Structural properties of fluids interacting via piece-wise constant potentials with a hard core

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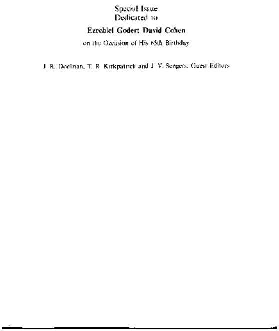
107 Statistical Mechanics Meeting, Rutgers May 8, 2012

Outline

Eddie Cohen

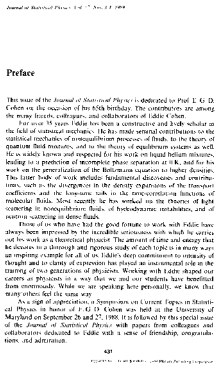
Eddie and Marina Cohen with my wife and me at the Rockefeller University on the occasion of Eddie's sixtieth birthday.

Eddie's Festchrift on the occasion of his sixty-fifth birthday.



Special Issue
Dedicated to
Ezechiel Godert David Cohen
on the Occasion of His 65th Birthday

J. R. Dorfman, T. R. Kirkpatrick and J. V. Sengers, Guest Editors


Journal of Statistical Physics Vol. 57, Nos. 3/4, 1989

Preface

This issue of the *Journal of Statistical Physics* is dedicated to Prof. E. G. D. Cohen on the occasion of his 65th birthday. The contributors are among the many friends, colleagues, and collaborators of Eddie Cohen.

For over 35 years Eddie has been a constructive and lively scholar in the field of statistical mechanics. He has made seminal contributions to the statistical mechanics of nonequilibrium processes of fluids, to the theory of quantum fluid mixtures, and to the theory of equilibrium systems as well. He is widely known and respected for his work on liquid helium mixtures, leading to a prediction of incomplete phase separation at 0 K, and for his work on the generalization of the Boltzmann equation to higher densities. This latter body of work includes fundamental discoveries and contributions, such as the divergences in the density expansions of the transport coefficients and the long-time tails in the time-correlation functions of molecular fluids. Most recently he has worked on the theories of light scattering in nonequilibrium fluids, of hydrodynamic instabilities, and of neutron scattering in dense fluids.

Those of us who have had the good fortune to work with Eddie have always been impressed by the incredible seriousness with which he carries out his work as a theoretical physicist. The amount of time and energy that he devotes to a thorough and rigorous study of each topic is in many ways an inspiring example for all of us. Eddie's deep commitment to intensity of thought and to clarity of expression has played an instrumental role in the training of two generations of physicists. Working with Eddie shaped our careers as physicists in a way that we and our students have benefitted from enormously. While we are speaking here personally, we know that many others feel the same way.

As a sign of appreciation, a Symposium on Current Topics in Statistical Physics in honor of E. G. D. Cohen was held at the University of Maryland on September 26 and 27, 1988. It is followed by this special issue of the *Journal of Statistical Physics* with papers from colleagues and collaborators dedicated to Eddie with a sense of friendship, congratulations, and admiration.

Piece-wise constant potential with a hard core

We consider discrete potentials of the form

$$\varphi(r) = \begin{cases} \infty, & r < \sigma, \\ \epsilon_1, & \sigma < r < \lambda_1\sigma, \\ \epsilon_2, & \lambda_1\sigma < r < \lambda_2\sigma, \\ \vdots & \vdots \\ \epsilon_n, & \lambda_{n-1}\sigma < r < \lambda_n\sigma, \\ 0, & r > \lambda_n\sigma. \end{cases} \tag{1}$$

- Hard core of diameter σ and n steps of "heights" ϵ_j and widths $(\lambda_j - \lambda_{j-1})\sigma$ $(\lambda_0 = 1)$
- $\lambda_n\sigma$ denotes the total range of $\varphi(r)$

- The sign of ϵ_j determines whether the j-th step is either a "shoulder" ($\epsilon_j > 0$) or a "well" ($\epsilon_j < 0$). The interaction potential at $r = \lambda_j\sigma$ ($j = 1, \ldots, n$) is repulsive if $\epsilon_j > \epsilon_{j+1}$ and attractive if $\epsilon_j < \epsilon_{j+1}$ ($\epsilon_{n+1} = 0$).

