this process is repeated until convergence is obtained.

DISCUSSION OF RESULTS

Table 1 shows the agreement between the values of B* calculated for the L-J potential function using both the analytical and numerical methods of integration and also the values of B* reported by Hirschfelder (4). The calculated and literature values of ε/k and σ in Table 2 are in reasonable agreement.

Similarly, Table 3 presents the agreement between the analytical and numerical results for the 13.5 - 6 potential function. The calculated values of ε/k and σ for common gases produced on detonation are listed in Table 4, along with those values currently in use in the TIGER code library for the JC3 EOS.

TABLE 1

Values of B*(T*) for the L - J Potential Function

T*	From Literature	From Gauss - Aitken Method	From Analytical Integration
0.3	-27.88058100	-27.88058209	-27.88058276
1.0	- 2.53808140	- 2.53808134	- 2.53808134
2.5	- 0.31261340	- 0.31261337	- 0.31261337
4.0	0.11541691	0.11541692	0.11541692
5.0	0.24334251	0.24334350	0.24334350
10.0	0.46087529	0.46087528	0.46087528
40.0	0.51857502	0.51857502	0.51857502
80.0	0.47979009	0.47979010	0.47979010
100.0	0.46406948	0.46406947	0.46406947
200.0	0.41143168	0.41143168	0.41143168
400.0	0.35835117	0.35835118	0.35835118

TABLE 2

Parameters for the L-J Potential Function

Parameters

Substance	$\varepsilon/k/K$		σ/nm	
	This work	Literature[1]	This work	Literature[1]
Ar	118 ± 4	122	0.349 ± 0.005	0.340
Xe	217 ± 8	217	0.422 ± 0.010	0.396
H_2	32 ± 2	29.2	0.278 ± 0.016	0.287
O_2	116 ± 6	118	0.354 ± 0.010	0.346
N_2	95 ± 5	95.5	0.379 ± 0.010	0.371
CO	99.9 ± 0.1	100.2	0.372 ± 0.001	0.376
CO_2	213 ± 5	205	0.392 ± 0.007	0.407
CH_4	144 ± 12	148.2	0.393 ± 0.009	0.382
C_2H_6	211 ± 12	243	0.479 ± 0.014	0.395
NO	107 ± 16	131	0.401 ± 0.035	0.317
N_2O	202 ± 25	189	0.433 ± 0.041	0.459
SO_2[3]	196 ± 27	252	0.655 ± 0.059	0.429
HCl[3]	203 ± 58	360	0.473 ± 0.079	0.331

1. Hirschfelder et al
2. neglecting quantum effects
3. derived from viscosity data

TABLE 3

Values of B*(T*) for the 13.5-6 Potential Functions

B*

T*	From Gauss – Aitken Method	From Analytical Integration
0.3	-25.61765821	-25.61765823
1.0	- 2.26327726	- 2.26327727
2.5	- 0.21203785	- 0.21203785
4.0	0.18213251	0.18213250
5.0	0.29979037	0.29979037
10.0	0.49915552	0.49915552
40.0	0.54855155	0.54855155
80.0	0.51021198	0.51021198
100.0	0.49479998	0.49479998
200.0	0.44317908	0.44317908
400.0	0.39084684	0.39084684

TABLE 4

Parameters for the 13.5 - 6 Potential Function

Substance	$\varepsilon/k/K$ Calculated	Library	σ/nm Calculated	Library
Ar	129 ± 10	–	0.345 ± 0.007	–
Xe	227 ± 4	–	0.427 ± 0.020	–
H_2[1]	35 ± 3	37.0	0.276 ± 0.018	0.334
O_2	126 ± 6	132.0	0.352 ± 0.013	0.373
N_2	103 ± 6	120.0	0.375 ± 0.009	0.405
CO	110 ± 1	120.0	0.370 ± 0.002	0.405
CO_2	233 ± 8	200.0	0.395 ± 0.026	0.420
CH_4	153 ± 6	154.0	0.395 ± 0.017	0.429
C_2H_6	236 ± 9	–	0.471 ± 0.007	–
NO	119 ± 18	105	0.393 ± 0.034	0.397
N_2O	220 ± 21	–	0.438 ± 0.029	–
SO_2	217 ± 30	–	0.642 ± 0.058	–
HCl	219 ± 59	360	0.469 ± 0.062	0.331

1. neglecting quantum effects

A comparison of the calculated values of B* using the numerical integration technique and the values given in the literature for the modified Buckingham-Corner potential function at $\alpha=14$, is included in Table 5. The parameters calculated for this potential function are in reasonable agreement with those reported by Hirschfelder et al (4), as shown in Table 6.

