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ANALYTIC PROPERTIES OF SYSTEMS WITH LENNARD-JONES TYPE POTENTIALS *

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The properties of a classical system with a n-m pair potential are analytic in a properly defined domain of two complex variables related to the fugacity or density and the temperature. For a Lennard-Jones potential these variables are $\rho\sigma^3(\beta\epsilon)^{\frac{1}{4}}$ and $(\beta\epsilon)^{\frac{1}{2}}$.

It was shown recently [1] that for classical systems with hard cores, (or lattice gases), the thermodynamic and correlation functions have convergent power series expansions in the reciprocal temperature β for small enough values of the fugacity z or density ρ. It was also proven there that the properties of a ferromagnetic Ising spin system, isomorphic to a lattice gas with attractive interactions, are analytic in real $\beta > 0$ in the presence of an external magnetic field. It is the purpose of this note to show that the reduced pressure and other functions of a classical system of particles interacting via a n-m pair potential

$$v(r) = \epsilon\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right], \quad n > m > \nu, \tag{1}$$

where ν is the dimensionality of the space considered, are analytic in the two complex variables ζ and λ or $\bar{\rho}$ and λ, $\zeta = z[\sigma^n \beta\epsilon]^{\nu/n}$, $\lambda = (\beta\epsilon)^{1-m/n}$, $\bar{\rho} = \rho[\sigma^n \beta\epsilon]^{\nu/n}$ for sufficiently small values of $|\zeta|$, $|\bar{\rho}|$, and $|\lambda|$.

To prove this we write the Mayer fugacity expansion for the grand-canonical pressure in the form

$$\beta_p[\sigma^n \beta\epsilon]^{\nu/n} = \pi(\zeta,\lambda) = \zeta + \sum_{l+2}^{\infty} b_l'(\lambda)\,\zeta^l \tag{2}$$

where the b_l' are the usual Mayer cluster integrals expressed in terms of the variable $y = (\beta\epsilon)^{-1/n} r/\sigma$, i.e.,

$$b_2'(\lambda) = \tfrac{1}{2}\int[\exp(-y^{-n} + \lambda y^{-m}) - 1]\,\mathrm{d}^\nu y \text{ etc.}$$

It follows then from the work of Ruelle [2] and Penrose [3] that this series converges and represents the thermodynamic pressure for

$$|\zeta| < 1/[eB'(\lambda)\,\mathrm{e}^{2\Phi'(\lambda)}] \tag{3}$$

where $B'(\lambda) = \int|\exp[-y^{-n} + \lambda y^{-m}] - 1|\,\mathrm{d}^\nu y$, and

$$\Phi'(\lambda) = \tag{4}$$
$$= -\inf_N \inf_{y_1,\dots y_N} N^{-1}\sum_{1\le i<j\le N}[y_{ij}^{-n} - (\mathrm{Re}\,\lambda)y_{ij}^{-m}] < \infty$$

is a generalization of the usual lower bound on the energy per particle for the case when the parameters of the potential may take on complex values.

The last inequality in (4) follows from the work of Fisher [4] and Dobrushin [5] for $n > m > \nu$. Now since the $b_l'(\lambda)$ are entire functions ** of λ and the series (2) is uniformly convergent on any compact set whenever (3) is satisfied, it follows that $\pi(\zeta,\lambda)$ is an analytic function of both complex variables in the domain specified by eq. (3). This domain clearly includes the origins of the complex ζ and λ planes and hence $\pi(\zeta,\lambda)$ may be expanded in a power series in λ for sufficiently small values of ζ.

The reduced density $\bar{\rho}$ has of course the same analyticity domain as $\pi(\zeta,\lambda)$ and so do the reduced l-particle distribution functions [2, 3]

$$\bar{n}_l(y_1,..y_l;\zeta,\lambda) = [\sigma^n\beta\epsilon]^{\nu l/n} n_l(r_1,..r_l;z,\beta). \tag{5}$$

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** This follows essentially from the uniform convergence of the cluster integrals: c.f. also ref. 1 where we prove the analyticity of the usual b_l as a function of β, for $Rl\beta > 0$.

The Ursell functions will also satisfy [6] the cluster property within the domain specified by (3).