- The density is measured by the packing fraction $\eta \equiv \frac{\pi}{6}\rho\sigma^3$.

- Hard-core diameter $\sigma = 1$ taken as the length unit.

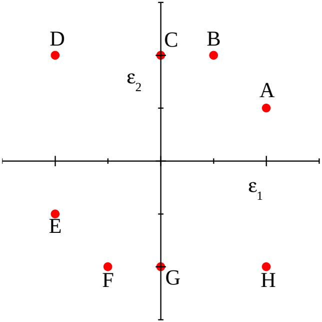
- Particular cases when $n = 1$ are the square-well and square-shoulder potentials

Why these potentials are interesting

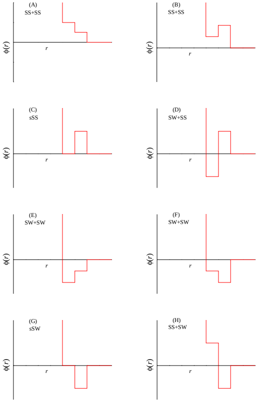
- Relative simplicity and versatility
- Applications (amongst others): chemical reactions, liquid-liquid transitions, colloidal interactions, anomalous density behavior of water and supercooled fluids and thermodynamic and transport properties of Lennard-Jones fluids.
- Scarcity of studies of structural properties

Chosen potentials

We will consider here cases with $n = 2$



$\lambda_1 = 1 \cdot 25$ and $\lambda_2 = 1 \cdot 5$



Structural properties

Static structure factor $S(q)$ and radial distribution function $g(r)$

$$
\begin{aligned}
S(q) &= 1 + \rho \int \mathrm{d}\mathbf{r}\, \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}}[g(r) - 1] \\
&= 1 - 2\pi\rho \left. \frac{G(s) - G(-s)}{s} \right|_{s=\mathrm{i}q}, \qquad (2)
\end{aligned}
$$

where ρ is the number density and

$$
G(s) = \int_0^\infty \mathrm{d}r\, \mathrm{e}^{-rs} r g(r) \qquad (3)
$$

is the Laplace transform of $rg(r)$.

The method

We define an auxiliary function $F(s)$ directly related to $G(s)$ through

$$\begin{aligned} G(s) &= s\frac{F(s)e^{-s}}{1+12\eta F(s)e^{-s}} \\ &= \sum_{m=1}^{\infty}(-12\eta)^{m-1}s[F(s)]^m e^{-ms}. \end{aligned} \tag{4}$$

Laplace inversion of Eq. (4) provides a useful representation of $g(r)$

$$g(r) = r^{-1}\sum_{m=1}^{\infty}(-12\eta)^{m-1}f_m(r-m)\Theta(r-m), \tag{5}$$

where $f_m(r)$ is the inverse Laplace transform of $s[F(s)]^m$ and $\Theta(r)$ is Heaviside's step function.

The contact value of the radial distribution function $g(1^+)$ is related to $F(s)$ through $g(1^+) = f_1(0) = \lim_{s\to\infty} s^2 F(s)$ and it has to be finite. Further, the behavior of $G(s)$ for small s determines the value of $S(0)$. Hence, $F(s)$ must satisfy two conditions:

$$F(s) \sim s^{-2}, \quad s \to \infty \tag{6}$$

and

$$F(s) = -\frac{1}{12\eta}\left(1 + s + \frac{1}{2}s^2 + \frac{1+2\eta}{12\eta}s^3 + \frac{2+\eta}{24\eta}s^4\right) + \mathcal{O}(s^5). \tag{7}$$

To reflect the discontinuities of $g(r)$ at the points $r = \lambda_j$ where $\varphi(r)$ is discontinuous, we decompose $F(s)$ as

$$F(s) = \sum_{j=0}^{n} R_j(s) e^{-(\lambda_j - 1)s}, \tag{8}$$

and assume the following *rational-function* approximation for $R_j(s)$:

$$R_j(s) = -\frac{1}{12\eta} \frac{A_j + B_j s}{1 + S_1 s + S_2 s^2 + S_3 s^3}, \quad j = 0, \ldots, n. \tag{9}$$

The approximation (9) contains $2n + 5$ parameters to be determined.