TABLE 5

Values of B*(T*) for Modified Buckingham - Corner Potential Function at $\alpha = 14$

B*

T*	From Gauss - Aitken Method	From Literature
0.4	-9.332257	-9.3320
1.0	-1.682281	-1.6823
5.0	0.178865	0.1789
10.0	0.317475	0.3175
20.0	0.352159	0.3522
50.0	0.328168	0.3281
100.0	0.288627	0.2885
200.0	0.243787	0.2438
400.0	0.199435	0.1994

TABLE 6

Parameters for the Modified Buckingham-Corner
Potential Function

					Parameters	
	r_m/nm		ε/k/K		α	
Subs-tance	This work	Litera ture[1]	This work	Litera ture[1]	This work	Litera ture[1]
H[2]	0.313 ± 0.023	0.334	33 ± 3	37.3	14.0	14.0
Ar	0.392 ± 0.007	0.387	122 ± 6	123.3	14.0	14.0
Xe	0.502 ± 0.034	0.445	201 ± 25	231.2	13.5	13.0
CH$_4$	0.450 ± 0.018	0.421	145 ± 17	152.8	14.0	14.0
N$_2$	0.414 ± 0.011	0.401	112 ± 7	101.2	17.0	17.0
CO	0.404	0.394	122	119.1	17.0	17.0

1. Hirschfelder et al

2. neglecting quantum effects

The calculated values of ε/k and σ from the 13.5 - 6 potential function have been used to replace the current values in the TIGER code. Calculations of detonation parameters and products have been made for the systems methylammonium nitrate + water (10) and ANFO. The results in Tables 7 and 8 are compared with those obtained using the "original" library values of ε/k and σ for the detonation products.

Although the detonation parameters are not affected significantly, the composition of the detonation products for the system methylammonium nitrate + water is altered substantially, when the new values of ε/k and σ are used in the TIGER code calculations. The amounts of CO, H_2 and CH_4 are increased whereas the amount of NH_3 is decreased and there is no C(s) predicted. Furthermore, as a result of the change in molecular parameters used in the TIGER code library, the potential classification of this system has changed from an explosive acceptable for underground use based on its fume characteristics to one that is no longer acceptable. Also, the detonation products are now predicted to include a significant proportion (~9 mol %) of combustible gases i.e. H_2 and CH_4.

In the case of ANFO, the detonation pressure is reduced significantly and the amounts of NH_3 and H_2 are, respectively, decreased and increased.

It is noted here that these calculations were done without altering the TIGER code library values of the parameters for H_2O and NH_3. The origin of these values is unknown but it is significant that n-m potential function calculations give drastically different values of ε/k and σ for these substances. Finally, it is well known that simple potential functions do not adequately describe such polar and hydrogen bonded species, for which the U(r) is clearly angle dependent.

TABLE 7

Detonation Parameters and Products for

Methylammonium nitrate + water

Detonation Parameters

Source of parameters	p/kbar	V/cm³/g	T/kK	-E/kJ/g	D/km/s
original	101.4	0.605	2.11	8.41	5.77
calculated in this report	96.3	0.601	2.06	8.25	5.58

Composition of Detonation Products/mol/kg

Product	Original	Calculated in this report
H_2O	20.04	19.77
NH_3	9.94	7.05
CO_2	7.40	7.16
N_2	4.18	5.61
CO	0.34	1.11
H_2	0.11	3.10
CH_4	0.07	0.88
C(s)	1.33	—

TABLE 8

Detonation Parameters and Products for ANFO

Detonation Parameters

Source of parameters	p/kbar	V/cm³/g	T/kK	-E/kJ/g	D/km/s
original	79.3	0.739	2.80	8.27	5.51
calculated in this report	71.0	0.734	2.80	8.24	5.17