Similar results may be obtained for the reduced pressure and other thermodynamic and correlation functions considered as functions of $\bar{\rho}$ and λ,

$$P(\bar{\rho},\lambda) = (\sigma^n \beta\epsilon)^{\nu/n}\, \beta_p = \bar{\rho}[1 - \sum_{l=1}^{\infty} \frac{l}{l+1}\, \beta_l'(\lambda)\, \bar{\rho}^l] \tag{6}$$

where $\beta_2'(\lambda)$ are the irreducible Mayer cluster integrals in the reduced variable y. It was shown by Lebowitz and Penrose [7] that the series converges, and represents the thermodynamic pressure for $|\bar{\rho}| < 0.28952/B(1+e^{2\beta\Phi'})$. We may therefore expand, for sufficiently small $\bar{\rho}$, $P(\bar{\rho},\lambda)$ in a power series in λ, $P(\bar{\rho},\lambda) = \sum a_l(\bar{\rho})\,\lambda^l$. When $n \to \infty$, the reference system obtained by setting $\lambda = 0$, corresponds to a fluid of hard spheres and the expansion in λ becomes an expansion in β discussed in ref. 1. For the Lennard-Jones potential on the other hand this is an expansion in $\sqrt{\beta\epsilon}$ for fixed $\rho\sigma^3(\beta\epsilon)^{\frac{1}{4}}$ and is to be contrasted with the customary [8] empirical representation of the experimental data as a series (finite) in $\beta\epsilon$ for given $\rho\sigma^3$. The latter expansion is difficult to characterize in an unambiguous way since in the limit $(\beta\epsilon) \to 0$, $\rho\sigma^3$ fixed, the system with L-J potential behaves like an ideal gas rather than as a gas of hard spheres which is usually used as a reference system. It would therefore appear useful to plot the experimental and computer data for the inert gases as a function of the parameters $\bar{\rho}$ and λ. Extrapolation of the results to $\lambda = 0$, (if possible), should then correspond to those of a reference system with a purely repulsive r^{-n} potential.

From a purely formal point of view it is also possible, as has been done by many authors [9], to separate the potential given in eq. (1) into a positive and negative part introducing a parameter η: $v(r;\eta) = v(r)\,H(\sigma - r) + \eta\, v(r)\,H(r-\sigma)$, where $H(x)$ is the Heaviside function. Our previous argument can then be used to prove analyticity of the pressure, and other functions, in η for small values of $\rho\sigma^3$ and $\beta\epsilon$. The method can also be extended to other types of potentials with parameters. This can include for example parameters characterizing three (and higher) body potentials which may be of importance even for the inert gases.

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References

1. J. L. Lebowitz and O. Penrose, Commun. Math. Phys., to be published;
   for lattice systems: L. Gallavotti, S. Miracle-Sole and D. Robinson, Phys. Letters 25A (1967) 493 have shown analyticity for small β for all $z > 0$.
2. D. Ruelle, Ann. Phys. 25 (1963) 109.
3. O. Penrose, J. Math. Phys. 4 (1963) 1312;
   Statistical mechanics, foundations and applications, ed. T. A. Bak (W. A. Benjamin, New York, 1967) p. 98.
4. M. E. Fisher, Arch. Rat. Mech. Anal. 17 (1964) 377.
5. R. L. Dobrushin, Th. Prob. Appl. (USSR) 9 (1964) 646.
6. D. Ruelle, Rev. Mod. Phys. 36 (1964) 580.
7. J. L. Lebowitz and O. Penrose, J. Math. Phys. 5 (1964) 841;
   see also J. Groeneveld, in: Proceedings Kon. Ned. Akad. v. Wet. (Feb. 1968), where (9) is shown to converge in a larger domain without however proving that it represents the pressure there.
8. E. B. Smith and B. Adler, J. Chem. Phys. 30 (1959) 1190;
   H. L. Frisch, J. L. Katz, E. Praestgaard and J. L. Lebowitz, J. Phys. Chem. 70 (1966) 2016.
9. J. A. Barker and D. Henderson, J. Chem. Phys. 47 (1967) 4714;
   D. Levesque and L. Verlet, Perturbation theory and equation of state for fluids, to be published.

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