The exact expansion of $F(s)$ imposes five constraints among the $2n+5$ parameters, namely

$$A_0 = 1 - \sum_{j=0}^{n} A_j, \tag{10}$$

$$S_1 = -1 + B_0 - C^{(1)}, \tag{11}$$

$$S_2 = \frac{1}{2} - B_0 + C^{(1)} + \frac{1}{2} C^{(2)}, \tag{12}$$

$$S_3 = -\frac{1+2\eta}{12\eta} + \frac{1}{2} B_0 - \frac{1}{2} C^{(1)} - \frac{1}{2} C^{(2)} - \frac{1}{6} C^{(3)}, \tag{13}$$

$$B_0 = C^{(1)} + \frac{\eta/2}{1+2\eta} \left(6C^{(2)} + 4C^{(3)} + C^{(4)} \right) + \frac{1+\eta/2}{1+2\eta}, \tag{14}$$

Here,

$$C^{(k)} \equiv \sum_{j=1}^{n} \left[A_j(\lambda_j - 1)^k - kB_j(\lambda_j - 1)^{k-1} \right]. \tag{15}$$

A simplifying assumption is that the coefficients A_j ($j = 0, \ldots, n$) may be fixed at their zero-density values, namely

$$A_0 = e^{-\beta\epsilon_1} \tag{16}$$

and

$$A_j = e^{-\beta\epsilon_{j+1}} - e^{-\beta\epsilon_j}, \quad j = 1, \ldots, n. \tag{17}$$

On the other hand, since the cavity function $y(r) \equiv g(r)e^{\varphi(r)/k_B T}$ must be continuous at $r = \lambda_j$, the coefficients B_j $(j = 1, \ldots, n)$ are determined from

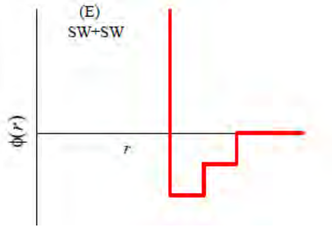
$$\frac{B_j}{S_3} = \left[e^{\beta(\epsilon_j - \epsilon_{j+1})} - 1\right] \sum_{\alpha=1}^{3} \frac{s_\alpha e^{\lambda_j s_\alpha}}{S_1 + 2S_2 s_\alpha + 3S_3 s_\alpha^2} \sum_{i=0}^{j-1} (A_i + B_i s_\alpha) e^{-\lambda_i s_\alpha} \tag{18}$$