Composition of Detonation products/mol/kg

Product	Original	Calculated in this report
H_2O	27.11	27.15
N_2	11.45	11.69
CO_2	3.92	3.87
NH_3	0.59	0.11
CO	0.29	0.33
H_2	0.22	0.90
NO	0.00	0.00

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Appendix A

n-m Potential Energy Functions

The n-m potential energy function is given by

$$U(r) = A/r^n - B/r^m \qquad [1]$$

for $n > m$, and where A/r^n is the repulsive term and B/r^m is the attractive term. Equation [1] can be transformed to one including σ and ε as follows:

$$\text{At} \quad U(r) = 0, \quad r = \sigma \text{ and } \sigma = (A/B)^{1/(n-m)}. \qquad [2]$$

Substitution of [2] into [1] gives

$$U(r) = A(B/A)^{n/(n-m)} [(\sigma/r)^n - (\sigma/r)^m] \qquad [3]$$

$$\text{At} \quad U(r) = -\varepsilon, \quad r = r_\varepsilon \text{ and } dU(r)/dr_\varepsilon = 0. \qquad [4]$$

Use of [4] in equation [3] yields

$$U(r) = \varepsilon \ (n/m)^{m/(n-m)} \ n/(n-m) \ [(\sigma/r)^n - (\sigma/r)^m] \qquad [5]$$

or

$$U(r*)/kT = f(n,m)/T*[1/r*^n - 1/r*^m] \qquad [6]$$

where $f(n,m) = (n/m)^{m/(n-m)} \ n/(n-m)$, $r* = \sigma/r$ and $T* = kT/\varepsilon$, all dimensionless quantities.

APPENDIX B

Analytical expression for B* for n-m potential functions

For a n-m potential function, B* is given by

$$B*(T*) = -a \int (m/r*^{(m-2)} - n/r*^{(n-2)}) \exp(-U(r*)/kT)dr* \qquad [1]$$

where $a = f(n,m)/T*$, and

$$U(r*)/kT = f(n,m)[1/r*^n - 1/r*^m]/T* \qquad [2]$$

Equation [1] can be integrated when [2] is substituted therein, by writing for the term

$$e^{a/r^m} = \sum_i (a/r^m)^{i-1}/(i-1)!. \qquad [3]$$

(Note that the * designation has been dropped)

The first term in the series is (omitting the integration limits)

$$-a \int (m/r^{(n-2)} - n/r^{(n-2)}) e^{-a/r^n} dr$$

which transforms to

$$- a \int t^{-3/n} e^{-at} dt + a(m/n) \int t^{-(n-m+3)/n} e^{-at} dt \qquad [4]$$

by substituting $t = 1/r^n$.

Use of the gamma function given by [5]

$$\Gamma(x) = b^x \int t^{x-1} e^{bt} dt \qquad [5]$$

in [4] gives

$$-a^{1-(n-3)/n} \Gamma([n-3]/n) + (m/n)a^{1-(m-3)/n} \Gamma([m-3]/n).$$

The second term in the series is

$$-a^2 \int (m/r^{(m-2)} - n/r^{(n-2)}) e^{-a/r^n} dr$$

which transforms to

$$-a^2 \int t^{(m-3)/n} e^{-at} dt + (m/n)a^2 \int t^{(2m-n-3)/n} e^{-at} dt \qquad [6]$$

and substitution of [5] into [6] gives

$$-a^{2-(n+m-3)/n} \Gamma([n+m-3]/n) + (m/n)a^{2-(2m-3)/n} \Gamma([2m-3]/n).$$

The subsequent terms in the series are obtained in a similar fashion and are listed in the Table.

TABLE 9

Terms in equation for B* for n-m potential functions

Term	Expression
1	$(m/n)a^{1-(m-3)/n}\ \Gamma([m-3]/n) - a^{1-(1-3/n)}\Gamma(1-3/n)$
2	$(m/n)a^{2-(2m-3)/3n}\ \Gamma([2m-3]/n) - a^{2-(1+[m-3]/n)}\ \Gamma(1+[m-3]/n)$
3	$(m/n2!)a^{3-(3m-3)/n}\ \Gamma([3m-3]/n) - (1/2!)a^{3-(1+[2m-3]/n)}\ \Gamma(1+[2m-3]/n)$
4	$(m/n3!)a^{4-(4m-3)/n}\ \Gamma([4m-3]/n) - (1/3!)a^{4-(1+[3m-3]/n)}\ \Gamma(1+[3m-3]/n)$
i	$(m/n[i-1]!)a^{i-f_1}\ \Gamma(f_1) - (1/[i-1]!)a^{i-f_2}\ \Gamma(f_2)$

$$f_1 = (im-3)/n$$

$$f_2 = (n+[i-1]m-3)/n$$

FIGURE 1

12−6 potential functions
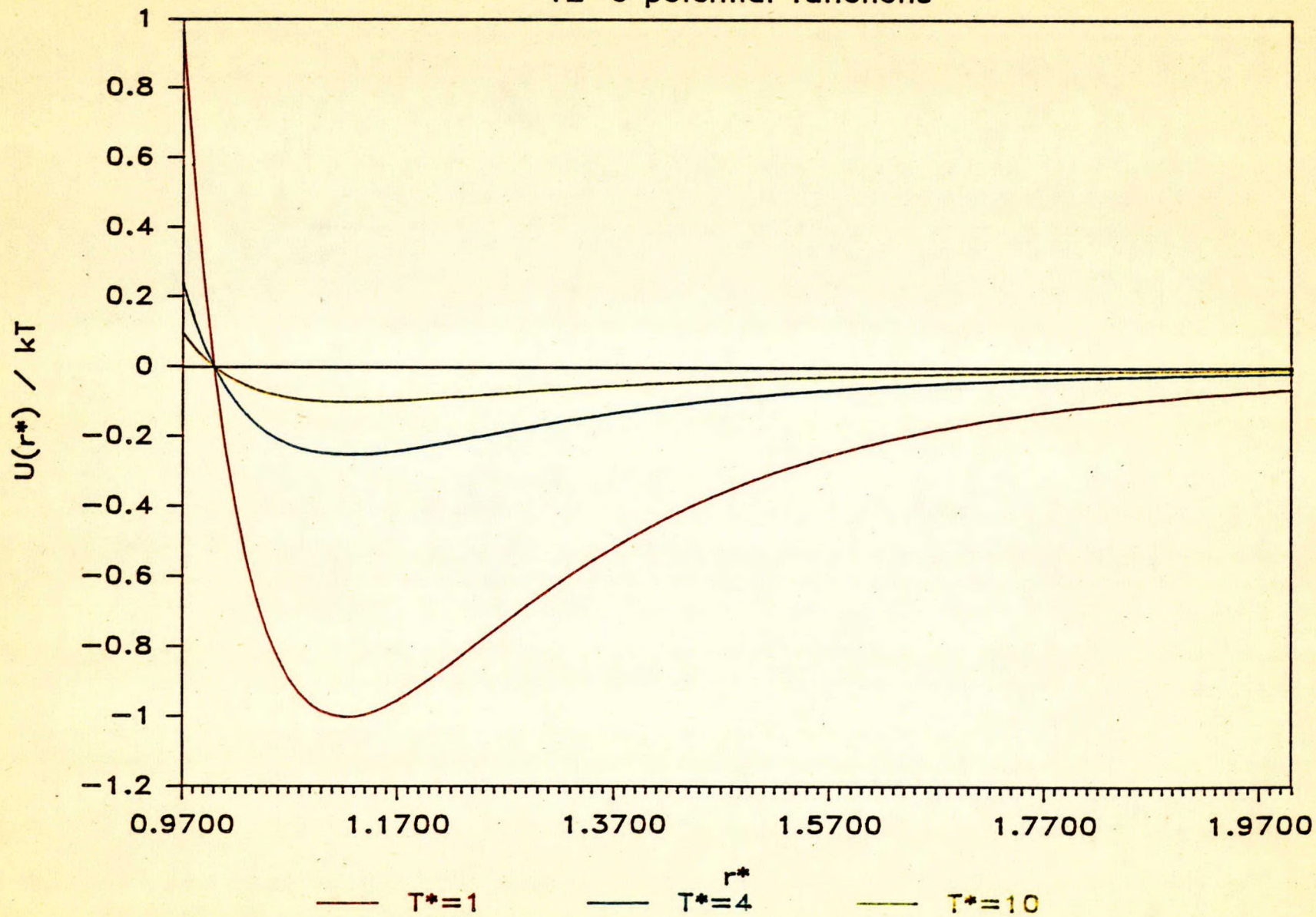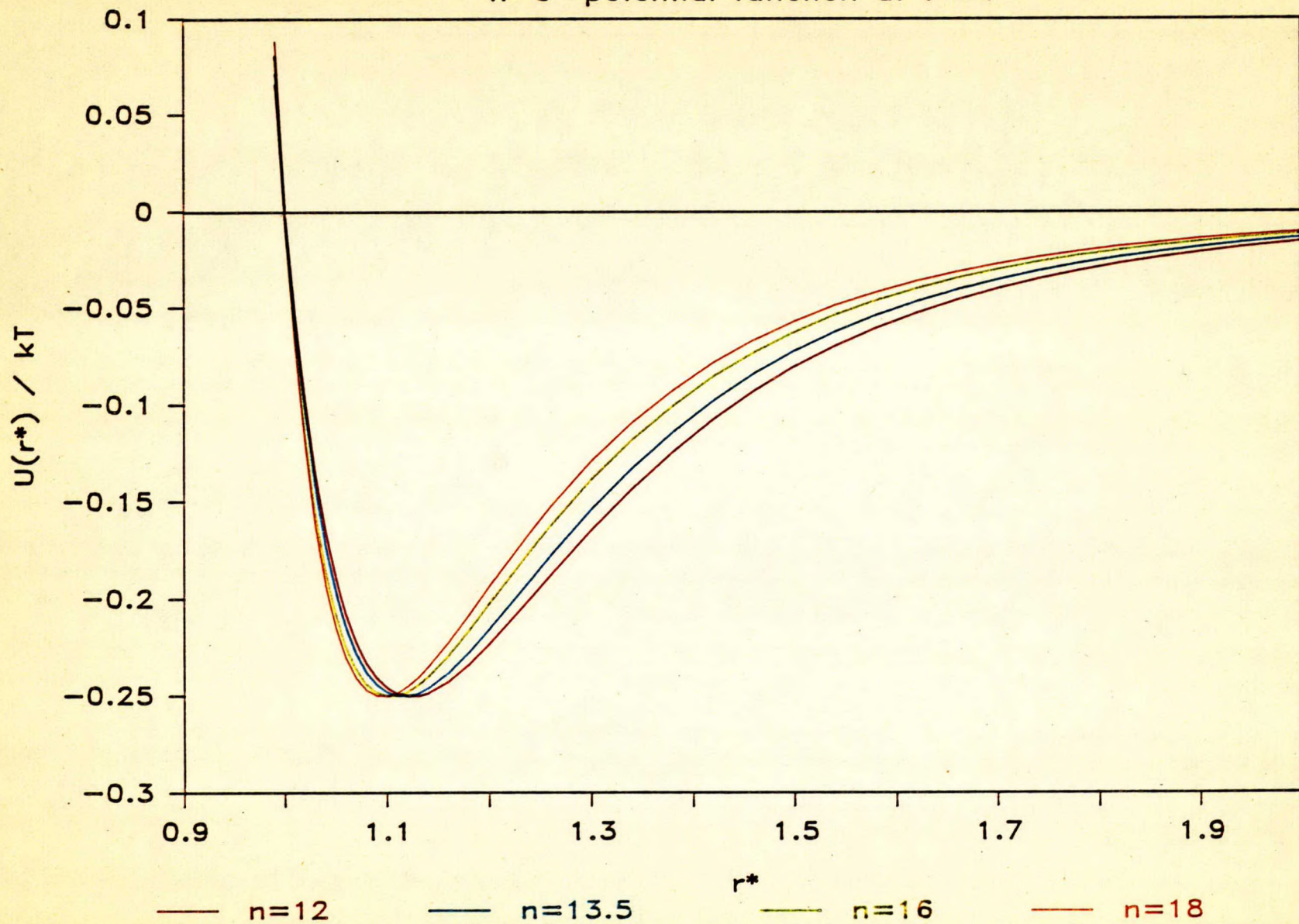
FIGURE 2