$$(j = 1, \ldots, n)$$

where s_α $(\alpha = 1, 2, 3)$ are the three roots of the cubic equation

$$1 + S_1 s_\alpha + S_2 s_\alpha^2 + S_3 s_\alpha^3 = 0 \tag{19}$$

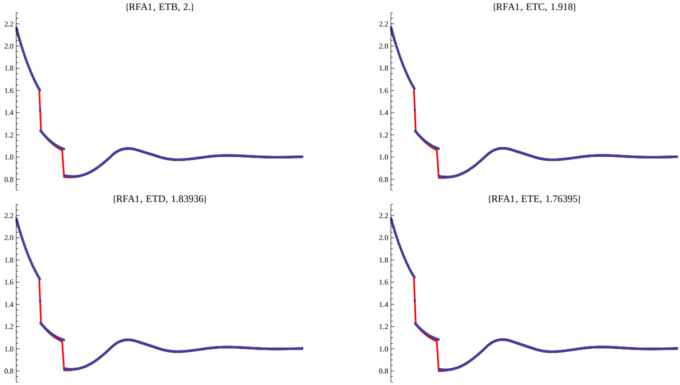
RESULTS

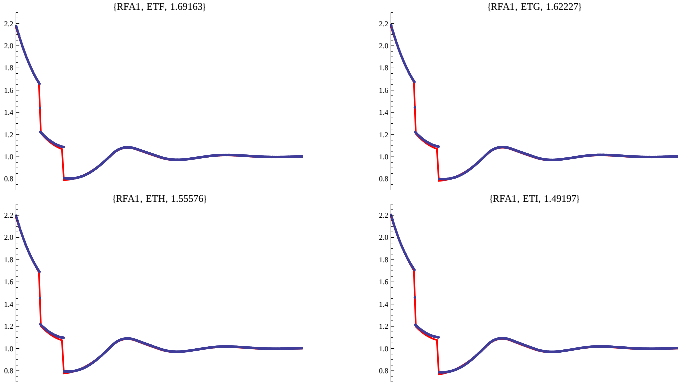


$$\rho\sigma^3 = 0 \cdot 5,$$

$$1 \cdot 26193 \leq k_B T/\epsilon \leq 2, \text{ (with } \epsilon = \max\{|\epsilon_1|, |\epsilon_2|\})$$

Red: RFA
Blue: Simulation

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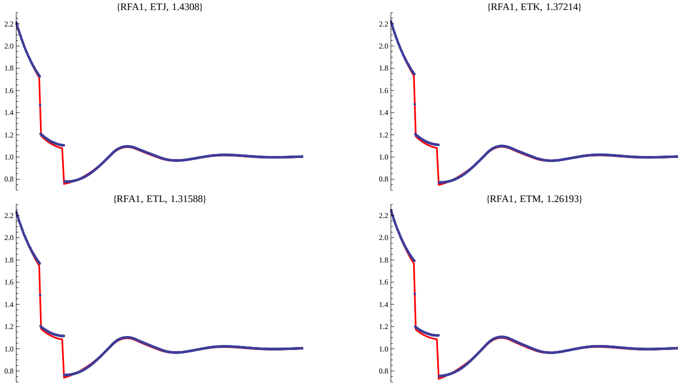
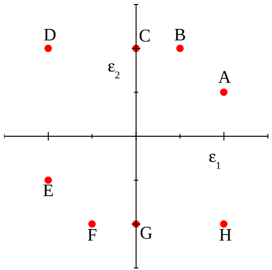
{RFA1, ETG, 1.62227}
{RFA1, ETH, 1.55576}
{RFA1, ETI, 1.49197}
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8

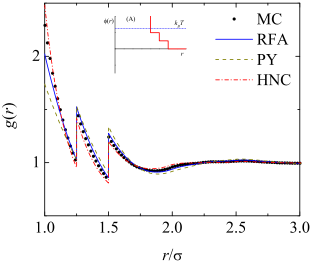

{RFA1, ETJ, 1.4308}
{RFA1, ETK, 1.37214}
{RFA1, ETL, 1.31588}
{RFA1, ETM, 1.26193}
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8

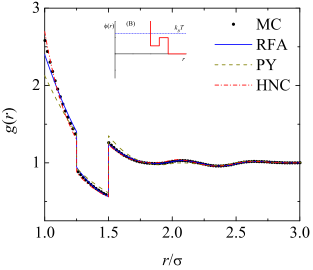
We further illustrate our findings taking $\rho\sigma^3 = 0 \cdot 5$ and $k_B T/\epsilon = 1 \cdot 261928$ in all cases. In units of ϵ, $\epsilon_1 = 0, \pm 0 \cdot 5, \pm 1$ and $\epsilon_2 = \pm 0 \cdot 5, \pm 1$, depending on the case.



Some side remarks

- The cases having $\epsilon_1 = \epsilon_2$ have not been considered since they correspond to having just one step.
- The four cases $(0, 0\cdot 5)$, $(0, -0\cdot 5)$, $(-0\cdot 5, 0\cdot 5)$ and $(0\cdot 5, -0\cdot 5)$ are identical to the cases $(0, 1)$, $(0, -1)$, $(-1, 1)$ and $(1, -1)$, respectively. In fact, given the choice $\epsilon = \max(|\epsilon_1|, |\epsilon_2|)$, at least one of the $|\epsilon_i|$ must be 1.
- The four cases $(-1, 0\cdot 5)$, $(-0\cdot 5, 1)$, $(0\cdot 5, -1)$ and $(1, -0\cdot 5)$ are topologically equivalent to the cases $(-1, 1)$, $(-1, 1)$, $(1, -1)$ and $(1, -1)$, respectively. It is only the relative scale between well and shoulder which changes. If ϵ_1 and ϵ_2 have opposite signs, we do not take any of the ϵ's to be $|\epsilon_i| = 0\cdot 5$.