n−6   potential function at T*=4
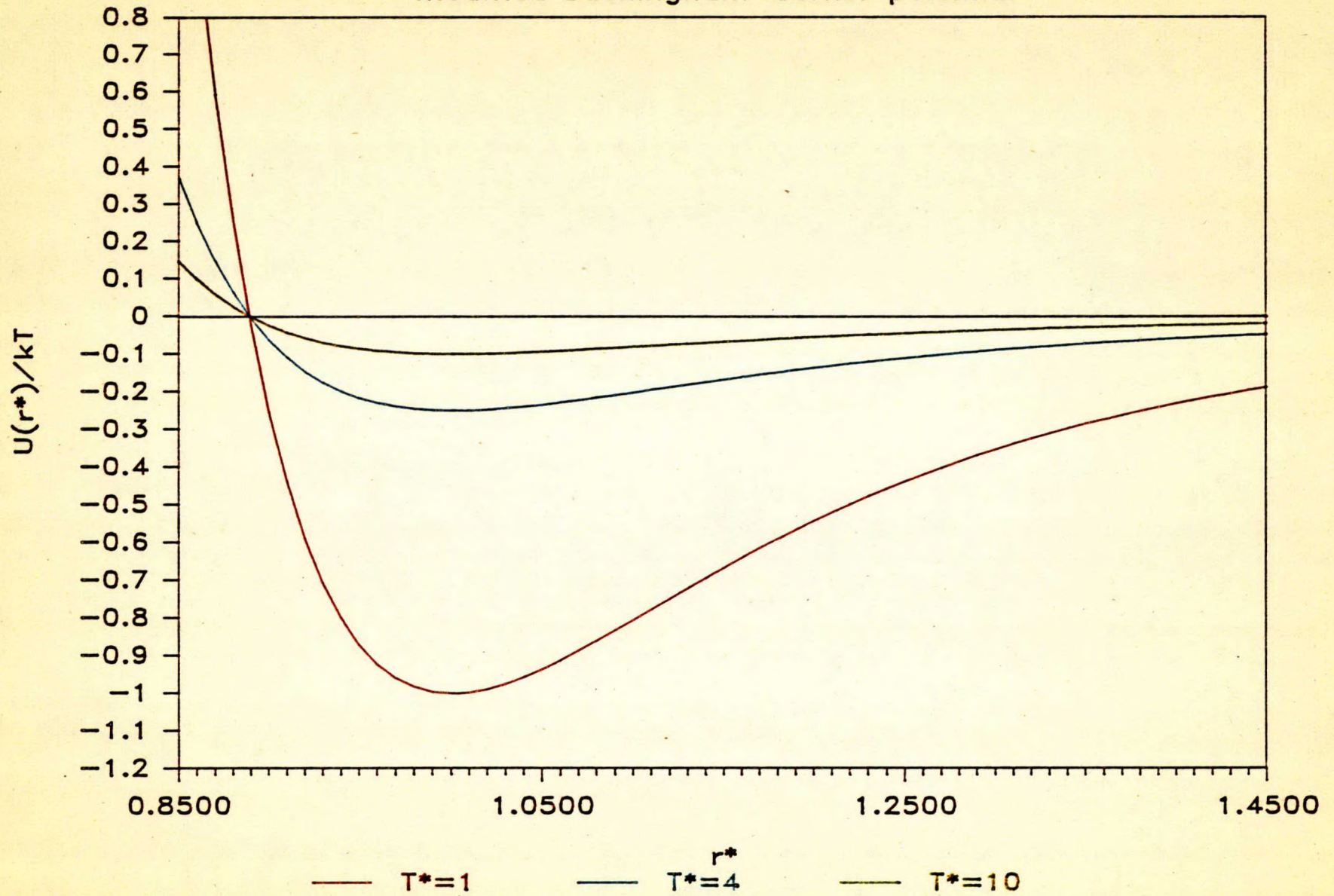
FIGURE 3.1

modified Buckingham—Corner potential

FIGURE 3.2
modified Buckingham–Corner potential

alpha=14   alpha=16   alpha=17   alpha=20
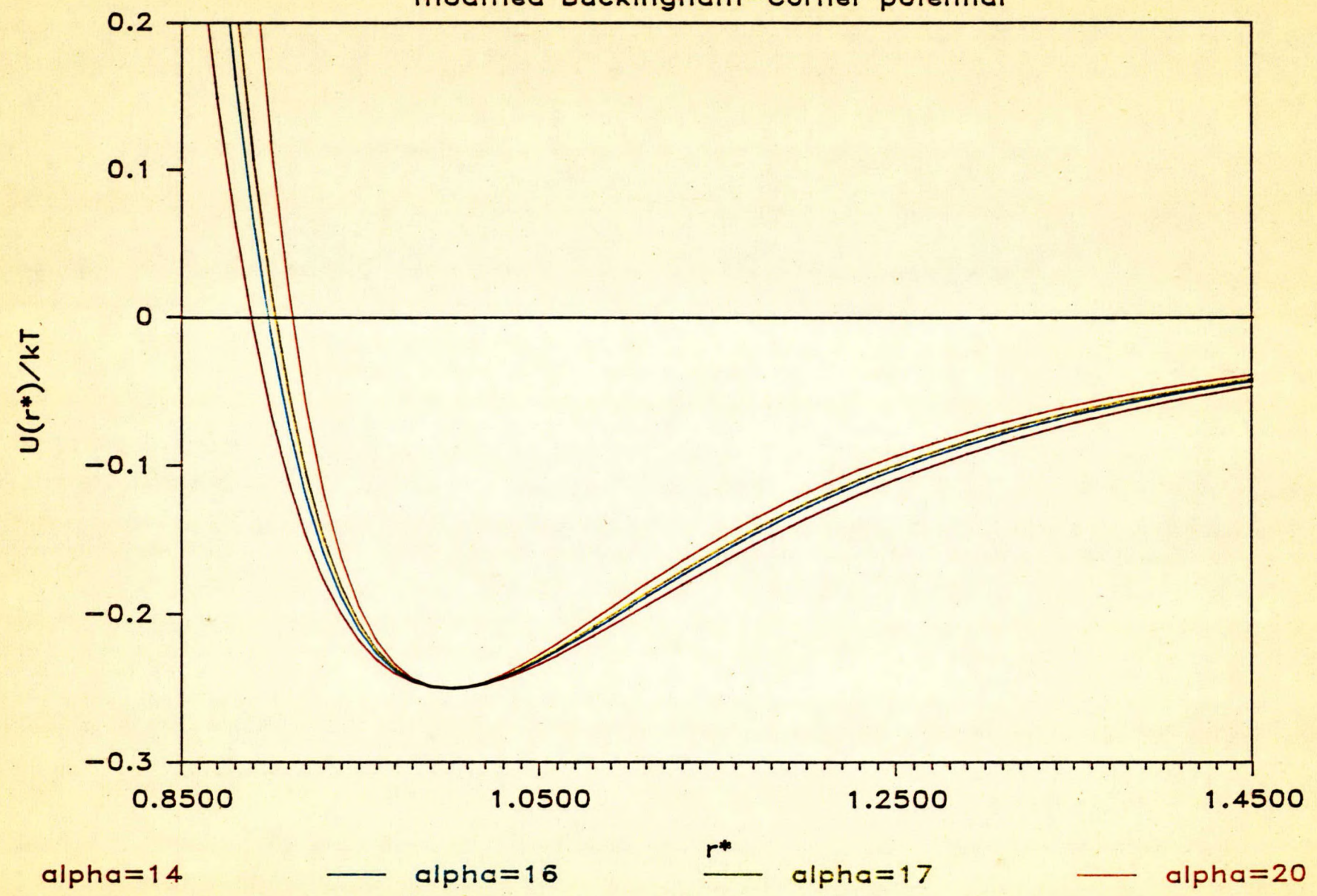