MC
RFA
PY
HNC
$\phi(r)$
(A)
k_BT
r
$g(r)$
r/σ
1.0
1.5
2.0
2.5
3.0
1
2


3
2
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g(r)
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3.0
r/σ
MC
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PY
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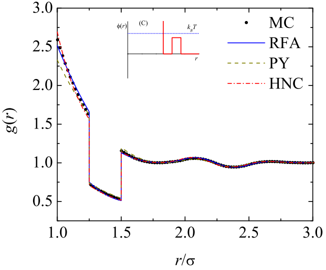
ϕ(r)
(B)
k_BT
r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(C)
φ(r)
k_B T
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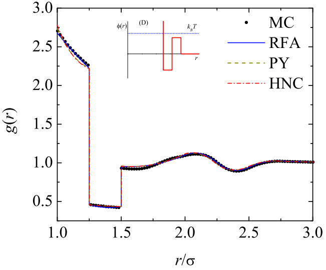
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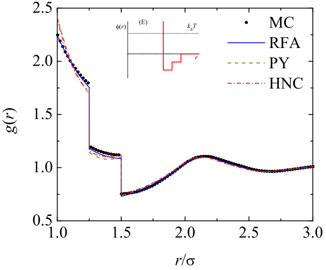
r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MC
RFA
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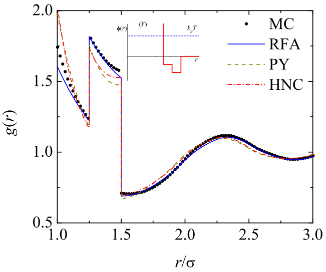
HNC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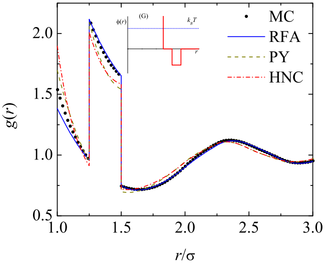
MC
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$k_B T$
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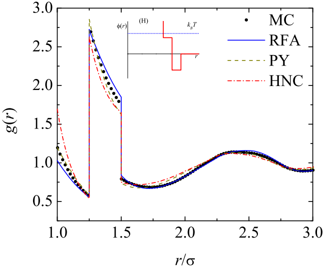
2.0
2.5
3.0


3.0
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r/σ
MC
RFA
PY
HNC
(H)
φ(r)
k_BT
r

Concluding Remarks

- This is yet another successful application of the rational function approximation method that we have used for the computation of the structural properties of hard-core fluids.
- Reasonable compromise between accuracy and simplicity (solution of n coupled trascendental equations).
- It certainly outperforms the PY approximation. (The RFA recovers the PY solution of the HS and the SHS fluids).
- In cases where $\epsilon_1 > 0$ and $\epsilon_2 > 0$ (*Cf.* cases A-C) the HNC approximation is better but if $\epsilon_1 < 0$ and/or $\epsilon_2 \leq 0$ (the rest of the cases) our approximation beats the HNC.
- The consideration of a greater number of steps seems worthwhile in the light of our findings.

Thanks!

Technical simulation details

The simulation data were computed by M. Bárcenas (Tecnológico de Estudios Superiores de Ecatepec) and P. Orea (Instituto Mexicano del Petróleo) with a Replica Exchange Monte Carlo method and a canonical ensemble. A cubic simulation box of dimensions $Lx = Ly = Lz = 10$ was used. Periodic boundary conditions were set in the three directions. Verlet lists were implemented to improve performance The initial configuration, consisting of a collection of 500 particles randomly arranged in the simulation box, was equilibrated by conducting 1×10^7 MC simulation steps. The radial distribution functions were calculated over additional 4×10^7 configurations. The attempted MC moves were accepted or rejected according to the Metropolis algorithm.