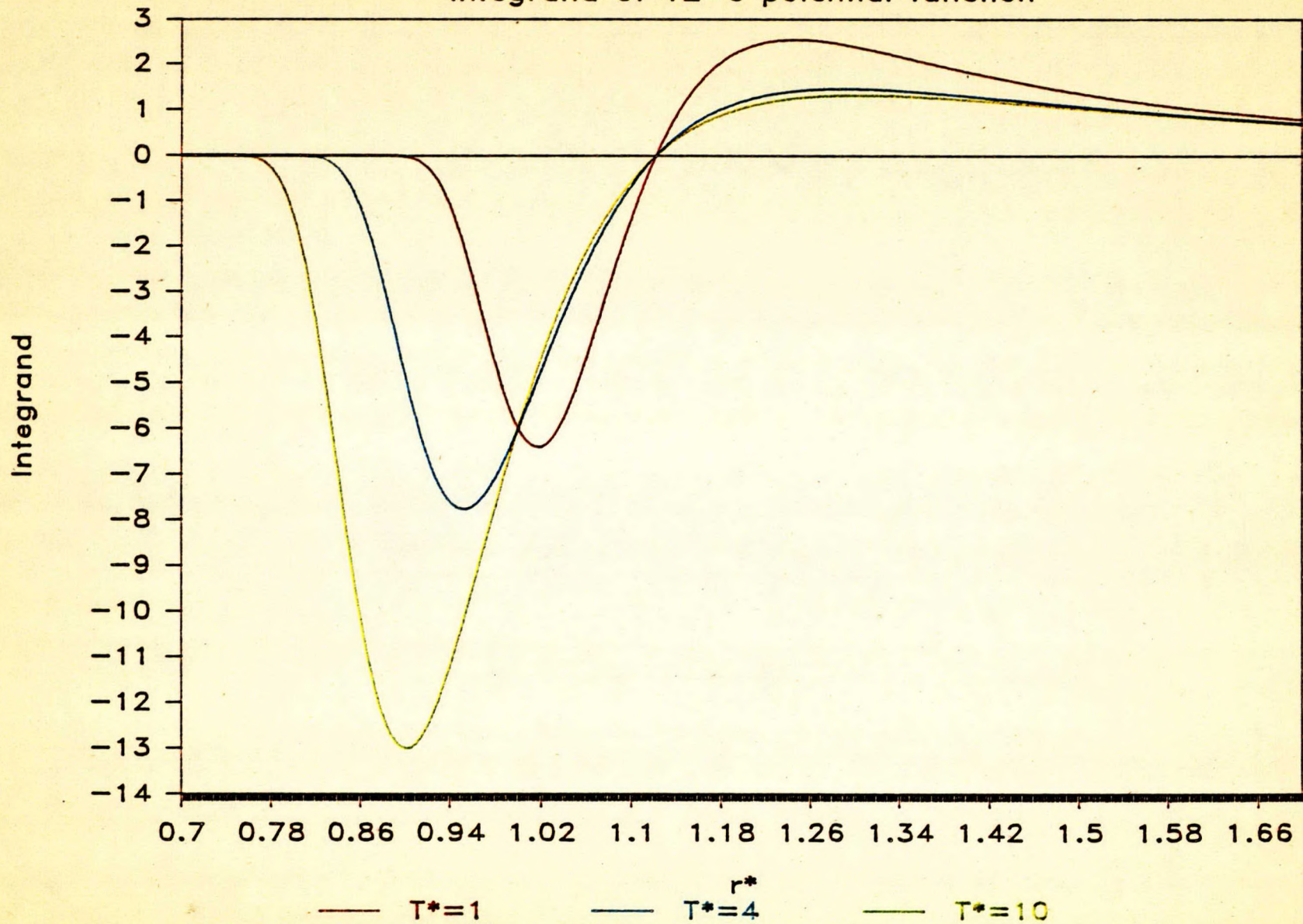
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FIGURE 4.1

Integrand of 12-6 potential function

FIGURE 4.2

Integrand of n−6 potential functions